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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.

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Responses to anonymous referee #4's comments

Q1. 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. Answer: VUV photoionization does have its limit. The VOCs which have the photoionization potentials higher than 10 eV, such as CH2O (10.88 eV), cannot be detected by the instrument with a Kr lamp as a VUV light source. However, most VOCs are detectable to this instrument. The

partially enlarged plot in Figure 1 shows that the signals from non-aromatic VOCs were obtained. Thus, we would like to keep the title in the Discussion.

Q2. 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. Answer: In fact, the prototype of the instrument is pretty big due to assembling with commercial high voltage supplies and separate electronics. The length $\times$ height $\times$ width of the instrument is 1200 mm $\times$ 1200 mm $\times$ 800 mm. However, the core part of the instrument, the orthogonal TOF, is 450 mm (L) $\times$ 220 mm (H) $\times$ 258 mm (W). It can be developed into a very compact instrument.

Q3. 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. Answer: Page 5878, line 20: The "in addition to methane" was deleted.

Q4. 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). Answer: The sentence "extremely low background noise was obtained" in page 5878, line 7 was changed to "an 8.7-fold improvement in the standard deviation of the noise was obtained"; The word "extremely" in page 5878, line 22 and 5879, line 6 were removed; The sentence "An extremely low noise level and excellent detection sensitivity were observed" in page 5879, line 28 was removed. The revision for the word "ultra": The "ultra" in the title was not removed; The "ultrasensitive" in page 5878, line 7 and page 5886, line 14 was removed; The "ultra" in page 5879, line 27 was removed.

Q5. Page 5879, line 6: I suggest the others provide specific reference for the LOD of a PTR-MS at 10 s 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 30-180 s signal averaging times. Answer: Thank the reviewer for calling for the LOD of a PTR-MS at 10 s integration time for benzene, which will offer better comparison. According to your suggestion, the sentence "The proton-transfer-reaction mass spectrometer (PTR-MS) has been demonstrated for the real-time measurement of trace gases with limits of detection (LODs) in the low ppbv to high pptv range." was changed to "The proton-transfer-reaction mass spectrometer (PTR-MS) has been demonstrated for the real-time measurement of trace gases in the atmosphere with limits of detection (LODs) in the pptv level."1.

Q6. 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? Answer: The biased comment will be deleted in the revised manuscript.

Q7.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. Answer: Table 1 shows the performances of instruments using different light sources. It is believed that the lights with similar wavelengths and photon fluxes from VUV lamps may have similar ionization rates. Of course, the structures of the ionizer, ion immigration optics, and TOF system would affect the LOD of instruments. Additionally, instruments with pulsed laser-based VUV light sources may be hard to achieve low LODs due to the lower duty circle of laser pulses, though pulsed laser-based VUV light sources can generate higher fluxes of VUV light.

Q8. Page 5880, line 21: What is the estimated pressure in the photoionizer for A and for B? Are they the same? Answer: The estimated pressures inside of photoionizers A and B are $\sim$100–300 Pa and $\sim$500–1000 Pa, respectively.

Q9. Page 5880 line 24: How does the lens configuration "focus" the ion beam? Is there any RF component here? Answer: The ions are focused by the static electric fields generated from the simple ion optics. However, the real situation in the ion immigration

region is very complicated. The trajectory of the ion cannot be simulated simply with the software SIMION 8.0 due to the presence of ion-molecule collision in the early part of the ion immigration region. There is no RF components used.

Q10. Page 5881, line 1: I am confused on the use of "collimated" for describing hardware? Answer: Page 5881, line 1: The sentence "the excitation tube of the VUV lamp, the photoionizer, and the ion-immigration optics are collimated" was changed to "the excitation tube of the VUV lamp, the photoionizer, and the ion-immigration optics are concentric".

Q11. 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 10 s? This must be the averaging time? Why 10 s? Why not save at 10 Hz and average in the analysis software. Answer: The extraction frequency is 35000 Hz. The signal of ions increases with the increase of the extraction frequency. The used maximum extraction frequency, 35000 Hz, is employed under the consideration for the desired mass range. In the manuscript, the acquisition time means the averaging time. There is no special reason for setting the averaging time (10 s). We simply used the acquisition software offered by the company of the digitizer and the 10 s averaging time yields signals strong enough for this experiment.

