

## ***Interactive comment on “PTR-QMS vs. PTR-TOF comparison in a region with oil and natural gas extraction industry in the Uintah Basin in 2013” by C. Warneke et al.***

**C. Warneke et al.**

carsten.warneke@noaa.gov

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We thank both reviewers for their comments. The comments, all of which we have addressed below, are clearly very insightful and have improved the manuscript. It is clear that the reviewer is a very knowledgeable expert on TOF operation and we gladly took all the suggestions.

Review of PTR-QMS vs. PTR-TOF comparison paper Warneke, et al., AMTD, 2014: This manuscript reports the comparison of two proton transfer reaction chemical ionization mass spectrometers, where the primary difference between the instruments

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lies in the mass analyzer – one using the traditional quadrupole mass filter, and the other using a new time of flight mass spectrometer. The ion-reaction portion of both instruments was similar in design and in operational conditions, such that a reasonable characterization of the differences between the mass analyzers was possible. Overall, this work shows quite clearly that the PTR-QMS and PTR-TOF work in much the same fashion for the field observations that were compared, and that, for almost all applications, the PTR-TOF will be the preferred instrument due to 1) its inherent ability to continuously monitor the entire mass range, and 2) its ability to separately quantify certain isobaric ions (given its superior resolution).

Recommendation: Overall, this paper is clear and well written, and appropriate for publication in AMT, which I recommend after consideration of the following points.

General: The text could be streamlined somewhat. There are several places where the same information is repeated.

Somewhere it would be good to define the term 'isobaric ions', distinguishing it from 'isomeric ions' arising from isomeric analytes, and point out that the latter are not separable using ToF separation, as they have exactly the same mass.

Answer: We have added the definitions of isobaric and isomeric ions and explained that the PTR-TOF can only distinguish isobaric ions on page 9.

Specific comments: P6567 L19: Reference Muller, et al., 2009 also for MS/MS PTRMS

Answer: We have added the reference.

P6569 L27-28: How were the apparent differences between the standards treated in the analysis? Not all of the compound sensitivities 'step' in sync with the tank change, i.e., m73 is different than m42, m33 (Fig2a); What is the reason for this?

Answer: The calibration standards are just different for each individual compound. They are not made individually and not from a single mother tank. Therefore it is not expected that all compounds would “step” in sync. For each compound in the calibra-

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tion standards, we have used historical calibration data (based on a large number of calibration tanks, MOCCS system measurements and known rate coefficients) to determine, which one of the tanks is likely the most accurate, and used those values in the final data analysis. The difference in the tanks is about 20%, which we have stated as our accuracy, even though the calibration values that we used are likely better than that. This is briefly explained in the text now on page 4.

P6570 L16: Extraction frequency of 250 kHz seems much too high for this instrument for a mass collection range of  $\sim 500$  amu. Recommend describing the ADC or TDC which was used.

Answer: The extraction frequency was 25 kHz. It is now correct in the text. A PCI based HPTDC (high performance time-to-digital converter) was used for the TOFMS data acquisition. It has eight channels with 25 ps time bin width. For TOFMS we do not run a faster time resolution than 100 ps bin width. The number of fast channels is 7 plus one trigger channel. The dead time is 10-20ns and the event size is 4 byte. This description of the HPTDC was added to the text.

P6572 L8: Poisson distribution.

Answer: We have added the Poisson distribution to page 6.

P6572 L11-12: Perhaps specify that this occurs for instruments operated in ion counting mode, and the under-counting is related to the ion-count-rate and the ion pulse-width (dead time).

Answer: We have added the discussion of the electron multiplier dead time to page 7.

P6573: I suppose for the reader to better understand this section it would be good to describe more details of the ToF operations, including the raw signal baseline stability (was the ADC/TDC temperature controlled), threshold level (was this dynamically varied or static?), average single ion peak height relative to threshold and how did this vary over the experiment. Was there a mass dependence to the average single ion

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peak height for the detector gains used in this experiment? What reagent ion signal is used to normalize the other signals ( $m/z$  19 or  $m/z$  21)?

Answer: The HPTDC was not temperature controlled and the threshold level was static. The single ion peak height and mass dependent changes were not systematically checked during the campaign; instead we performed frequent calibrations with a gas standard with compounds covering the mass range of interest, which is generally the preferred way of keeping track of the instrument sensitivity. We have added this discussion to the text. We used  $m/z$  21 to normalize to the primary ion signal. We have added this to the instrument description section.

P6577 L6: Insert 'individually' before 'measurable'

Answer: We have added "individually" as suggested.

Figure 4a: To the extent that these sensitivities are based solely on authentic calibrations, this shows that after correction for the well-known discrimination in the ToF pulser, the remaining mass-dependent discrimination for both the quadrupole and ToF analyzers is very similar. This might be worth some added discussion in the text.

Answer: We have added on page 6 that the remaining mass discrimination is similar between the instruments, because the PTR-QMS mass discrimination is relatively small.

Figure 7: Labels read  $m_{21}$ , but counts seem to be for  $m_{19}$ ?

Answer: We have corrected the Figure and the label reads  $m_{21} \times 500$  now.

Figure 9: This figure might be enhanced if the high resolution ToF peak-fits are added to the lower two panels, and add molecular assignments. What are the units for the ToF data? Counts/extraction/? Can these be made the same as those used for the QMS data?

Answer: We have tried to add the high resolution fits to this plot, but the plot gets too

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crowded and the main information is not clear anymore. Instead we have added labels for some example peaks. This clearly demonstrates the advantage of the PTR-TOF versus the PTR-QMS for identifications of various  $m/z$ . We have also changed the label to counts/extractions. We prefer to leave the units as the raw data units given in the Figure.

Technical corrections: P6566 L7: insert 'to charge ratio' after 'mass'.

Answer: We have used mass to charge ratio now in the abstract.

Figure 2: solid red and solid magenta colors are difficult to distinguish in the print version. Suggest making these symbols more different.

Answer: We have changed the color and symbol for the m69 trace.

References: Müller, M, Mielke, LH, Breitenlechner, M., McLuckey, SA, Shepson, PB, Wisthaler, A, and Hansel, A: MS/MS studies for the selective detection of isomeric biogenic VOCs using a Townsend Discharge Triple Quadrupole Tandem MS and a PTR-Linear Ion Trap MS, *Atmos. Meas. Tech.*, 2, 703-712, doi:10.5194/amt-2-703-2009, 2009

In addition to the replies to the reviewers we have also found a mistake for  $m/z$  107 in Figure. The hydrocarbon and single oxygen VOC contribution were switched. We have corrected this figure.

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