

Interactive comment on “Introducing the Extended Volatility Range Proton-Transfer-Reaction Mass Spectrometer (EVR PTR-MS)” by Felix Piel et al.

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Response to Reviewer #1:

We thank the reviewer for carefully reading our manuscript and for providing highly valuable comments, which we have addressed in detail below.

Major comments:

In the abstract, lines 18-20, the EVR configuration is presented primarily as an improvement by passivating surfaces, with “further improvement” by heating to 120 C. However, as far as I can tell, there is no data presented in the manuscript about how much the passivated surfaces changed the response times. If the authors want to highlight the passivation, this type of information needs to be

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included in some form. Otherwise, the temperature increase, for which there is clear data (e.g. Fig. 3a), should be presented as the main improvement. And in that case, the novelty of this manuscript (and the EVR inlet) is questionable, as there are a wealth of PTR studies where inlets and inlet lines have been heated in order to improve response times and detection of less volatile species (see e.g. section 2.4.5 in Yuan et al., 2017, Chem. Rev.). The authors need to make very clear what exactly causes the improvement of response times in this manuscript, and how this is different enough from earlier work that it deserves publication in AMT.

We have found data from two experiments wherein the signal decay of *cis*-pinonic acid was measured with the same instrument, before and after being modified to the EVR configuration. All other experimental parameters were kept identical. The signal decay time dropped from $\tau_{1/e} = 181$ s to $\tau_{1/e} = 4$ s. In the revised manuscript, we are presenting these data as the first results in the Results section, clearly demonstrating and highlighting the benefit of surface passivation.

Lines 55-58 at the end of the introduction do not even mention the temperature issue, suggesting that the material changes are the main topic of this manuscript. This requires verification.

We refer to our comment above, but agree that the effect of temperature should be mentioned in the Introduction. The revised paragraph reads as follows:” Herein we will demonstrate how the use of heated inlet capillaries made of passivated stainless steel (SS) and of a heated drift tube with passivated metal surfaces significantly improves the time response performance of PTR-MS analyzers. We will show that the heated and passivated instrument responds fast to low-volatility analytes, both for gas-phase and particle-phase measurements.”

A related point is the lack of any schematic diagram of the EVR in the manuscript. It may be understandable if the design itself did not change, but rather only ma-

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terials were exchanged, yet it would still be beneficial for a reader to see a figure showing these changes. As it is, the only reference on PTR in section 2.1 is the Yuan et al (2017) review, which itself doesn't have a schematic of the exact system used in this work. This makes it very laborious for a reader to understand the changes, and consequently to properly assess the novelty of the changes and the manuscript itself.

This is a valuable suggestion and we have included a figure (new Fig. 1) showing the drift tube and inlet system with all passivated surfaces in the Experimental section.

Specific comments:

1. Lines 28-29: Since these measurements were done using NH₄⁺ adducts, I don't think it should any longer be called "PTR-MS".

PTR-MS instruments can nowadays be operated with different chemical ionization reagent ions (H₃O⁺, NO⁺, O₂⁺, NH₄⁺, others), and most of them do not react via proton transfer reactions (PTR). It is debatable if it makes sense to introduce additional acronyms for different operation modes of the same instrument. In the past, the acronym "eTR-MS" has been proposed for the O₂⁺ mode but it was never taken up by the community. Our operation mode should probably be called "AAF-MS" (AAF: Ammonium Adduct Formation). We think that introducing new acronyms for different operation modes of the same instrument would just create confusion. Note that we are referring to the PTR-MS instrument and not to PTR-MS as a chemical ionization method.

2. Lines 69-70. Since T_{drift} is used later as a parameter, it is important for a reader to have a clear picture of how the drift tube looks. Also here a schematic would be useful.

As stated above, we have included a figure showing the drift tube and inlet system in the Experimental section.