Q12. 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. Answer: The uncertainty analysis for the triple stages of dilution was described as follow. Firstly, a 1000 μL micropette pipettor (Eppendorf Co. Limited) was used in the first dilution stage. The uncertainty for this stage is $\pm$ 0.8% on the base of the uncertainty of the micropette pipettor (systemic error + random error). Secondly, a 100 μL micropette pipettor was used in the second dilution stage. The uncertainty for this stage (systemic error + random error) is $\pm$ 1%. Finally, a 1 ml injection

syringe was used in the third dilution stage. The uncertainty for this stage is ± 3.5% on the base of the uncertainty of the injection syringe (systemic error + random error). The whole uncertainty for the dilution is < 5% (systemic error + random error). This information will be added in the revised manuscript.

Q13. Page 5883 line 4: More discussion is needed on the source and energy of the photoelectrons that are generating N2+ and O2+ in the source region. Specifically, with input radiation of 10 eV and the associated work function of the metal surface, where is the energy coming from to ionize N2+? I must be missing something? Answer: For photoionizer A, a large amount of VUV light illuminates the ion optics biased at dozens of volts, so lots of N2+ and O2+ are generated. The observed N2+ and O2+ survive due to the low pressure in the region of ion immigration. For photoionizer B, the baffle doesn't block 100% VUV light from entering the region of the ion optics and tiny amount of VUV light still enters the region of the ion optics.

Q14. 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? Answer: Thanks a lot for great comments. According to Q20 below, we analyzed the data and concluded that the contribution ratio from photoionization and the proton transfer may be ∼5.6:1 for photoionizer B. See the answer to Q20.

Q15. 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? Answer: The spectrum on ambient air with photoionizer B is shown in Figure 2. The tiny observed N2+ may be formed outside of the photoionizer B and survive due to less ion-molecule collisions. The baffle in photoionizer B doesn't blacks 100% VUV light from entering the region of the ion optics and tiny amount of VUV light can still enters the region of the ion optics. The answer to Q20 discusses the role of water in the ionization process.

Q16. Page 5883 line 20: Why does the baseline at m/z of 78 decrease with photoion-

izer 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? Answer: We speculate that the noise at m/z of 78 under the condition of photoionizer A mainly results from the secondary ions induced by photoelectrons generated in the ion immigration region and the TOF system. These secondary ions are not controlled by the designed ion optics. The working pressures of the TOF regions for photoionizer A and B are ∼2ïĆť10-3 and ∼3ïĆť10-3 Pa, respectively.

Q17. Page 5884 line 10: I suggest referencing benzene concentrations in the atmosphere and not VOC mixing ratios. Answer: The sentence "The benzene concentrations employed in the calibration were in the low ppbv range considering that trace gases are present in the atmosphere at ppbv levels or lower." is changed to "The benzene concentrations employed in the calibration were in the low ppbv range considering that benzene is present in the atmosphere at several μg m-3."8.

Q18. 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? Answer: The sentence was rephrased as "The slope of the fitted line indicates that the detection sensitivity of the VUV-PIMS is ∼1.25 ïĆś 0.02 counts pptv-1 with 10 s of the averaging time." The uncertainty 0.02 was obtained from 5 measurements. We did not measure the relative humidity during the experiment. In the experiment of the sensitivity measurement, high-purity nitrogen and oxygen were used as buffer gas. We estimate that RH was very low during the experiment. We didn't conduct the experiment to study the dependence of the signals on RH. We will study the dependence on RH in the future.

Q19.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. Answer: The sensitivities of similar instruments are listed in Table 1. We think that the gain in the sensitivity of

this instrument mainly results from the powerful VUV lamp we used and the short ion immigration region.

