

Interactive comment on “A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H_3O^+ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere” by B. Yuan et al.

Anonymous Referee #1

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General comments:

This paper introduces a H_3O^+ ToF-CIMS, an instrument based on PTR-MS technology using a time-of-flight mass spectrometer instead of a quadrupole employed in classical PTR-QMS.

The abstract of the manuscript creates the impression that the use of a time-of-flight mass spectrometer represents the major novelty of this instrument, which is clearly not the case. As the authors mention in the text, PTR-TOF-MS are available since more than 10 years and were commercialized several years ago. The first PTR-TOF-MS

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used an electrostatic lens system to transfer ions from the chemical ionization region to the TOF-MS. A recent paper by Sulzer et al. (2014) describes an PTR-Qi-TOF using a quadrupole to transfer the ions to the time-of-flight mass spectrometer, similar to the H_3O^+ ToF-CIMS presented in this manuscript. Therefore I have difficulties to recognize the novelty of this instrument. The authors repeatedly point to the advantages of the H_3O^+ ToF CIMS compared with a PTR-QMS. However, the PTR-TOF-MS or even better, the PTR-Qi-TOF, would be much more appropriate for comparison.

Given the described high humidity dependence of the H_3O^+ CIMS, its applicability in field experiments might be questioned, since it strongly complicates data post-processing and interpretation.

A pretty long part of the manuscript is dedicated to the inability of the small segmented quadrupole (SSQ) to map the primary ion distribution present in the drift tube onto the detector. However, for proper data analysis it is crucial that the signals at the detector represent the actual conditions in the chemical ionization region, since normalization of protonated VOC signals to a not well defined number of primary ions could introduce large errors. I'd assume the simplest way to test this is to use two VOCs of similar mass, one of which is reacting with H_3O^+ only, while the other reacts with H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. That way it should be possible to infer if the measured ratio of H_3O^+ to $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ions corresponds to the ratio present in the drift tube of the instrument.

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Specific comments:

Line 79: Although isobaric compounds cannot be separated by a PTR-QMS, they are still measurable.

Line 136ff: I guess you mean catalytically cleaned air was passed to the instrument for 90 s every 30-40 min and the catalytic converter was continuously flushed with ambient air. Nevertheless, I doubt that you were able to measure a proper background

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of semi-volatile, sticky compound masses in such short time periods.

Line 140: same here for sticky compounds probably contained in the calibration gas standard.

Line 141: Why did you add calibration gas to ambient air? This way varying concentrations of compounds contained in ambient air and measured at the same mass-to-charge ratios as the calibration gas compounds could affect your calibration results.

Line 143ff: since you measured up to m/z 500 trichlorobenzene is not really suitable to calibrate the mass scale at the high end of the m/z range.

Line 163ff: I can imagine that in H_3O^+ TOF-CIMS the signals at m/z 19 and m/z 37 are in saturation and therefore not suitable to calibrate the mass axis.

Line 294: Why do you normalize to the H_3O^+ ion signal only, although you write that H_3O^+ is likely to cluster with other water molecules in the SSQ? Normalization to the sum of H_3O^+ and $H_3O^+(H_2O)$ ions seems to be more suitable in this case.

Section 426: this part is completely redundant. Why should the mass resolution of the H_3O^+ TOF-CIMS be different from that of other instruments using the very same TOF-MS? Also the advantages of a TOF-MS compared with a QMS have been extensively discussed previously.

Line 433: isobaric ions have per definition the same nominal mass.

Line 490ff: it is common knowledge that (VOC) instrument backgrounds change with instrument running time and humidity!

Line 649: Given the high humidity dependence of the H_3O^+ TOF-CIMS caused by the SSQ, its removal might ameliorate this issue. This would result in an instrument similar to the mentioned PTR-QiTOF-MS, for which systematic investigations of the humidity dependence introduced by the quadrupole interface are obviously missing so far.

Fig. S3: how comes you have double data points for some BSQ voltages?

Fig. S6: any explanation for the outlier around m/z 110

Fig S8: pretty brave to specify the masses with four decimal places...

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