

# ***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 anonymous referee #1 for reading the manuscript and providing many useful comments that we will address in the revised version. We strongly believe that this work is valuable and can be useful for the CIMS community.

1. 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  $\text{H}_3\text{O}^+$  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.

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In this paper we focus on characterization of the ability to detect n-alkanes under different mechanisms available in the mixed ionization mode. We did not focus on crude oil evaporation, but one motivation for this work was developing an analytical method suitable for the detection of a broader suite of compounds than is possible with any of the common pure ionization modes possible with PTR-MS. This has never been done before and we found that the mixed mode can be sensitive not only to n-alkanes but also to most VOCs which can be protonated by  $\text{H}_3\text{O}^+$ . The contribution from the  $\text{NO}^+$  channel was relatively small ( $\sim 10\%$ ), but the ions sensitive to  $\text{NO}^+$  can also be detected if they are highly abundant. The main benefit of the mixed mode is that no switching is required making the real time data available simultaneously. While this mode is more challenging to interpret, we explicitly emphasize these challenges such as fragmentation and interferences. Furthermore, we point to where this method could be useful (e.g. matrices dominated by n-alkanes and aromatics such as fossil fuel emissions).

2. A few recent papers have shown that  $\text{NO}^+$  primary ions are a promising method for detecting n-alkanes. In this paper a mixture of  $\text{H}_3\text{O}^+$ ,  $\text{O}_2^+$  and  $\text{NO}^+$  is used for primary ions, which results in various reaction channels and therefore multiple product ions for each n-alkane, severely complicating the detection.

We agree that  $\text{NO}^+$  is a very promising mode, but as nicely reviewed by Koss et al., 2016 this mode is only useful for branched chain and long chain alkanes. We think that our development is highly complementary to pure  $\text{O}_2^+$ ,  $\text{NO}^+$ , and  $\text{H}_3\text{O}^+$  modes. We demonstrated that  $\text{O}_2^+$  is the best primary ion to detect n-straight alkanes  $> \text{nC}_5\text{H}_{12}$  via charge transfer as opposed to hydride abstraction. The detection of n-straight chain alkanes is less sensitive via hydride abstraction than by charge transfer (a factor of 2-3), as illustrated in figure 5. The detection is generally complex but this is also true to some extent for pure modes where the impurity ions can be 1-2 orders of magnitude lower, while the measured concentrations often span 6 or more orders of magnitude. The pure mode in PTR-MS should still be regarded as mixed mode because there remain

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contributions and interferences that will necessarily depend on the studied matrix and concentrations. For example, if there is 1% of O<sub>2</sub><sup>+</sup> in the pure NO<sup>+</sup> mode, 100 ppb of pentane in a plume can make a relatively large signal due to O<sub>2</sub><sup>+</sup>, which would interfere with cyclopentane. We would also like to point out that while individual n-alkanes are most uniquely detected by GC-MS, the mixed mode offers a good time-dependent tracer for a sum of all alkanes which can serve as a link between detailed chemical composition of alkanes (GC-MS) and high time resolution of the varying emissions or concentrations (PTR-MS in mixed mode).

3. 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.

While crude oil evaporation was not the focus, we will add examples of measuring mixtures of alkanes and estimating the concentrations of n-alkanes. In our method, we take into account n-alkane fragmentation by using the calibrated fractions from individual n-alkane experiments. We show that the larger alkane fragments are successfully subtracted from the lower alkanes ions, and demonstrating that this method works reasonably.

4. In addition, it is well known that O<sub>2</sub><sup>+</sup> reacts with alkanes, which is the main reaction channel used here, so I am wondering what is new here.

It is well known that O<sub>2</sub><sup>+</sup> reacts with alkanes, but except for SIFT studies (e.g. Francis et al., 2007), the O<sub>2</sub><sup>+</sup> mode and its mechanisms have not been evaluated on PTR-MS. We find that this mode is indeed very useful for alkane detection and we show optimizations to achieve high sensitivity, and suppress excessive fragmentation. We also explore in great detail which mechanisms produce the highest sensitivities as a function of carbon number. For n-hexane and lower n-alkanes the most sensitive mechanism was hydride abstraction, while for higher n-alkanes, the most sensitive mechanism was

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charge transfer. This is new information that will be valuable to the broader community. While our in-depth characterization of O<sub>2</sub><sup>+</sup> ionization mechanisms is presented with the goal of O<sub>2</sub><sup>+</sup> detection, it should be clear that this detailed characterization will also be useful to those who will regard O<sub>2</sub><sup>+</sup> as an impurity in other detection schemes. Our characterization of the O<sub>2</sub><sup>+</sup> ionization will thus enhance interpretation of data for complex mixtures using any ionization scheme. In addition, the mixed mode utilizes H<sub>3</sub>O<sup>+</sup>, and to a smaller extent NO<sup>+</sup> for enabling measurement of a much broader range of compounds simultaneously.

5. 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.