Q20. 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. Answer: The carbon isotope ratio, 12C/13C, is 98.893 : 1.107. Considering 6 carbon atoms of benzene, the theoretical ratio of signal intensities at m/z 78 and 79 (I78/I79) should be 1 : 0.067. Figure 3 shows the signal intensities at m/z 78 and 79 are 4957 and 1212, respectively, which is equal to 1 : 0.24. The experimental result shows that the proton transfer reaction may contribute to the formation of m/z 79 if no other VOC can contribute to m/z 79. Deducted by the isotopic contribution, $\sim$874 counts at m/z 79 can be assigned to 12C6H7+. So roughly, the contribution ratio from photoionization and the proton transfer may be 4957 : 874 ($\sim$5.6 : 1). We speculate that water molecules are ionized by photoelectrons accelerated by the field between the metal flange of VUV lamp and the photoionizer, and the proton transfer reaction would occur inside of the photoionizer. The pressure of sampled gas drops rapidly outside the photoionizer. The study of pressures and ion-molecule interaction times will be interesting. Limited by the experimental data we obtained, we hope that we can discuss this issue in a separate paper in the future.

Q21. Page 5885 line 26: What is the bias voltage between the VUV lamp and the photoionizer and how will this eliminate the water clusters? Answer: The bias voltage between the metal flange of the VUV lamp and the photoionizer is 38 V. A piece of metal mesh is attached to the side of photoionizer connecting to the VUV lamp, which eliminates most protonated water and water clusters. Otherwise, the protonated water

and water clusters would reach 105 cps.

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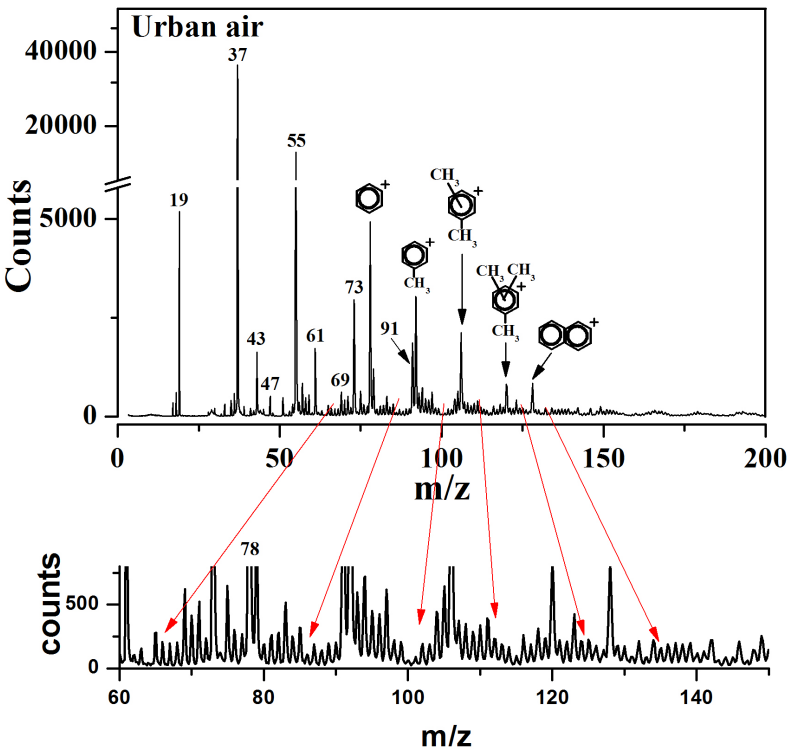

