

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

Anonymous Referee #2

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This manuscript presents the development and characterization of a new type of inlet for PTR-MS instruments that allows for detection and quantification of less volatile compounds. The authors demonstrate how the new instrument can be integrated with the CHARON setup and used for online measurements of gas- and particle-phase organics. This kind of instrument development is quite valuable, and I think these data (including intercomparison of response times for various CIMS instruments) should be available for the CIMS community. However, on a whole the presented data and discussion are somewhat limited, and the paper does not cover some important parameters of the new instrument that are critical for its full characterization. While the paper is fairly well-written, it would require some major revisions before being published in Atmospheric Measurement Techniques.

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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.

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).

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_4^+ 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 quantification of these compounds.

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 non-oxidized 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.

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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.
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.
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 b_1 and b_2 ? I believe this is not explicitly discussed in the paper.
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.
6. Lines 140-141: It would be beneficial if the authors could include high-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?
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?
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 yel-

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low 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.

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

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.

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.

Technical corrections:

1. Line 307: remove "in an"

References:

1. Hansel, A., Scholz, W., Mentler, B., Fischer, L., Berndt, T. (2018). Detection of RO_2 radicals and other products from cyclohexene ozonolysis with NH_4^+ and acetate chemical ionization mass spectrometry. *Atmospheric Environment*, 186, 248-255.
2. Zaytsev, A., Breitenlechner, M., Koss, A. R., Lim, C. Y., Rowe, J. C., Kroll, J. H., Keutsch, F. N. (2019). Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH_4^+ CIMS) to oxygenated volatile organic compounds. *Atmospheric Measurement Techniques*, 12(3), 1861.

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