

First of all, we would like to thank again the reviewers for their comments on the manuscript. The changes made to the revised manuscript are summarized below.

### **Response to referee #1:**

*I believe the authors response to most of my comments. The technique this work deployed is advanced, and the data are beautiful. However, my only concern is that the current manuscript is, not precisely, in between of a research paper and a measurement report paper. The data analysis is covered by the techniques. It's far beyond a analytical chemistry paper, but still defective as an atmospheric chemistry paper. If the authors insist to submit it as a research paper, I have to say no with regret.*

We certainly insist to publish it as a research paper. However, to take into account the remarks of the referee #1 and as suggested by the editor, we shortened the technical section 2 moving important part of the technical description and details (about 6.5 pages and 2 tables) into the supplementary material (S1, S2 and S3). The technical section is now 1.5 pages which is more reasonable and makes the article more balanced with the result section being 4.5 pages (plus 1 table and 8 figures) and the discussion section being 7 pages (plus 1 table and 5 figures).

### **Response to referee #2:**

*1. Concerning the quantification of VOCs with a PTR-MS, I am not entirely sure I understand the answer provided by the authors. From the manuscript I understand that for each VOC both the  $H_3O^+$  and  $H_3O^+(H_2O)$  signals were used for quantification. If this is the case then my comment has not been addressed. While the formula used for VOC quantification is correct (I have never questioned that), its application must change depending on the relevant proton transfer reactions:*

*- for VOCs that react with  $H_3O^+$  only and do not react with the water cluster, only the  $H_3O^+$  signal should be used for the quantification because the  $VOC+H^+$  signal will depend only on the proton transfer reaction with  $H_3O^+$*

*- for VOCs that react with  $H_3O^+$  and with  $H_3O^+(H_2O)$  via proton transfer, then both the  $H_3O^+$  and  $H_3O^+(H_2O)$  signals should be used for the quantification*

*- for VOCs that react with  $H_3O^+$  via proton transfer reaction and with  $H_3O^+(H_2O)$  via ligand switching reaction, the product ion will appear at two different masses corresponding to  $VOC+H^+$  and  $VOC+H_3O^+$ . If the author decides to base the quantification only on the  $VOC+H^+$  signal, which is produced by the main reaction pathway, then only with  $H_3O^+$  signal should be used for the quantification because the reaction between the VOC and  $H_3O^+(H_2O)$  does not produce the  $VOC+H^+$ .*

We agree with the reviewer that the normalization procedure used for VOC quantification should not be the same for all VOCs and be dependent of the way it reacts with the reagent (i.e.  $H_3O^+$  and/or with  $H_3O^+(H_2O)$ ). This is actually the case in our quantification method since a factor ( $X_r$ , see eq. 1), which is compound dependent, is applied to the signal of  $H_3O^+(H_2O)$ . This factor is determined experimentally for each quantified VOCs and allows to take into account the different reaction pathways leading to the protonation of each VOC. In other word, if a VOC does not react with  $H_3O^+(H_2O)$  or if its reaction with  $H_3O^+(H_2O)$  proceed via ligand switching rather than by proton transfer, this factor will be zero and quantification will only be

performed normalizing the signal by  $\text{H}_3\text{O}^+$ . This has been clarified in the revised supplement S2 where the description of PTR-MS data acquisition protocol has been moved (see response to referee #1):

“ $X_r$  is a factor introduced to account for the effect of humidity on the PTR-MS sensitivity (de Gouw and Warneke, 2007) and is determined experimentally through calibrations performed at various relative humidity for each individual quantified VOCs. It therefore also allows to take into account the reaction pathways of each individual VOC with the reagent ions (i.e.  $\text{H}_3\text{O}^+$  and/or with  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ .”

*2. The evaluation of recovery and matrix effects should be part of the validation of any new analytical protocol. Considering that there were discrepancies between the results obtained with different methods I strongly recommend completing the method validation and add this information to the manuscript.*

Actually, recovery and matrix effects have been evaluated for our analytical method during its development phase. These optimization and evaluation tests have been conducted introducing known amount of standards in an atmospheric simulation chambers (CESAM, Wang et al., 2011) and a laboratory test chamber (Gonzalez-Flesca and Frezier, 2005) for various humidity conditions and complexity of mixtures and are discussed by Rossignol et al. (2012).

In addition, recovery and matrix effects are taken into account in the way we perform the quantification in our analytical method. For quantification, we use external calibrations performed in the same conditions as atmospheric samples, doping the collecting support (i.e. whether filter or adsorbent cartridges) with known amount of standards. This way, response coefficient used for quantification include the derivatization and extraction efficiency and the matrix effects.

Our answer to the previous comment of the referee #2, stated that we did not investigated this specifically to explain the disagreement observed for malonic and tartaric acids, which was the original question of the referee #2. We apologize for the misunderstanding. We add a statement to clarify this in the revised supplement S1 where the internal and external calibration protocol of TD-GC-MS analysis has been moved (see response to referee #1):

“In addition of this internal calibration protocol, external calibrations are performed in the same conditions as atmospheric samples, doping the collecting support (i.e. whether filter or adsorbent cartridges) with known amount of external standards (list of external standards can be found in the supplementary material 4). This way, response coefficient used for quantification include the extraction and derivatization efficiency and the matrix effects. In addition, recovery and matrix effect evaluation for the method can be found in Rossignol et al. (2012)”

*3. Please add to the manuscript the information about the activity coefficients used for equation 3. I see the information in the answers to the reviewers, but I haven't spotted it in the manuscript (unless it is there, and I missed it).*

This information has been added in the revised manuscript, as follow:

“ $\zeta_i$  has been set to 1.27 as suggested by Rossignol (2012)”

*4. Concerning my comment on page 21 about the Henry's law constant, please add to the manuscript that you are discussing the transfer from gas phase to deliquescent aerosol. It was not obvious to me, I thought you were discussing the transfer of analytes from the particles to liquid water inside the PILS.*

This information has been added in the revised manuscript, as follow:

“Some of the compounds identified and quantified by TD-GC/MS, especially carboxylic acids, are soluble in aqueous phase and their presence in aerosol phase could proceed through the transfer from gas phase to deliquescent aerosol.”

## References

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