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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "Real-time monitoring of trace-level VOCs by an ultrasensitive compact lamp-based VUV photoionization mass spectrometer" *by* W. Q. Sun et al.

**Anonymous Referee #4**

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Summary and General Comments:

Sun et al., describe a lamp based photoionization mass spectrometer for the measurement of benzene. Low detection thresholds are achieved (3 ppt, 2 sigma, 10s) and measurement of ambient air, sampled from the author's laboratory window are reported. The paper is likely publishable, following the authors attention to the following points:

Title/abstract: This paper demonstrates a detection method for benzene. As such, the title should reflect this, not VOCs. The authors have not shown that this technique is a

specific, sensitive measurement for VOCs.

Abstract: The word “compact” is used to describe the instrument in the abstract, however dimensions, weight and power demand are not given in the manuscript to justify this relative to other ToF mass analyzers used in the field.

Page 5878, line 20: It is not clear what the authors are stating here with respect to methane? Is it that non-methane hydrocarbon concentrations are often sub ppb? This is true in some locations, but not all. This needs to be clarified and referenced.

Page 5878, line 21: The use of words such as “extremely” and “ultra” are present throughout the manuscript. These adjectives are meaningless without context. I suggest they be removed and the instrument metrics be described in objective terms (e.g., LOD).

Page 5879, line 6: I suggest the others provide specific reference for the LOD of a PTR-MS at 10s integration time for benzene for specific comparison as this is the measurement now most commonly used. For many VOC, detection limits for PTR-MS can be sub ppt for 30-180s signal averaging times.

Page 5879, line 8: The authors need to be more specific on the mechanisms for the matrix effects that PTR-MS suffers from, for what VOC? For benzene?

Page 5880, line 9: How does the photon flux from this lamp compare to those of other laser based systems. Is it expected that the ionization rates would be comparable? There should be some discussion of the trade-offs for the lamp vs laser systems in terms of power and wavelength.

Page 5880, line 21: What is the estimated pressure in the photoionizer for A and for B? Are they the same?

Page 5880 line 24: How does the lens configuration “focus” the ion beam? Is there any RF component here?



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Page 5881, line 1: I am confused on the use of “collimated” for describing hardware?

Page 5881, line 6-12: What is the extraction frequency? The m/z dependent ion duty cycle is directly dependent on this number. How was it chosen, what is the sensitivity to this number? How is the acquisition time 10s? This must be the averaging time? Why 10s? Why not save at 10Hz and average in the analysis software.

Section 2.2: An uncertainty analysis needs to be included for the final concentrations of benzene that were used for calibration. There are multiple stages of dilution used and each flow and volume measured carries uncertainty. This propagated uncertainty should be included.

Page 5883 line 4: More discussion is needed on the source and energy of the photo-electrons that are generating N2+ and O2+ in the source region. Specifically, with input radiation of 10eV and the associated work function of the metal surface, where is the energy coming from to ionize N2+? I must be missing something?

Page 5883: If N2+ and O2+ are present in the ionization region for either photoionizer, can’t the ionization mechanism also be charge transfer? To what extent is this playing a role?

Page 5883: What does the spectrum look like on ambient air? Specifically, I would be very surprised to see N2+ peaks in the presence of water vapor as it should charge transfer. What is the role of water in the ionization process?

Page 5883 line 20: Why does the baseline at m/z of 78 decrease with photoionizer B? What is the mechanism? It seems like the authors argue that the signal at 28 and 32 are directly impacting the baseline at 78? This does not make sense to me for a properly tuned ToF. Again, what are the differences in system pressures for the two designs?

Page 5884 line 10: I suggest referencing benzene concentrations in the atmosphere and not VOC mixing ratios.



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Page 5884 line 16: It should be stated what the averaging time is for this (10 s), also, what is the uncertainty in this number? Is this a calibration done at 0% RH? What is the dependence on RH?

Page 5884 line 27: Is it reasonable to assume a factor of 3 improvement in ion transmission? If this is true, I think it warrants more discussion on the comparison of these techniques as this represents a significant advance.

Page 5885 line 9: The ambient spectra of figure 4 looks very similar to a PTR-MS spectra if the drift tube was at high pressure (permitting larger water clusters to form). Looking at this spectra, the ionization mechanism for benzene could very easily be proton transfer as well. It would be very helpful to see a zoom in of the spectra at 78, 79 and a calculation of the 78/79 ratio to confirm that the ionization mechanism is photoionization and not proton transfer. Also, along these lines how is water ionized in this design? Again, discussion of pressures and ion-molecule interaction times would be very helpful.

Page 5885 line 26: What is the bias voltage between the VUV lamp and the photoionizer and how will this eliminate the water clusters?

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 5877, 2015.