Atmospheric
Measurement
Techniques
Open Access

Discussions

EGU

AMTD

Interactive
comment

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 #1

Received and published: 11 June 2016

This paper describes a method for the detection of n-alkanes using a standard PTR-MS instrument with different settings. n-alkanes are not detectable with H3O+ primary ion chemistry, but n-alkane measurements are of increasing importance due to their emissions from oil&gas developments and crude oil evaporation and the authors mention crude oil evaporation as the main motivation for this work. A few recent papers have shown that NO+ primary ions are a promising method for detecting n-alkanes. In this paper a mixture of H3O+, O2+ and NO+ is used for primary ions, which results in various reaction channels and therefore multiple product ions for each n-alkane, severely complicating the detection. The paper also does not show measurement results of mixtures of n-alkanes or for example crude oil evaporation, so that possible overlap

from fragments of larger alkanes or other compounds cannot be judged from the data presented. I suspect that fragmentation and overlap will make this method not very useful. In addition, it is well known that O2+ reacts with alkanes, which is the main reaction channel used here, so I am wondering what is new here. If the manuscript can be improved to demonstrate the usefulness of this method, this paper might be acceptable, but certainly not in its current form. I have several major comments and some minor ones that need to be addressed. The major comments basically all deal with the usefulness and the novelty of the method as presented here.

Major comments:

- As I mentioned above, I am not convinced that this method as described here, is actually useful, not even for oil evaporation, where the contributions of other species besides alkanes is minimal. The main primary ion at the tested instrument settings for the reaction with the n-alkanes is O2+. H3O+ is also present, but does not react with the alkanes. Various groups, foremost D. Smith and co-workers, have investigated the use of O2+ over the years, including for n-alkanes, and O2+ has basically been abandoned due to strong fragmentation in the charge transfer reactions with most compounds, except maybe for NH3 (Norman et al 2007). Fragmentation from O2+ with n-alkanes has also been documented in several more recent papers; a good example is by Francis et al 2007. The main issue is that larger alkanes fragment onto the same masses, where smaller alkanes are detected, such that in more complex alkane mixtures none of the individual species can be detected unambiguously. Recently the use of NO+ has become more popular in the PTR-MS community and it was shown that NO+ is a very promising primary ion for alkanes, but still suffers from fragmentation resulting in compound overlap; especially the work by Inomata et al 2014 and Yamada et al 2015 but also a very recent paper by Koss et al AMTD 2016 discuss this issue. In the method used here, one not only has to deal with fragmentation, but also competing reaction channels from NO+ and H3O+. Fragmentation, the main complication in all the other papers, is basically ignored in this manuscript; only the unfragmented

products from proton transfer (PT), charge transfer (CT) and hydrogen abstraction (HA) are discussed. Fragments are mentioned briefly in the text and a mass spectrum of n-decane is shown in the SI, and those clearly show the strong fragmentation with this current setup. In my opinion, the fragmentation will be the most restricting factor to the usefulness of this setup and I think a rigorous discussion of the fragmentation patterns needs to be added to the manuscript. This should include the actual fragmentation patterns of all investigated alkanes, a discussion of the contribution of larger alkanes to smaller alkanes and a detailed comparison to the ample literature of the reaction products from NO+ and O2+.

- The authors describe that their PTR-MS was not equipped with SRI and therefore it was easier to de-tune the ion source to generate NO+ and O2+ ions. This seems like a weak argument to me. To make NO+ one has to only replace the water reservoir with a synthetic air tank on the PTR-MS. This takes less than an hour to do. The optimum instrument setup for NO+ is well described by Jordan et al 2009 and Inomata et al 2014. A better justification is needed for why this method of producing clean NO+ was not used.

- With the competition between PT, CT and HA each measured compound likely has different product ions. How can you know for an unknown compound mixture which is the dominant reaction channel? Just a simple example: mass 71 is the HA product from n-pentane, PT product from MVK+MACR, and PT product from cyclopentane, which is an important constituent of crude oil (Yuan et al 2014). In addition mass 71 is a fragment of larger alkanes. Were you planning to use an analysis similar to Figure 3 for identification?

- Nothing demonstrates the usefulness of a method better than an example. A good one would be to calibrate all the n-alkanes simultaneously and show that you can identify and quantify all the alkanes correctly with the method described here. A mass spectrum of a crude oil sample with all the n-alkane peaks identified would be also very useful. A comparison with a standard method such as GC-MS would be even better.

An example is really needed!

Minor comments:

Line 55: I think it would be appropriate to use references from other groups for large alkane sources and abundances as well.

Line 83: Also here it would be appropriate to add a few more references such as Yamada et 2015, Knighton et al 2009, Koss et al 2016.

Line 92: There are several newer PTR-MS references that should be added here as well.

Line 117: You are varying all primary ions not only O2+.

Line 173-180: The description of Figure 2 does not include a discussion of the primary ions that are shown in the Figure. There also seems to be a mistake in the y-axis in Fig 2a. I also assume that Fig 2a shows the HWF case and Fig 2b the LWF case, at least for the primary ions. This needs to be explained.

Line 179: Here would be a very good place to start discussing the fragmentation products.

Line 188: How are the isotopes taken into account? Did you subtract the isoptopic signal from the PT channel for this ratio? If not, this should be done.

Line 196: A similar discussion should be added for PT. It is mentioned in several places in the text that the PA of alkanes is too low to react with H3O+, but it should be discussed more explicitly.

Line 204: Have you looked at cycloalkanes as well? They are a large fraction of crude oil and undergo slow, but measureable PT. Those will have a large influence on your measurements. Do you know how they will vary with E/N?

Line 265: I would call R7 a ligand switching reaction. This is a prominent channel at

low E/N as you have here.

Line 292: Figures 3 and 5 are somewhat inconsistent. The sensitivity shown in Figure 5 is higher than in Figure 3. Is this because of different water flow used 1sccm vs 2sccm?

Line 297: What are the averaging times that you used for the detection limits?

Figure 5: The y-axis is divided by 10e4. Where does that come from? This is not consistent with the rest of the manuscript.

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