

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

### **Anonymous Referee #1**

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The paper by Mikoviny et al. describes the construction and characterization a new high temperature version of the proton transfer reaction mass spectrometer (PTR-MS). There is considerable motivation for the development of such an instrument as there is a clear need for a chemical ionization instrument that can be easily and efficiently coupled to a particle collection/thermal desorption apparatus. Thermal limitations of traditional PTR-MS instruments have seriously limited the application of this versatile technique to the study of particle-bound organics. The instrument described in this paper overcomes these restrictions without sacrificing performance. The new hollow cathode ion source design described in this paper is also particularly notable and will be interest to PTR-MS practitioners using conventional instruments. The ability to elim-

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inate photon-induced background without having to “bend” the drift tube is a tremendous asset as the bending process is tedious and often leads to unwanted leaks. I believe this paper and the instrument it describes will be of significant interest to many researchers and with some minor clarifications will be suitable for publication. This is by far one of the best papers that I have been asked to review in past several years. A very nice piece of work!

### Comments

Page 89, 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.

Page 89 – 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.

Page 89, line 10 – The authors state there are “ three 0.5mm 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.

Page 89, line 21 – The Varian pump is a TriScroll 600 – the “s” in Triscroll” should be capitalized.

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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.

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.

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.

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.

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.

Page 193, line 11 – This is a picky detail. I compute the  $2\sigma$  level for the parameters given to be  $\sim 150$  ppt. I would ask the authors report a value of 150 ppt. The 100 ppt

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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.

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.

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