

## ***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 #2:**

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

#### **Major comments:**

***1. The purpose and the focus of the manuscript are a little unclear. Is it just to estimate the signal-decay times for a new instrument or to assess its performance more holistically? If so, the effects of interactions with inlet walls and humidity should be discussed in this paper.***

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The main purpose of this manuscript is to establish the EVR PTR-MS instrument in the scientific literature. More than two dozens of EVR PTR-MS instruments are nowadays in use, and we think it is important that the users can refer to an instrument paper when presenting their own data. We want to present a new type of PTR-MS instrument and exemplify its improved performance, rather than systematically investigating material, temperature or humidity effects.

***2. The effect of the drift tube temperature is interesting and important for more comprehensive evaluation of the instrument measurement capability, but is weakened by the very small number of compounds used to derive the conclusion that 120°C is the optimal temperature at which the instrument should be operated. It would be of interest to conduct similar measurements with a larger set of compounds, especially with the ones that tend to thermally decompose at higher temperatures, such as hydroperoxides (i.e., cumene hydroperoxide and dicumylperoxide discussed later in the paper).***

While the suggested thermal decomposition study would certainly be interesting, we feel that such work would go beyond the scope of a first instrument paper (see reply to comment 1). Please also note that we are not claiming that 120 °C is the optimal operation temperature. In fact, the operation temperature must be adapted to the type of analytes that are to be measured. We are explicitly stating this in the revised manuscript.

***3. I do not fully understand how detection of particle-phase highly oxidized organic compounds produced via ozonolysis of limonene fits in this paper. The authors neither discuss the signal-decay times for these compounds nor try to estimate the respective wall losses. It has been shown several times that softer ionization techniques, such as NH<sub>4</sub><sup>+</sup> CIMS, can be used for detection of highly oxygenated compounds in the gas and particle phase (i.e., Hansel et al., 2018; Zaytsev et al., 2019). Hence, the authors should clarify why they present these data and how implementation of the new inlet improves detection and quantifi-***

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**cation of these compounds.**

We agree that we did not properly convey the information we wanted to give. Limonene ozonolysis was just a way for generating highly oxidized compounds up to O<sub>8</sub>, which were not among the pure substances (up to O<sub>6</sub>) available for our study. We have taken up the suggestion by the reviewer and show the signal decay of an O<sub>8</sub>-compound. This demonstrates that even for highly oxidized analytes (ELVOC)  $\tau_{1/e}$  remains below 20 s.

**Specific comments:**

**1. Lines 49-54: From reading this paragraph one might get a false impression that PTR-MS has the best measurement capability among all CIMS instruments. While it is true that the ionization efficiency does not vary too much among oxidized and nonoxidized compounds, the overall measurement capability of PTR-MS instruments is significantly limited by ionic fragmentation and wall losses. Hence, the authors should edit this paragraph and make their description of PTR-MS more balanced.**

We have only stated the H<sub>3</sub>O<sup>+</sup> ion chemistry detects a broader spectrum of organic analytes than other CI techniques, which is certainly true from a pure ion chemistry point of view. This does *per se* not imply that PTR-MS has a better measurement capability, because the latter depends on additional factors (e.g., inlet losses, detection limit). Since Reviewer 1 also did not like our comparative statement, we have removed it.

**2. Lines 55-58: The effects of drift tube temperature are not mentioned here, however they seem to play a fairly important role as outlined in the Discussion section. The particle-phase experiments should also be mentioned at the end of Introduction.**

This has also been pointed out by Reviewer 1 and we mention the effect of temperature in the revised paragraph. We also mention the particle experiments. The revised

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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.”

**3. Section 2.1: This section is missing a schematic of the EVR PTR-MS instrument. I suggest moving Fig S1 to the main text and significantly expanding it to demonstrate what parts of the instrument were replaced or coated. As of now, these changes might not be obvious especially for a reader who is not fully familiar with IONICON PTR-MS instruments.**

The drift tube and capillary inlet system (including the passivated parts) are sketched in Figure 1 of the revised manuscript.