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3. Lines 50-51: “H₃O⁺ ion chemistry thus detects a wider spectrum of analytes than any other chemical ionization method for atmospheric organic carbon.” This is a strong statement and would need a citation. Instruments like the NH₄⁺-Cl₃-TOF or C₃H₇NH₃⁺-APi-TOF (Berndt et al., 2018, *Angew. Chem. Int. Ed.* 2018, 57, 3820–3824) seem to detect almost all organic compounds (including radicals) except hydrocarbons. Can the authors show references where H₃O⁺ ion chemistry would have detected a broader spectrum than that?

Well, basic ion chemistry tells us that H₃O⁺ ions react with a broader spectrum of organic species than NH₄⁺ or C₃H₇NH₃⁺ ions. The scope of this paper is, however, not to discuss the pros and cons of different reagent ions. Since Reviewer 2 also did not like our comparative statement, we have removed it.

4. Lines 73-75. These two sentences need to be reformulated. “was measured as the time that evolved until” is hard to understand.

We changed our wording to: “ $\tau_{1/e}$ is the time it took the analyte signal to decay to 1/e (36.8%) of its initial value. τ_{90} is the time it took the analyte signal to decay to 10% of its initial value.”

5. Fig. S1. The part inside the red dashed box is presumably the inlet and drift tube of the PTR? This needs to be clarified, as it is not easy to read for someone not highly experienced with the system.

Fig. S1 has been revised to better show the experimental set-up. Additional details are shown in the newly included Fig.1.

6. Lines 108-109: This leaves the reader with the question “why?”.

It was more difficult to generate low volume mixing ratios with these substances. This is now explained in the text.

7. Lines 133-134: This also leaves the reader with the question “why?”.

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The solid *cis*-pinonic acid sample was heated to 70 °C for generating a measurable concentration in the gas phase. Using lower instrument temperatures would have resulted in condensation on the walls. This is now explained in the text.

8. Section 3.2: The discussion is about T_{drift} , and the text suggests that it is only the drift tube temperature that is changed. But Fig. S1 suggests that the entire inlet is one temperature-controlled entity. Please clarify. This again would be easier to understand if there was a proper schematic included.

Fig. 1, which has been newly included in the Experimental section, should make it clear what parts are heated in the temperature-controlled instrument enclosure.

9. Lines 138-139: This seems consistent, but Fig. S2 shows that the dependence of τ on C^0 is very weak, with compounds of the same C^0 easily having an order of magnitude or larger differences in τ . Were these two compounds selected to be shown because they happened to match?

Both our data and literature data indicate that for long-chain ketones and carboxylic acids $\tau_{1/e}$ exhibits the expected increase with decreasing $\log C^0$, while for saccharides and substituted phenols other factors seem to play a role. We thus show data for one long-chain ketone and one carboxylic acid. This is explained in the text:” For long-chain ketones (Pagonis et al., 2017; Krechmer et al., 2018) and carboxylic acids (Fig. S2), $\tau_{1/e}$ exhibits the expected increase with decreasing $\log C^0$. Since $\log C^0$ depends upon temperature, changes in T_{drift} should lead to predictable changes in $\tau_{1/e}$. We thus measured $\tau_{1/e}$ for 2-tridecanone_(g) and *cis*-pinonic acid_(g) at variable T_{drift} (Fig. 5).”

10. Line 144: Why are you now shifting from $\tau_{1/e}$ to τ_{90} ?

Some of the literature data were only reported as τ_{90} .

11. Line 145: It is unclear which data from this study is used in Fig. 4. This should be made clear, so that a reader would be able to compare responses

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compound by compound. In addition, there is a nice monotonic trend of tau vs C0 in Fig. 4, which is hard to understand given the huge spread of points in Fig. S2. One is left wondering how the authors selected the 5 data points shown in Fig. 4 for the EVR.