Fig. 1. Partially enlarged plot of outdoor air VUV-PIMS spectrum at m/z 60-150

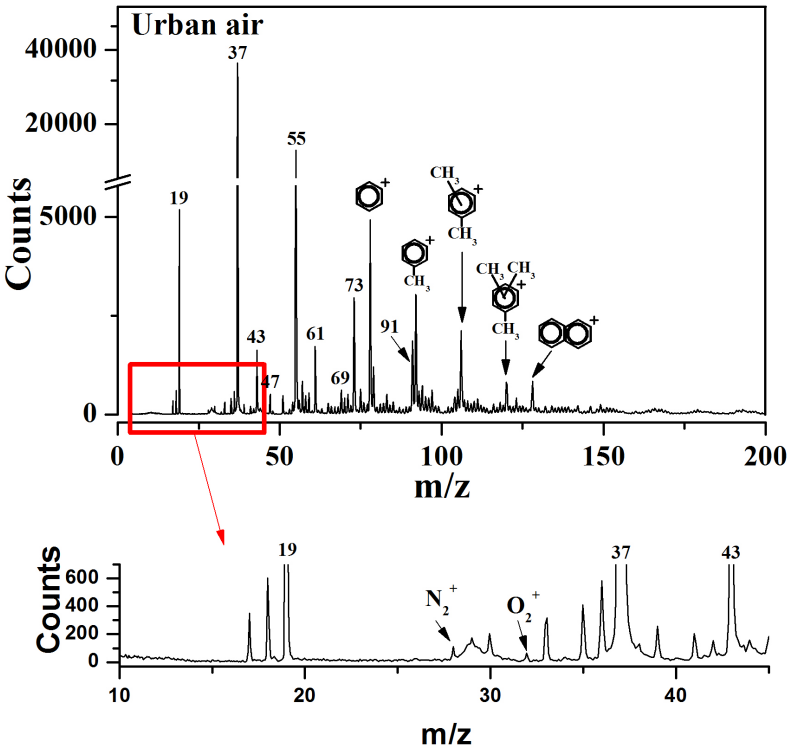

Fig. 2. Partially enlarged plot of outdoor air VUV-PIMS spectrum at m/z 10–45

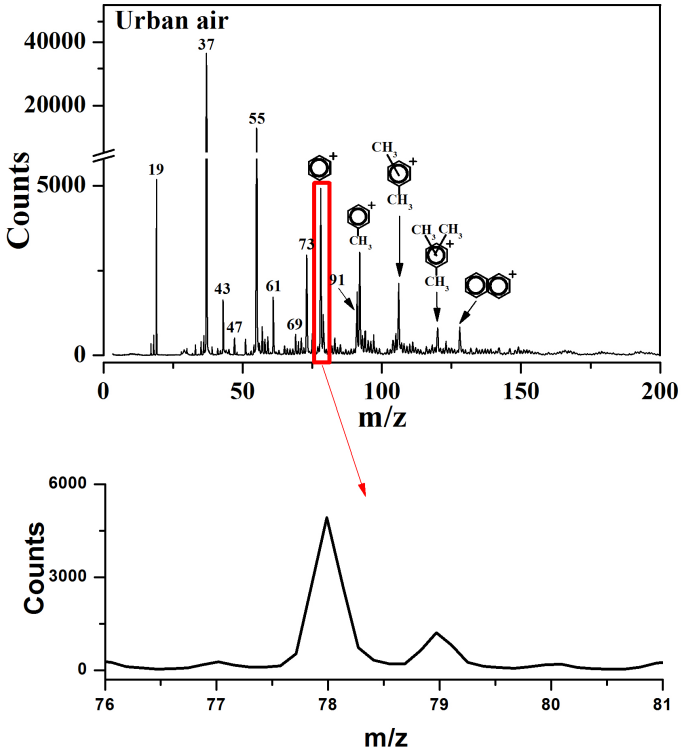

Fig. 3. Zoom in of the spectra at 78, 79

Table 1. The performances of instruments using different light sources

Type of VUV	Photon flux (photon/s)	LOD	Type of MS	Year	ref
radio frequency-powered VUV lamp	~5×10^{14}, Kr, 121.6 nm	3 pptv for benzene	TOF	2015	this study
laser	~1.6×10^{18}, 118 nm	10 ppbv for benzene	TOF	2010	2
electron-beam-pumped rare gas excimer VUV lamp (EBEL)	3×10^{17}, kr_2* excimer, 147nm	2 ppmv for benzene	TOF	2002	3
EBEL	1.9×10^{19}, Ar*, 126nm	50 ppbv for benzene	TOF	2005	4
EBEL	~1.5×10^{13}, Ar*, 126nm	50 ppbv for benzene	Quadrupole	2005	5
lyman-α atomic radiation based microwave discharge lamp	~10^{14}, H_2/He, 121.6 nm	10 pptv for trichlorobenzene	Ion trap + TOF	2005	6
Commercial Kr VUV lamp	10^{11}, Kr, 121.6 nm	35 ppbv for toluene	TOF	2011	7

Fig. 4. Table 1. The performances of instruments using different light sources