

Interactive comment on “Development and characterization of a High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS)” by T. Mikoviny et al.

T. Mikoviny et al.

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We thank the referee for her/his careful reading and positive feedback. We have adopted most of the suggested changes.

Page 189, line 2 - I would suggest replacing the “and” at the end of this line with “or”. This sentence would then read: “; from now on referred to as the high E/N mode) or 87 Td I recommend this minor change since the instrument can be operated in either the high E/N or low E/N mode but not both simultaneously.

C128

We have applied the suggested correction.

Page 189 - description of the new hollow cathode (HC) ion source design. Traditional HC ion sources have a water flow exhaust line that is pumped. This new design seems to lack this feature. Is this an oversight in the schematic or can the HC source be operated without this pumped exhaust line? It is my understanding that the HC ion source must operate at a pressure lower than the drift tube. The authors need to comment on this change or adapt their schematic to show the presence of this exhaust line.

The reviewer is correct. We had overlooked this detail. The schematic has been adapted.

Page 189, line 10 - The authors state there are “three 0.5 mm diameter orifices which were aligned with the hollow cathode cylinders.” I guess I don’t understand this statement. I see that the drift tube is bound on either end by apertures and that there is another aperture at the entrance to the quadrupole mass spectrometer. Are the authors referring to these apertures? If so, I ask that the authors expand their discussion to more clearly identify the location of the three apertures being referred to.

To clarify the details, we have expanded our discussion and have also adapted our schematics (Fig. 1). “The exit anode lens had one central orifice of 0.8 mm diameter and three 0.5 mm diameter orifices which were aligned with the cathode hollow cylinders. The three off-axis orifices had the primary function of reducing the pressure in the discharge region, thus improving the discharge stability.”

Page 189, line 21 - The Varian pump is a TriScroll 600 - the “s” in “Triscroll” should be capitalized.

We have applied the suggested correction.

C129

Figure 1 - It seems that there should be a valve or second aperture in front of the scroll pump on the inlet line, otherwise the drift tube pressure would be reduced to the backing pressure of the scroll pump.

The schematic has been adapted to include this important detail.

Page 190, line 22 - I don't understand the sentence: "HT-PTR-MS sampling times were compound specific and ranged from 20 ms to 1 s." Are the authors referring to ion signal averaging times? This seems that this is case.

We have modified this sentence to include the signal integration times (see also comment from referee #2). "Ion signal dwell times were compound specific and chosen as follows: dimethyl sulfoxide (m/z 79: 0.1 s), ammonia (m/z 18: 20 ms), monoethanolamine (m/z 62: 0.5 s), levoglucosan (m/z 85: 0.5 s), oxalic acid (m/z 91: 0.5 s), cis-pinonic acid (m/z 167: 1 s)."

Page 191, Ion source performance - In this section the authors' state that that they optimized the quadrupole for high m/z signals and that this reduced the detection efficiency of the primary ions. This is useful statement, although it also infers that other low mass ions are being discriminated against. I find myself objecting to the final sentence in this section. Maximizing the reagent ion signal is somewhat of a senseless exercise as detecting more primary doesn't in any way translate into higher sensitivity. Absolute sensitivity is controlled by the density of the primary ions in the drift tube and is not affected by how we tune our mass spectrometer. The process of correcting ion intensities for transmission bias compensates for any observed variation in primary signal related with detection efficiency. I would ask the authors to omit the last sentence. They report response factors as cps/ppb. Anyone using a PTR-MS knows that this is the true figure of merit for expressing sensitivity and not the stated primary ion count rate.

C130

We fully agree with the reviewer's assessment, except on her/his final statement: "Anyone using a PTR-MS knows that . . .". It is our experience that the mass spectrometers in most PTR-MS instruments have been optimized for maximum primary ion signal detection. In addition, it is common usage in the community to compare the performance of different PTR-MS instruments by simply looking at primary ion numbers. Our description makes clear that different results are obtained with different mass spectrometer settings. It also allows to compare the performance of the HT-PTR-MS to standard PTR-MS instruments with different settings. We feel it is important to have these aspects explicitly stated in the literature and we thus suggest not to modify this paragraph.

Page 192, line 14 - Consider replacing "... both hexanal and decanal." with ... either hexanal or decanal. I think this makes the sentence a little easier to read.

We have applied the suggested correction.

Page 192, line 16 - Consider replacing "induces" with promotes. Increasing the temperature "promotes" the fragmentation of the protonated species. Both of these compounds fragment at 25C and so promotes seems to be a better description than induces.

We have applied the suggested correction.

Page 193, line 11 - This is a picky detail. I compute the 2σ level for the parameters given to be ~ 150 ppt. I would ask the authors report a value of 150 ppt. The 100 ppt level reported in the abstract is reasonable since S is stated to 50 - 100 cps/ppt in which case the average would be about 100 ppt.

We think the reported number is correct.

S = 50 cps/ppb ; BG = 7 cps , t = 1 s

C131

$$DL = 2\sigma/S \text{ with } \sigma = \sqrt{BG} \text{ therefore } DL = 2\sqrt{7}/50 = 106 \text{ ppt} \sim 100 \text{ ppt}$$

Figure 2 - Axis labels - Consider showing the units in parentheses (cps), (ppb) rather than / cps or / ppb. The backslash / could be inferred that the units in the denominator.

IUPAC recommends this format in its Green Book.

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C132

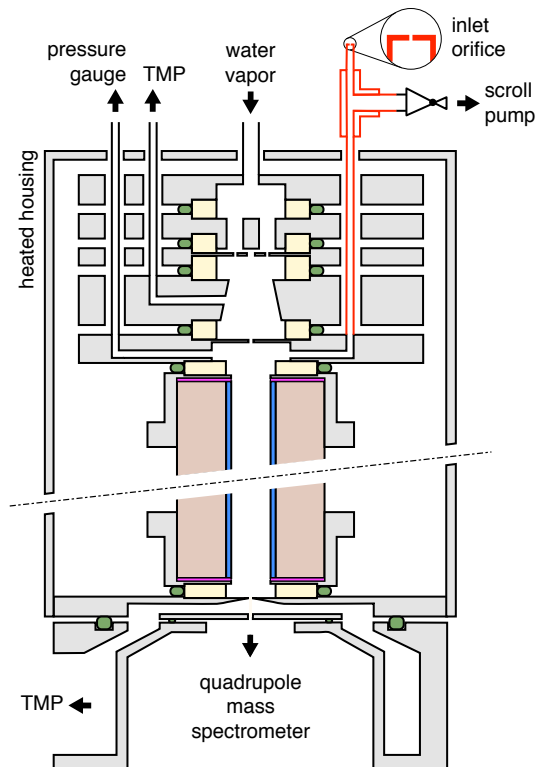


Fig. 1.

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