We strongly disagree with this comment. In addition to alkanes, oil contains a large fraction of aromatics, so the mixed mode is much more useful than the pure modes because it allows for simultaneous tracking of alkanes and aromatic compounds without the need for ion switching. Again, we did not focus on determining alkanes in oil. Our main focus was on determining the mechanisms for detection of alkanes and optimizing the use of mixed-mode conditions. We are confident that the mixed mode, first proposed here, is novel and can be very useful for numerous applications where air is dominated by VOCs such as aromatics, and alkanes. We include the example of a complex alkane+VOC matrix which shows that the mixed mode can be promising also for complex matrices although not all (e.g. biogenics). There are very few studies on O<sub>2</sub><sup>+</sup> detection of alkanes and the mixed mode has never been proposed before. The double hydride abstraction mechanism in O<sub>2</sub><sup>+</sup> is a particularly novel finding in our study and more specific for the detection of some alkanes. We have not only described

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optimizations and characterizations of this method, but the revised paper further emphasizes the novelty and usefulness of the method as well as highlights the known and less known challenges more clearly.

6. The main primary ion at the tested instrument settings for the reaction with the n-alkanes is  $O_2^+$ .  $H_3O^+$  is also present, but does not react with the alkanes. Various groups, foremost D. Smith and co-workers, have investigated the use of  $O_2^+$  over the years, including for n-alkanes, and  $O_2^+$  has basically been abandoned due to strong fragmentation in the charge transfer reactions with most compounds, except maybe for  $NH_3$  (Norman et al 2007). Fragmentation from  $O_2^+$  with n-alkanes has also been documented in several more recent papers; a good example is by Francis et al 2007.

We directly addressed the expected challenges of  $O_2^+$  ionization that have limited previous investigations by systematically studying a very large and comprehensive matrix of instrumental (voltages etc.) and experimental (humidity etc.) conditions. It is true that the  $H_3O^+$  does not react with alkanes, which is desirable in this study. The role of  $H_3O^+$  in the mixed mode is not the ionization of alkanes but of the other compounds. Crude oil is just an example, but there can be other environments where alkanes and other classes of VOCs (e.g. aromatics) need to be analyzed simultaneously. The number of studies using  $O_2^+$  ionization is actually extremely small relative to those on  $NO^+$  and  $H_3O^+$  and almost exclusively comes from the SIFT community, where strong fragmentation is more difficult to suppress or account for. For example, Francis et al., 2007 used CIMS and focused only on short alkanes. We comprehensively evaluate the ionization mechanisms available in the mixed mode and increase understanding of the  $O_2^+$  mechanism using a PTR-MS instrument. As mentioned earlier, we also characterized the mechanisms responsible for the highest sensitivities as a function of the carbon number and point out that hydride abstraction dominates the sensitivity for n-hexane and smaller hydrocarbons, while charge transfer is the most sensitive mechanism for larger alkanes.

7. The main issue is that larger alkanes fragment onto the same masses, where smaller

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alkanes are detected, such that in more complex alkane mixtures none of the individual species can be detected unambiguously. Recently the use of  $\text{NO}^+$  has become more popular in the PTR-MS community and it was shown that  $\text{NO}^+$  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  $\text{NO}^+$  and  $\text{H}_3\text{O}^+$ .

The reviewer suggests that  $\text{NO}^+$  mode on its own is better than the mixed mode. This may be true, but only in some applications.  $\text{NO}^+$  is indeed promising for alkane detection, but has similar, although perhaps less pronounced, challenges in terms of fragmentation and multiple ionization mechanisms (CT, HA,  $\text{NO}^+$  association). We think that  $\text{O}_2^+$  is highly complementary to  $\text{NO}^+$  because it is not sensitive to branched alkanes and is more sensitive to straight chain alkanes in the range where  $\text{NO}^+$  is not sensitive. Also, the alkanes follow a clear fragmentation pattern in  $\text{O}_2^+$  mode, which we show can be accounted for.

8. 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  $\text{NO}^+$  and  $\text{O}_2^+$ .

We did not mean to ignore the fragmentation of alkanes. In contrast, we highlighted that this is an important issue which should be taken into account in complex alkane mix-

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tures. While the earlier version of the manuscript focused on simple alkanes to characterize their detection, in response to this review, we include the algorithm to quantify the signal of individual alkanes in complex mixtures by subtracting the fragment fractions. We show that this method works reasonably well for a mixture of n-alkanes and is easy to apply.

9. 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  $\text{NO}^+$  and  $\text{O}_2^+$  ions. This seems like a weak argument to me. To make  $\text{NO}^+$  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  $\text{NO}^+$  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  $\text{NO}^+$  was not used.

We are unsure which sentence was misleading. We certainly did not want to depreciate the value of SRI, which is very useful and available in recent versions of the instruments sold by Ionicon. In fact, we believe the mixed method can be made even more useful for instruments with SRI, where the proportions of each ionization agent can be adjusted to maximize detectability in complex matrices. In addition, we never intended to double the effort on the pure  $\text{NO}^+$  mode, which has nicely been reviewed recently by Koss et al. and other groups. Instead, we focused on the novel mixed ionization mode featuring  $\text{O}_2^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{NO}^+$  simultaneously. We think that this development is unprecedented and highly innovative. Of course we fully recognize that this method is not free from the challenges that are present in other adaptations of PTR-MS instruments as well.

