EGUsphere, referee comment RC3
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Comment on egusphere-2022-880

Anonymous Referee #3

Referee comment on "Online measurements of cycloalkanes based on NO^+ chemical ionization in proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS)" by Yubin Chen et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-880-RC3, 2022

General comments on "Online measurements of cycloalkanes based on NO^+ chemical ionization in proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS)"

The authors investigate the simultaneous detection of cycloalkanes and acyclic alkanes using a PTR-TOF-MS with NO^+ ionization chemistry. The measurement technique was tested in a laboratory before applied in the field, here the city of Guangzhou, China and at a chassis dynamometer. The authors confirm that cyclic alkanes are ionized via hydride ion transfer while isomers of alkanes, alkenes, cluster with NO^+. Using a gas standard containing cyclic and acyclic molecules their sensitivity was determined. Effects of humidity and tubing were also considered by the authors. Their motivation is the contribution of cyclic and bicyclic alkanes to the formation of SOA in urban environments or from vehicle exhaust. They also report different ratios for cyclic and acyclic alkanes in diesel and gasoline exhaust.

Further investigation of the application of PTR-TOF-MS with NO^+ ionization chemistry is of great interest for the field if VOC detection. The results provide a new dataset for C10 to C20 alkanes under polluted conditions. I thus recommend that the work is published.

Specific comments:

Line 100: This sentence sounds as if cycloalkanes and acyclic alkanes have never been measured simultaneous in ambient air before, but Koss et al., 2016 did that to my knowledge.

Line 118: The authors show one part of the ionization sequence, but the formation of NO+ ions in the ion source is more complex. See Karl et al., 2012 (doi:10.5194/acp-12-11877-2012).

Line 120: The authors state that impurities are minimum, but no values are given. Also it is known from Yuan et al., 2016 that primary ion signals as well as signals of the impurities can be influenced by the ion guide. This study used an instrument including an ion guide, thus it would be important to rule out artefacts arising from that.

Line 130: VOCs can also cluster with H3O+, I suggest writing: Compared to proton transfer reactions occurring mostly between H3O+ ions and VOCs species…

Line 209: As far as I understood the interferences can still be up to 15 %. To my opinion this is worth mentioning like (< 15 %).

Line 211: The authors mention before that the calibration experiments were done with a gas standard containing compounds listed in Table S1, but the information would be very helpful in this chapter as well.

Line 238: The authors show how vehicular emissions drop to 10 %, but how did they measure that technically. Was the inlet brought close to the cars exhaust? How was the switching from detecting exhaust to clean air done? I imagine they used a dilutive flow of synthetic air, but this is not described in the manuscript.

Line 249: Did the authors calculate average sensitivities for cyclic and bicyclic alkanes separately? The fragmentation seems to be different.

Line 269: Since there are also cases where cyclic alkanes are more abundant than acyclic alkanes I suggest writing: … suggestion they predominantly came from same emission sources.

Line 289: The authors report completely different emission pattern from diesel vehicles compared to gasoline. Has this been detected before for other compounds? Is there a known explanation for the difference?

Line 315: For some alkanes (C_{15}, C_{16}, C_{18}) the ratio observed in London is much larger than detected in this work. This is not similar. I would appreciate a more detailed discussion at this point.

Figure 8: Here it would be very helpful to see error bars. AS the authors present averaged values the variability is important to proof significance, especially for the comparison of the ratios.

Technical corrections:

Line 31: For a better reading I recommend writing: Appling this method, cycloalkanes were successfully measured at an urban site in southern China and during a chassis dynamometer study for vehicular emissions.

Line 35: These results demonstrate that NO+ PTR-ToF-MS…

Line 45: Components and concentration levels of organic compounds largely affect atmospheric chemistry, …

Line 75: For a better understanding I recommend writing: Based on measurements of gas chromatographic techniques, the signals of unspeciated cyclic compounds can be determined. This is done by subtracting the signal of speciated IVOC from the total signal

for each retention time bin according to the series of *n*-alkanes.

Line 103: Typo: … ambient air and from emission sources…

Line 105: I suggest to write: The results of laboratory experiments to characterize product ions,…

Line 113: mass resolution instead of mass resolving

Line 147: In this study, we investigate characteristic ions of cycloalkanes generated by the NO+ ionization…

Line 149: I suggest using species instead of chemicals.

Line 160: Typo: sensitivities

Line 186: The sentence is confusing to me, I suggest writing: As mentioned above, the characteristic peaks of cycloalkanes under NO+ ionization are consistent with the ions that

are received at the attempts to utilize H3O+ PTR-MS. For the latter method though sensitivities are reported to be lower.

Line 193: The isomers… (without ‘as’)

Line 202: I recommend adding: …which are similar fragmentation ions from NO+ ionization of the two species and …

Line 212: Figure S4 is never mentioned in the manuscript.

Line 241: Typo: …but relatively lower than determined for those acyclic alkanes.

Line 307: Fig. 8b instead of Fig. 9