**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Quantification of hydroxyacetone and glycolaldehyde using chemical ionization mass spectrometry" *by* K. M. Spencer et al.

**Anonymous Referee #1**

Received and published: 25 October 2011

Referee report Spencer et al., Quantification of hydroxyacetone and glycolaldehyde using chemical ionization mass spectrometry, Atmos. Chem. Phys. Discuss., 11, 23619–23653, 2011

Report for authors and discussion forum:

Summary This paper reports the application of CIMS technology to quantify hydroxy-acetone (HA) and glycolaldehyde (GA). It seeks to demonstrate the applicability of a well-established chemical-ionization method (CF3O- CIMS) to two compounds that are present in fire plumes and are late generation products of isoprene and MBO oxidation. The authors present calibration data for the two compounds for different water concen-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

trations for their CI-QMS and the CI-QqQ-MS instruments. CI-QMS data from airborne measurements (fire plumes during ARCTAS-CARB) are shown and discussed. Data from ground based CI-QqQ-MS measurements are shown and compared to as simplified photo-oxidation box model. The paper concludes that the presented technique provides robust quantification of hydroxyacetone and glycolaldehyde.

General comments The focus of this paper is on the analytical capabilities of CF3O-CIMS rather than the scientific results of the measurement of HA and GA, or scientific conclusions in the field of atmospheric chemistry. From a paper with such a technical aspect one would expect a broader and deeper introduction of techniques that have been shown to quantify and identify HA and GA. In this paper some chromatographic techniques are listed and other methods mentioned here and there but neither in a systematic way nor to an extent that would allow the comparison of this new application to established techniques. The authors need to introduce the literature on the measurement techniques for HA and GA (GC, HPLC, FTIR, other CIMS,...) more thoroughly so it allows the reader to decide what the advantages of this new method are and why the scientific community should care. Typically, such technical papers also compare the new technique and its performance to existing techniques in a direct inter-comparison with other instruments, either in a lab-setup or in the field. Such a direct comparison provides for obvious reasons much stronger means to decide if a new technique is at least a good as existing ones. If such data exists they should be presented here to support the authors argument that their technique allows for robust quantification of GA and HA. The authors mention an interference of propionic acid at m159 but provide little support that this interference is negligible in fire plumes; on the contrary the paper they cite (Yokelson et al 2009) to support their case shows that propionic acid has enhancement ratios similar to HA. Are the authors claiming that what was measured by the Caltec-CIMS during the Yucatan biomass burning study is actually HA? If so, this is an important finding, it needs to be discussed thoroughly and they might want to give a recommendation on the interpretation of already published propionic acid data measured by their CIMS instrument. Even an errata for the Yokelson paper (John Crounse

and Paul Wennberg are co-authors there too) should be considered. Please, clarify and make changes to the manuscript where needed.

Specific comments

1 Introduction p23620L18+ add yields of HA and GA from isoprene and MBO oxidation to quantify how important these compounds are in the respective oxidation scheme.

2.1. Instrument description Presumably HCN data shown as results was measured with the same instrument and should be mentioned here too.

2.2 Calibration p23626L25+ How does the scrubber work and how much (quantitatively) of the compounds does it remove? Either show experimental results or at least give a reference. Can the authors show that the scrubber does not change the water content in the sample stream? If yes, show it – if no, discuss implications.

3.1. Signal in CIQMS m159: Hydroxyacetone; the authors claim that little interference with propionic acid from fire plumes is expected because concentrations of propionic acid in the biomass burning plumes were small in previous experiments (Yockelson 2009). This reference seems to be used as a 'quick and convenient fix' for an interference that was not quantified by the authors. Yokelson et al (2009) do (a) not report concentrations propionic acid but (b) enhancement ratios (or normalized excess mixing ratio, as it is called there and interpreted as emission ratio (ER) for very fresh plumes) relative to CO of 0.0015 (1.5ppt/ppb). Those propionic acid ER are in the same range as the enhancement ratios of hydroxyacetone the authors present in their ARCTAS-CARB fire plumes. Hence propionic acid concentrations should be expected to be in the same range of what the authors quantify here with the same technique from m159 and a substantial portion of what the authors claim to be exclusively hydroxyacetone might in fact be propionic acid. The authors need to clarify this in the experimental description and in the results, discussion and conclusion of the paper.

3.2.1 HA in CI-QqQ-MS m159m85: in what respect is it similar to QMS and how does

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

that sentence add information to the manuscript?

4. Observations The 'explanation' of increased hydroxyacetone, glycolaldehyde and acetic acid at BEARPEX deserves more depth. The authors state in this chapter, observations, the coincidence of temperature increase and observed increase of HA, GA and AA and conclude causality between the two observations with no appropriate reasoning. Here, the authors should introduce their observations; they need to build their arguments in the discussion and may conclude what is supported by data and discussion in the conclusion chapter.

5.2. BEARPEX How did the authors take dispersion/dilution into account in their box model? Did the authors run MCM with partly modified reaction rates and branching ratios? If so, please express that more clearly. How does the model represent the measurement data? Does a range of realistic scenarios cover the range of HA and GA (and their ratios) measured at the field site. Since the authors show the production ratio of GA and HA in the model they might want to add a panel in Fig 6 that shows [GA]/[HA] measured at the field site. It is not entirely clear to me what the purpose of the box model is if there is hardly any connection made to the measured data.

6. Conclusions With the propionic acid interference not solved I disagree that single quad and QqQ technique are equally capable to measure HA. QqQ MS might allow to separate isobaric species and the authors might want to look into that. There is no scientific conclusion for the experimental data.

Recommendation for editor: The paper has a couple of shortcomings that need to be addressed. The calibration work was done satisfactorily but there is no direct comparison with existing techniques and in this light a very strong literature introduction and comparison is necessary to allow the reader to decide what's new here. The second point is the propionic acid interference at m159; was m159 from the Caltec CIMS previously interpreted as propionic acid and now the interpretation has changed? If this is the case then there is a strong point to make in this paper, and John Crounse and Paul

Wennberg should consider an errata for the Yokelson at al. (2009) publication. I do believe that CF3O- CIMS can measure HA and GA but this paper does not convince me that CI-QMS is free of interference and potential misinterpretation. The only real conclusions of this paper – CIMS is a robust technique to quantify (and necessarily identify) HA and GA – is not (yet) satisfactorily supported by the manuscript. I recommend publication if the authors address all the issues in their response and a revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23619, 2011.