10. 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

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for identification?

We found typically no or little competition between PT, CT, and HA for most ions. PT is not applicable to alkanes less than C10 and the sensitivity of cyclopentane (and its relative abundance in common mixtures such as oil) is very low compared to other alkanes. In addition, MVK+MAC is very low far away from biogenic sources and is only an issue for PTR-MS systems using a quadrupole detector. A potential interference with cyclopentane and pentane needs to be taken into account also for pure NO<sup>+</sup> where O<sub>2</sub><sup>+</sup> (even if reduced to a few %) can have an important interference from much more abundant alkanes. Overall, detection of most compounds is dominated by a single ionization mechanism. Thus, overlap is mainly a problem when detecting compounds with very different concentrations. This can be true for any ionization scheme with reagent-ion impurities. Our comprehensive study of the ionization schemes at a minimum allows us to determine the major components of a sample and may often allow much more detailed characterization than has previously been possible.

11. 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!

We thank the reviewer for this useful suggestion. We agree that the example of more complex mixture, and comparison with GC-MS method, would be useful for the readers. In fact, we did this work already but were planning to include it to another manuscript. In response to this comment, we will add to the manuscript the quantification of n-alkanes in crude oil using GCxGC-MS and show a simple method how the fragment contributions can be accounted for.

Minor comments: Line 55: I think it would be appropriate to use references from other

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groups for large alkane sources and abundances as well. We now include more references.

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. These references are now included.

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

Line 117: You are varying all primary ions not only O<sub>2</sub><sup>+</sup>. This has been now made clear.

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. The primary ions and water flow cases are now clearly explained.

Line 179: Here would be a very good place to start discussing the fragmentation products. As suggested, we start discussing the fragmentation products here.

Line 188: How are the isotopes taken into account? Did you subtract the isotopic signal from the PT channel for this ratio? If not, this should be done. As we wrote in p. 4, lines 127-128 and 146-147, the <sup>13</sup>C isotopic signals were subtracted from the preceding ions.

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 H<sub>3</sub>O<sup>+</sup>, but it should be discussed more explicitly. We implemented this suggestion in the revised manuscript.

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? Yes, we did measurements

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on cycloalkanes. As the reviewer noted, PT ions have very low sensitivity and in some cases suffer interference by HA from alkanes. This is a challenge for both  $\text{NO}^+$ ,  $\text{O}_2^+$  and the mixed mode. We focus on the most abundant compounds such as n-alkanes, and aromatics. Because, cycloalkanes and alkanes fragment differently, one way to discriminate between cycloalkanes and alkanes would be to vary the E/N ratio but we do not want to focus on this in this manuscript.

Line 265: I would call R7 a ligand switching reaction. This is a prominent channel at low E/N as you have here. The manuscript has been updated accordingly

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? The water flow rate affected the absolute count rate of primary ions. The scales in these figures are not the same. Figure 3 shows the absolute sensitivities while Figure 5 shows the normalized sensitivities to sum ( $\text{O}_2^+$ ,  $\text{NO}^+$ ). Normalized sensitivities resulted in more consistent values for the CT reactions.

Line 297: What are the averaging times that you used for the detection limits? The average time was 0.2 s

Figure 5: The y-axis is divided by  $10^4$ . Where does that come from? This is not consistent with the rest of the manuscript. In p8 lines 281-290, we explained that normalized sensitivity (ncps/ppbv) is recommended to account for the variability of levels of  $\text{O}_2^+$  due to changing water flow in PTR-MS instruments (Jobson et al., 2005; Warneke et al., 2001). We calculated the normalized sensitivities to sum ( $\text{O}_2^+$ ,  $\text{NO}^+$ ) to account for the variability between experiments. Because the response in signal of  $\text{NO}^+$  and  $\text{O}_2^+$  are extremely high compared to response of the n-alkanes, the scale in y-axis was divided by 104

Once again, we thank the reviewer for stimulating the discussion which resulted in further improvement of the manuscript.

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References: Francis, G. J., Wilson, P.F., Milligan, D.B., Langford, V.S., McEwan, M.J.: GeoVOC: A SIFT-MS method for the analysis of small linear hydrocarbons of relevance to oil exploration. *International Journal of Mass Spectrometry*, 268(1):38-46, 2007. Knighton, W. B., Fortner, E. C., Herndon, S. C., Wood, E. C., and Miake-Lye, R. C.: Adaptation of a proton transfer reaction mass spectrometer instrument to employ NO<sup>+</sup> as reagent ion for the detection of 1,3-butadiene in the ambient atmosphere, *Rapid Commun. Mass Sp.*, 23, 3301-3308, 10.1002/rcm.4249, 2009. Koss, A. R., Warneke, C., Yuan, B., Coggon, M. M., Veres, P. R., and de Gouw, J. A.: Evaluation of NO<sup>+</sup> reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds, *Atmos. Meas. Tech. Discuss.*, doi:10.5194/amt-2016-78, in review, 2016.

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