The compound names have been included on the upper x-axis of the figure. Comparing the time response of different instruments to different compounds is obviously difficult, and one needs to be careful not to compare apples with pears. Our data suggest that at least for carbonyls and carboxylic acids the observed trends in $\tau_{1/e}$ can be explained by differences in C_0 , which is why we have only included such compounds in the figure. We explain this in the revised text: "The upper horizontal axis lists the compound names; the lower horizontal axis shows in which log C^0 range molecules are classified as volatile organic compounds (VOCs), intermediate volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs). Since the instruments did not measure the same SVOCs, we only use our carboxylic acid data for the log C^0 -based comparison."

12. Line 153: C13 ketones are referenced, but I do not know where I should be looking to find this data.

The compound names have been included on the upper x-axis of the figure.

13. Fig. 4: It took me a while to realize that the unit of tau changes between Fig. 2 and Fig. 4, from sec to min. Why not keep them the same? Now both the time unit and the decay reference (1/e vs 90) change, and it makes things much harder to follow. I suggest to make all of these the same, as it would make the reading much smoother and avoid confusion.

All times are now reported in seconds.

14. Fig. 4: If I understand the plot correctly, the non-EVR PTR-TOF from this study seems to work much better than the EVR. All measured response times

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are on the order of 0.01min, while in the EVR all points are at 0.1 min or higher. Does this mean that the EVR setup has actually made the response times worse compared to the original design (as long as the inlet is heated)?

Unfortunately, the reviewer has misinterpreted the figure. $\log C^0$ is a measure of volatility and the compounds studied include volatile organic compounds (VOCs), intermediate-volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs). We have added a classification bar on the x-axis for including this information. As a general trend, τ_{90} increases with decreasing volatility or decreasing C_0 . What the figure shows is the following:

1. For VOCs and the more volatile IVOCs ($\log C^0 \geq 5$), τ_{90} is close to the volumetric exchange time of the drift tube for both the EVR and the conventional PTR-ToF-MS instrument, as long as the drift tube is heated to 120 °C. Conventional unheated PTR-MS instruments have a much slower time response.
2. For the less volatile IVOCs ($\log C^0 \leq 3$) and SVOCs, surface passivation reduces τ_{90} by two orders of magnitude (*cis*-pinonic acid), even if the drift tube is heated to 120 °C in both the conventional and the EVR PTR-ToF-MS analyzer. The heated EVR PTR-ToF-MS responds as fast as state-of-the-art CIMS instruments.

We have adapted the text to convey the above information.

15. Line 155: The fact that temperature explains the major part of the differences, and this fact is only mentioned in one sentence in the main text, makes Fig. 4 very misleading. For example, one would read from Fig. 4 that the reason the PTR-TOF in this study was 3-4 orders of magnitude better than the PTR-qMS from Pagonis et al is related to the quad vs tof, since that is the only clear difference. Not to mention the comparison to other instruments, which were not run at elevated temperatures. Please put the operating temperatures into the

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figure legend, since these values are the most critical parameter to understand the major differences in the figure.

Temperature is certainly an important factor and we have included the operating temperatures in the figure legend. The key information is, however, that for the less volatile IVOCs ($\log C^0 \leq 3$) and SVOCs an increase in the drift temperature to 120 °C alone does not do the job. It is the surface passivation that drops τ_{90} by two additional orders of magnitude.

16. Lines 171-172: Again, the fast changes are attributed to the materials, and temperature is not mentioned at all. This needs to be clearly validated before making this claim.

We have extensively addressed this issue in previous comments and in the revised manuscript.

17. Conflict of interest statement: Ionicon analytik is said to be “commercializing (CHARON) PTR-MS”, but they are also advertising directly the EVR setup presented here (<https://www.ionicon.com/accessories/details/extended-volatility-range-evr>). Why is this not mentioned here?

We are now explicitly mentioning that IONICON Analytik commercializes PTR-MS, CHARON and EVR.

Technical corrections:

1. Line 97 and line 107: Caption, not legend.

This was corrected.

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