

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

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We thank the anonymous referee #2 for reading the manuscript and providing many useful comments which we have now addressed in the revised version.

1. The paper describes a mixed mode operation of a standard PTR-MS instrument (i.e., H_3O^+ , NO^+ and O_2^+ 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

C1

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 efficiency 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.

We appreciate these useful comments and we are pleased that the reviewer is finding our work useful for the PTR-MS community and acceptable in AMT. As suggested, we will include the tables with the fragment ions and their branched ratios. We agree that a typical mode of PTR-MS is also a mixed mode due to other reagent ion impurities and this is what the community often does not realize. Unlike with GC, a fully unambiguous identification is a general issue with CIMS and in particular when compounds are fragmenting it can very be difficult to discern signals for individual molecules but we are now showing the examples of the mixtures of alkanes and we are bracketing the potential bias to estimate the concentrations of n -alkanes, where larger alkane fragments are successfully subtracted from the lower alkanes ions using a calibrated fragmentation algorithm.

2. 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.

We generally agree that the atmospheric detectability using the mixed mode is challenging. However, relative to early instruments (Hansel et al. 1995) with lower ppb range detection limits for alkanes, the sensitivity to alkanes in the mixed mode is quite impressive (of the order of tens cps per ppb) and the detection limits in the lower ppt range. This sensitivity is only within a factor of 2-3 lower than the sensitivity of the pure

C2

mode but must be at cost of more complicated spectra and therefore the detection limit will be disproportionally higher. The higher effective detection limits are due to interferences with fragments which have to be accounted for. Overall, we hope that our research is useful to keep in mind the alkane ions which may be present in the pure modes if alkane concentrations are relatively high and possibility of usefulness of the mixed mode in studies of evaporation or alkanes in pollution plumes. We rephrased the parts which may have been interpreted as overly optimistic. We also updated the references with Karl et al. 2012.

3. 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. We rephrase the sentence: "However, proton transfer reaction products are mostly unobserved for alkanes because the proton affinity of most alkanes is lower than that of water or in case of longer alkanes ($C \geq 10$) it is only very slightly higher than water leading to potential backward reactions"

4. Line 92: I cannot imagine better references describing "operation and fundamental principles of PTR-MS" here and therefore disagree with Reviewer #1. We thank the reviewer for this positive comment. We therefore keep these references, and we also add the references suggested by Reviewer #2.

5. Line 103: To produce NO^+ primary ions, usually a mixture of O_2 and N_2 is used as described in Karl et al, not pure NO . Thanks.

6. 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. We replaced "monitored ions" with "corresponding ions". The same change was reflected in table 1.

C3

7. Line 170: The use of the term saturated is misleading here "primary ion was saturated" has been replaced with "which led to decline in primary ions"

8. Line 279: " $H_3O^+ = 1$ sccm" Done

9. 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).

Further to our response to comment #2, the detection limits presented in the manuscript are the lower bounds for the detection limits which are valid if the atmosphere is dominated by a single alkane but we are now making it clear in the text that they may be significantly higher in complex alkane mixtures and this will depend how complex the mixture is and what the dominating alkanes are. 10. Line 330: the term "highly sensitive" should be avoided here; in PTR-MS community this term is usually used for compounds being ionized at a kinetic rate, which is not the case here We refrained from using "highly sensitive". However, the sensitivities are typically only up to 2-3 factors lower than those at a kinetic rate, so are relatively sensitive.

11. 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 ($NO^+ + O_2^+$ for M; H_3O^+ for M+H etc.) We thank the reviewer for spotting these inconsistencies in the previous version of the manuscript. To be consistent with the PTRMS community terms, we are now consistently using the word "ncps" for the PT mechanism normalized to 1 million cps of H_3O^+ . The CT and DHA mechanisms in the case of alkanes are due to O_2^+ so we show "weighted" sensitivities wcps (to distinguish from PTR terms) where are normalized to 1 million cps of O_2^+ . In the case of HA mechanisms which can undergo

C4

either O₂⁺, or NO⁺ ionization or both, we show “weighted” sensitivities wcps which are normalized to 1 million cps of the sum of NO⁺ and O₂⁺. We think this is appropriate because in the mixed mode, the relative proportion of NO⁺ to O₂⁺ is relatively constant (~10%) and correlated so this simple standardization of sensitivities does not require the knowledge of whether a given alkane is ionized by NO⁺ or O₂⁺. We hope that the revised figure can be a useful summary of how these mechanisms distribute over the carbon numbers. To further increase the clarity we divided the figure into four panels. The PT panel uses normalized sensitivities to 1M of H₃O⁺ (ncps/ppb), the HA panel shows weighted sensitivities panel normalized to 1E6 cps of the sum of O₂⁺ and NO⁺ (wcps[O₂⁺,NO⁺]), the CT and DHA panels use weighted sensitivities normalized to 1E6 cps of O₂⁺ (wcps[O₂⁺]). Another reason why the weighted sensitivities by relevant primary ions make sense is that in different configurations the absolute number of ions and therefore absolute sensitivities can be different or variable. This is one standardized way which should account for primary ion levels which are also provided for transparency, so that the user can easily un-normalize/un-weight.

Once again, we thank the anonymous reviewer 2 for these valuable comments which will significantly improve the manuscript.

References: Hansel, A.; Jordan, A.; Holzinger, R.; Prazeller, P.; Vogel, W. and Lindinger, W.: Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, *Int. J. Mass Spectrom. Ion Proc.*, doi:149/150, 609-619, 1995. Karl, T.; Hansel, A.; Cappellin, L.; Kaser, L.; Herdinger-Blatt, I. and Jud, W.: Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO⁺ ionization mass spectrometry, *Atmos. Chem. Phys.*, 12, 11877-11884, doi:10.5194/acp-12-11877-2012, 2012.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/amt-2016-64/amt-2016-64-AC2-supplement.pdf>

C5

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-64, 2016.

C6