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Atmospheric Chemistry and Physics Discussions

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

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We thank the two reviewers for their constructive comments. Our response to each comment, including changes to the manuscript text, is below.

Reviewer 1 Comment: Are the authors claiming that what was measured by the Caltech-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.

Response: The propionic acid data in the Yokelson et al. (2009) paper was obtained by monitoring m/z 93, the fluoride transfer mass, rather than m/z 159 (the cluster mass). Hence there was no hydroxyacetone interference in that data set.

Comment: 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.

Response: We appreciate the goal of this reviewer comment. However, because this paper does not introduce new chemistry and because of the complexity of the chemistry, with hydroxyacetone and glycolaldehyde yields from isoprene and MBO oxidation being a function of the relative concentrations of HO2 and NO, the NO/NO2 ratio, and the RO2 lifetime, we believe the reader is best served by referring to the cited references to understand the chemistry in the context they are interested in.

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

Response: Yes, the HCN data are from the same instrument. To clarify, section 2.1 begins with:

Negative ion chemistry of CF3O- has been shown to provide sensitive detection of many atmospheric trace gases (Huey et al., 1996; Amelynck et al., 2000a,b; Crounse et al., 2006; Spencer et al., 2009; Paulot et al., 2009a,b; St. Clair et al., 2010) and was exploited in this work to detect hydroxyacetone, glycolaldehyde, acetic acid, and hydrogen cyanide (HCN). The measurement of HCN by the Caltech single quadrupole CIMS has been described previously (Crounse et al., 2006, 2009).

Comment: 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.

Response: The two methods employed for background signal measurement in the Caltech CIMS are more extensively described in Crounse et al., 2006, which is referenced in the text for this purpose in Section 2.2. The scrubber approach was used for the data presented here. The scrubber does alter the water content to some degree, as discussed in the 2006 paper. To the extent that the background signal for a given compound is water-dependent, that water dependence is captured when the background data are considered for a whole flight or day's data.

Comment: 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 ARCTASCARB 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.

Response: The single-MS signal for m159 in the ARCTAS-CARB fire plumes is most likely some combination of hydroxyacetone and propionic acid. Outside of fire plumes the concentration of propionic acid is sufficiently low that the m159 signal is representative of the hydroxyacetone concentration. In an analogous manner to removing the acetic acid contribution to the signal at m145, it is possible to remove the propionic acid contribution to the signal at m159 using the signal at m/z 93. Text has been added to the manuscript to clarify this point (Section 3.1.1). Unfortunately m/z 93 was

not observed during ARCTAS-CARB and consequently the hydroxyacetone data from ARCTAS-CARB has been removed from the manuscript.

Comment: 3.2.1 HA in CI-QqQ-MS m159m85: in what respect is it similar to QMS and how does that sentence add information to the manuscript?

Response: The noted similarity was in reference to a lack of additional data work-up steps such as those employed in the glycoaldehyde work-up. For brevity, the sentence in question has been removed. Section 3.2.1 now begins with:

The MS/MS ion signal m/z = 159 $\rightarrow$ m/z = 85 was used to measure hydroxyacetone with the tandem CIMS instrument.

Comment: 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.

Response: To address this point, the discussion of temperature and concentration trends was moved from 'Observations' to the 'Results and Discussion' section.

Comment: 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.

Response: The scope of the modeling effort was intended to be limited. The purpose was to show that the hydroxyacetone and glycolaldehyde measurements at the BEARPEX site were consistent with a simple model implementing isoprene and MBO oxidation mechanisms.

The model chemical mechanism was based on Paulot et al. (2009a,b) with modifications mentioned in the text.

A dilution scheme was not implemented in the model, but dilution of compounds en route to the BEARPEX site was approximately accounted for by choosing the initial isoprene and MBO mixing ratios to yield the measured mixing ratios at the site after reacting for the known transport time.

Figure 8 shows the [GA]/[HA] measured at the field site, and can be compared to the model output at 300 min shown in Figure 9B, as discussed in the text. A point was added to Figure 9B at 300 minutes to mark the value determined from Figure 8.

Comment: 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.

Response: Section 3.1.1 now clarifies the capability of the single quad technique to measure hydroxyacetone. It now reads:

Hydroxyacetone clusters with the reagent ion CF3O- and is detected at m/z 159. There is a known atmospheric interference at that m/z: propanoic acid. Analogous to using m/z 79 to remove the acetic acid contribution to m/z 145 (Section 3.1.2), it is possible to use m/z 93 to remove the propanoic acid contribution to m/z 159. Because propanoic acid has not been observed in large quantities relative to hydroxyacetone outside of biomass burning plumes, the m/z 159 data can generally be used for hydroxyacetone without correction.

Reviewer 2 Comment: The authors could do more to verbally highlight the unique aspects of this data that would not be possible without the CIMS techniques.

Response: To better highlight the benefits of the CIMS techniques, the typical temporal resolution of the derivatization-based techniques was added to contrast with the time scale of the CIMS measurements:

Two shortcomings of these techniques are the intensive sample processing required and the time lag between sample collection and concentration measurement. Typical measurement periods are 5 min - 2 hr. In contrast, both single quadrupole and triple quadrupole (tandem) chemical ionization mass spectrometry enable online, rapid, in situ measurements with no sample processing. In these techniques, the ambient sample enters the instrument directly and reaches the detector rapidly (<1s), enabling immediate detection of these compounds and providing a potentially high temporal resolution data set.

Comment: The authors present schemes for detecting HAC and GLYC simultaneously using both single-quad and tandem CIMS. I would appreciate the addition of a brief summary passage directly comparing the two techniques and their pros and cons.

Obviously the mass interference by acetic acid is problematic for the single quad but the authors seem to have eliminated this problem in the data analysis. I may be wrong, but the acetic acid subtraction procedure doesn't sound much more involved than analyzing MS-MS data from the tandem instrument. Are there other reasons to choose the single quad over the tandem instrument (sensitivity, detection limit time response, weight, etc.)?

Response: We added Section 3.3 to clarify the main tradeoff between the two instruments when measuring glycolaldehyde and hydroxyacetone:

The Caltech single quadrupole CIMS instrument has higher ion transmission, and consequently higher sensitivity, than the tandem CIMS instrument. Measurement of an

analyte by the single quadrupole instrument is therefore preferable to measurement by the tandem CIMS instrument, when there are no interferences at the observed m/z. For analytes such as glycolaldehyde, the benefit of the higher precision for the single quadrupole CIMS is offset by the uncertainty introduced by subtracting a portion of the signal due to interfering compounds. As the signal from the interfering compound constitutes a larger fraction of the total observed signal, the uncertainty in the final glycolaldehyde mixing ratio increases. Because acetic acid is much more prevalent in the atmosphere than propanoic acid, relative to glycolaldehyde and hydroxyacetone, respectively, the tandem CIMS technique benefits the measurement of glycolaldehyde more than the measurement of hydroxyacetone.

Comment: Figures 6, 7 – the colored dots in the legend are too small to distinguish, maybe use colored lines.

Response: The dots in the Figure 6 legend are now larger. With the removal of the hydroxyacetone data, Figure 7 now has only one color.

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