Review of amt-2021-355 (Antonia Zogka et al. 2022)

General comments

The manuscript proposed by Antonia Zogka et al. present the application of a Selected Ion Flow Tube Mass Spectrometer (SIFT-MS) to the measurement of 2 challenging gases (glyoxal and formaldehyde), at different relative humility.

The introduction is well constructed, and the subject well presented. The objectives are clearly defined, and the method explained with details. The results are worth publishing, but I think a deeper exploration of the results can be performed. For the moment, my opinion is that the results do not entirely support the conclusions raised by the authors (see my remarks below). I see 2 main points that can be explored by the authors to improve the paper:

- It is clearly showed in the paper that the humidity affects the sensitivity of the instrument. An interesting point discussed by the author is how humidity affect the protonation, giving about the chemical reactions that take place in a drift tube. The fragmentation is clearly discussed, but less attention is paid to clustering with H3O+. This should more extensively discussed. In addition, the sum of ions that can be attributed to one species (its fingerprint on the mass spectra) must be investigated, to see if their sum is constant with humidity. The effect of the normalization by primary ions (including water clusters) as frequently performed for PTRMS sometimes help to reduce the effect of humidity. This must be investigated and further discussed. Finally,
- The sensitivity of the SIFT MS to formaldehyde or glyoxal shows a nice relation with I_{37}/I_{19}, which traduces the ambient humidity variations. A proposition of a correction factor, in other words a formula to calculate the sensitivity as a function of this ratio can be obtained form these experiment to be used for monitoring studies. I suggest that the authors estimate the correct formula and discuss its use. This would improve the output of the paper and make a new step forward to ambient measurement of glyoxal and formaldehyde.

My recommendation is that the paper should published only after the authors addressed the points raised here.

Specific Comments

Is the ap2e ProCeas calibrated? Did the authors regularly check the blanks/background of the instrument? As this instrument is used as a reference to evaluate the sensitivity of the SIFT-MS, that is necessary. In addition, why not using the theoretical concentration based on dilution calculation to evaluate the SIFT sensitivity? As the concentrations in the standards are known and the flows are controlled by MFC, the theoretical concentration in the lines can be easily calculated.

A long path FTIR is used for several occasion in the experiments performed by the authors. Please provide at least a brief description of the instrument.

L.232-233: *"m/z =59 (C2H3O2+) and m/z=88 (C2H2O2·NO+), originating from H3O+ and NO+ respectively are used."* Why only these two ions are used? Are other potential ions (fragments, clusters, …) investigated?

L.250-291: This part is not results ad discussion but rather material and methods. Please move this part to the appropriate section in the manuscript

L.325: "*The background [H2O] has been estimated in the range of 10^{10} molecule cm^{-3}*". I do not see an explanation about how background [H2O] is calculated/measured.

L.342-343: "*sensitivity is not impacted by water presence when the relative ratio of I37/I19 is below ca. 0.55, irrespectively of the SIFT-MS operation mode.*" This is of great importance, because it implies that in CC, the ambient humidity will affect the sensitivity when RH is above 30 %, which almost always the case. So, unless a correction as a function of humidity is applied, CC cannot be used for ambient measurement of FM in H_3O^+ mode.

Section 3.1 In this section, the authors discussed the primary ions and the first water cluster under SC and CC. In the CC, the pressure is higher, with a lower residence time. I am thus wondering whether the 2nd water cluster ($H2O.H2O.H3O^+$) behave in this condition? Can it be important? Should it be considered? In addition, the figure S1 shows that there are more water clusters that H3O+ at 70 %. What can be the implication? Are these operating conditions valuable for humidity higher than 70 %, where the water cluster will be even more important?

It would also be interesting to comment (even briefly) about other possible clusters from NO^+ and O_2^+ ionization, and the whether the increasing pressure in the reactor increase the level of impurities that may arise from the source.

L.428-428: "*under SC the calibration factor at m/z 31 remains constant within the experimental uncertainties, and thus (R3) seems to have insignificant impact on the sensitivity of the instrument*" This sentence is true considering the uncertainty at 70 %, but it seems that higher RH will decrease (maybe a little) the sensitivity. I think that it should be noticed, or at least please precise that your sentence is true only for RH between 0 and 70 %, and for higher humidity more experiments would be needed.

Figure 6: This figure is interesting and shows that the effect of RH is not really a decreasing sensitivity but rather a change in distribution of ions, due to several reactions that occurred in the drift/reaction tube such as protonation, charge transfer, fragmentation, or clustering. The figure 6 only shows the fragmentation for glyoxal, which is already interesting. But it would be necessary to show other ions such as water clusters. Finally, it raises the following question: are VOC.H+ ions the most appropriate ones to monitor formaldehyde and glyoxal in ambient air (or in humid conditions in the lab)?

L. 610-612: Again, this shows that in real ambient conditions where RH is always higher than 10 %, that GL.H+ might not be the main ion formed in the drift, so maybe not the good one to follow if one wants to measure glyoxal

L. 676-677: I do not agree with the authors. The sensitivity shows a strong dependance on humidity, except for GL when NO^+ is used as primary ion, where only a small change is observed. Thus, it cannot be concluded that the instrument is stable as function of relative humidity.

L. 689-690: Because of the humidity dependance of the sensitivity, I am not convinced that it is suitable for indoor, where humidity can change depending on activities (for example, window opening, cooking, etc.). In my opinion, the only conditions suitable are lab experiment at controlled humidity.

L. 693-695: In my opinion, the sensitivity (several ppbs) in the NO+ ionization does not make it suitable for ambient monitoring, where low levels can be encountered.

Conclusion: please update the conclusion according to the remarks above.

Minor Comments

L.23: “using SIFT MS” – redundant with SIFT-MS in the line above…

L.24: Of course, SIFT-MS provides a nice opportunity to measure many organic gases, as demonstrated by many studies since several years. I do not the interest to place such a sentence here, as a main conclusion of the study. A sentence about what the measurement of glyoxal and formaldehyde by SIFT MS can bring to the atmospheric community (in term of monitoring, for example, to identify processes or whatever) would be much appreciated.

L.136: please remove i and ii. They are sub list of 2 item included in a list of i and ii. The sentence will be easier to read without this second list.

Section 2.1: Here, formaldehyde and glyoxal are sometimes written in full letters, and sometimes abbreviation. Please chose one form, and keep consistency through the paper (I noted few cases later in the manuscript)

L.141: What is the uncertainty on the formaldehyde concentration the cylinder?

L.168-169: Keep the same tense in the sentence

L.177: VOCs < 0.1 ppb. I guess this is for each individual VOC, not for the sum of VOCs. This precision must be added.

L.194: a space is missing between 1 and ppb

L.204-205: Please indicate the temperature of the flow reactor and the sampling port.