**4. Line 95: Why did the authors use the double exponential decay for fitting the signals? How did the authors calculate  $\tau_{1/e}$  from fitted parameters b1 and b2? I believe this is not explicitly discussed in the paper.**

We did not calculate  $\tau_{1/e}$  from the fit.  $\tau_{1/e}$  is simply the point in time when the analyte signal had dropped to 36% of its initial value. This is explicitly stated in the manuscript (§2.2). The fit was just included for guiding the eye; the fit function was included upon request of the editor.

**5. Figure 2: What do different circles/data points for the same compound represent? The authors should clarify this and discuss why the difference between some data points is fairly large, for example for 2,6-dimethoxyphenol and diglycolic acid it can be up to a factor of 2.**

See figure legend. Also see figure caption: „The size of the dots indicates the initial steady-state mixing ratio (0.1–100 ppbv) used in the respective experiment.”

**6. Lines 140-141: It would be beneficial if the authors could include high-**

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**resolution mass-spectra in the Supplement to demonstrate that studied compounds did not thermally decompose. Many of observed compounds are known to undergo ionic fragmentation (e.g.,  $C_6H_9O + 4$  is an ionic fragment of levoglucosan as discussed later in the paper), so how do the authors know that there is no additional thermal decomposition resulting in formation of those fragments?**

The reviewer raises a good point; our statement was too general. What we can state is that we did not observe any decarboxylation products. This has been corrected in the revised manuscript: "Exposing the sample gas to heated surfaces in an analyzer, may thermally degrade some analytes. It is important to note that none of the acids studied in this work decarboxylated at  $T_{drift} = 120^\circ C$ . It may, however, be necessary to use a lower  $T_{drift}$  when more thermally labile analytes are targeted."

**7. Section 3.3: The authors should provide a table in which they should list compounds that were used to compare performances of various instruments. What ketones, carboxylic acids and hydroxycarbonyls were used in this study?**

The compound names have been included in the figure.

**8. Figure 4: It seems to me that the authors did not measure response times for the same compounds using a conventional PTR-MS and a new EVR PTR-MS as yellow and dark red points are located far from each other (for yellow dots  $5 < \log C_0 < 7.3$  while for dark red dots  $0.5 < \log C_0 < 5$ ). I suggest that the authors include additional data points on this figure to demonstrate how the performance of the EVR PTR-MS instrument compares with a conventional IONICON PTR-MS for the same group of compounds.**

We agree that including more data points would be valuable, but in this case adding more data from the conventional IONICON PTR-MS would not give additional information. We show that for 2-tridecanone ( $\log C_0 \sim 5$ ) the response is almost identical to that of the EVR-type instrument. Since the instrumental response time is already very close to the volumetric exchange time of the drift tube, we refrained from study-

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ing shorter-chain and thus more volatile ketones. We also show that for *cis*-pinonic acid ( $\log C_0 \sim 3$ )  $\tau_{90}$  is close to 2000 s for the conventional PTR-ToF-MS instrument, meaning that the three SVOCs we studied with the EVR-type instrument are simply not measurable with a conventional analyzer. It would certainly be interesting to compare the performance in the  $3 < \log C_0 < 5$  range, but there we do not have any data (except for glycolic acid) and it would become a disproportionate effort to perform additional measurements study with two instruments.

**9. Figure 4: I agree with the Referee 1 that operational temperatures should be clearly stated in the legend of this figure.**

We have included the operational temperatures in the legend.

**10. Figure 6: The authors state that mass concentrations of observed compounds were calculated under the assumption that all of these compounds were detected at the collisional rate. The authors should clarify how this collisional rate was calculated. In addition, they should explicitly mention it in the text as this is a fairly important assumption and can strongly affect the authors' conclusion about mass yields of observed compounds.**

This figure has been moved to the Supplement and we provide additional details in the figure caption.

**11. Conflict of interest: I agree with the Referee 1 that the authors should mention the fact that IONICON has been advertising the EVR PTR-MS setup for quite some time now.**

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

**Technical corrections:**

**1. Line 307: remove "in an"**

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Done.

C7