Atmos. Chem. Phys. Discuss., 14, C351–C354, 2014
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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene" *by* A. P. Praplan et al.

**Anonymous Referee #3**

Received and published: 9 March 2014

The manuscript of Praplan et al. reports results from investigation of water-soluble organic acids from photooxidation of 1,3,5-trimethylbenzene (TMB) using an online system for ion chromatographic separation before mass spectrometric identification. The study is interesting since the authors have developed an an online IC-MS method for analysis of organic acids based on a previous work from the same group published a decade ago (Fisseha et al., 2004). Unfortunately, the method is hampered by high detection limits and uncertainty compared to the actual concentrations for some types of samples (typically particle samples). Generally the background, methods and results are well presented, but I have raised a number of specific issues below, which should



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be adequately answered before publication.

Abstract: There is no need to define the abbreviation PSI here, since it is not used further in the abstract. The last sentence of the abstract should be a bit further explained in order to be meaningful.

Page 986 Line 25. At least one reference is needed to support this.

Page 987: References are needed in lines 2 (... many different compounds) and line 5.

line 16-: Are online methods not prone to artefacts? Later in the discussion of the present manuscript, it seems that online methods may also have such problems.

line 22: "the method ... allows selective collection of organic acids". I assume the authors mean water-soluble species, not just organic acids.

Page 989 line 20: "hydroxy anion" should be changed to "hydroxide anion". What is the counterion (cation) in the eluent? The settings of ESI-MS should be clearly stated.

Page 991: line 7-9: Please provide more details on the sampling and extraction method.

line 21: It seems that "aerosol and gas phase" should read "gas phase and aerosol".

Page 994: Line 3: How can the particles formed be bigger? I assume you mean that they grow to larger aerosol diameters.

line 13: Please add that the black lights were additional sources of light.

line 21: What do you mean by "at least one chromatographic peak was identified of twenty-five masses.."?

Line 25: unambigious identification - did you have authentic standards for all compounds? Please also state in the experimental section, for which compounds you had authentic standards for quantification?

Page 995: Line 13: What were your detection limits?



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Line 25-28: This paragraph needs a little further explanation including references to relevant literature.

Line 29-: Can you quantitatively compare functionalisation/oligomerisation pathways and fragmentation pathways without complete mass balance?

Page 996 line 17-18: Since glycolic acid does not seem to depend on precursor concentration, I am wondering if it could be related to background concentrations in your system. Did you investigate this e.g. in experiments with light but without TMB?

Page 997: Lines 2-5: What is the uncertainty on these numbers?

Lines 12-16: The background for this statement is not clear to the reader. Please explain your reasoning.

Line 17: Remove "also" in the beginning of the sentence. The whole paragraph needs editing to improve style and grammar.

Add a reference to Table 2 for the discussion of the unknown compounds.

page 998 line 29: Which source for the carboxylate ions do you suggest/expect?

page 999 Line 2: "confirms" should read "suggests" due to the large associated uncertainties. line 20-21: References are needed here.

page 1000: The last statement only refers to the present method for determining Kp, correct?

Figure 3: "due to an instrumental limitation" - is it just lack of data or?

Figure 5: Why were the data not corrected for wall losses?

Figure 8: In my version, the legend is in the middle of the figure, which looks odd. Please explain that the data were normalized to the total aerosol mass from SMPS data.



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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 985, 2014.



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