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Discussions

Interactive comment on "Sensitive detection of
n-alkanes using a mixed ionization mode
Proton-Transfer Reaction – Mass Spectrometer"
by Omar Amador-Muñoz et al.

Anonymous Referee #2

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The paper describes a mixed mode operation of a standard PTR-MS instrument (i.e., H3O+, NO+ and O2+ primary ions present at the same time) to detect n-Alkanes. I agree with reviewer #1 that it will be extremely difficult to unambiguously detect these compounds in the real atmosphere using the approach described in the paper. However, I find the nicely conducted experimental work very useful for the PTR-MS community: Since a PTR-MS instrument always operates in a mixed mode (primary ion purity hardly ever reaches 95 %), information of product ions from n-Alkanes from the different precursor ions is valuable to many users, especially when interpreting PTR-TOF data from field campaigns. I strongly encourage the authors to include a table or figures in the paper or supplementary information, showing the full lists of fragment ions

and their branching ratio for each compound tested. If possible, corrected for mass-dependent transmission efficiy of the mass spectrometer (if not, please state clearly). After including this information and real world examples as suggested by reviewer #1 and held out in prospect by the authors' response, I find the paper definitely acceptable in AMT.

However, the phrasing in some parts of the paper (listed among other comments below) seem to be too optimistic in terms of atmospheric detectability of these compounds.

Additional comments:

Line 44: Hansel et al. 1995 is not the right citation here, back then the LOD was in the low ppbv range; a newer Ref would be appropriate

Line 63: According to table 1, the PA of none of the n-Alkanes listed is higher than the PA of water. There is some inconsistency here. A short discussion about sensitivities for compounds having only slightly higher PA's than water (like Formaldehyde, e.g.) and their water vapour dependencies due to backward reactions would be appropriate here.

Line 92: I cannot imagine better references describing "operation and fundamental principles of PTR-MS" here and therefore disagree with Reviewer #1

Line 103: To produce NO+ primary ions, usually a mixture of O2 and N2 is used as described in Karl et al, not pure NO

Line 128: "monitored ions" is misleading; as I understand, you made full mass scans; so you monitored all ions, including fragments. Giving only M-1, M-2, M and M+1 ions in the table, without mentioning that these ions were not the most prominent ones in many cases, is a bit of a whitewash here.

Line 170: The use of the term saturated is misleading here

Line 279: "H3O+ = 1 sccm"

Line 297: The phrasing seems too optimistic here, since it implies that these alkanes can be detected at these concentrations in the atmosphere, which I seriously doubt because of interferences. After the authors include results from mixtures, the LoD should be given for compounds in the presence of other n-Alkanes, rather than obtained from zero-air (as examples, demonstrating the range of detectabilities).

Line 330: the term "highly sensitive" should be avoided here; in PTR-MS community this terms is usually used for compounds being ionized at a kinetic rate, which is not the case here Figure 5: ... is really hard to interpret; I agree with reviewer #1 and I am not convinced by the answer from the authors to this comment. Ncps/ppbv should always be used the same way: cps/ppbv for 1e6 primary ions per second; primary ions are these ion species which lead to the specific product ions (NO+ + O2+ for M; H3O+ for M+H etc.)