

Interactive comment on “Measurement of formic acid, acetic acid and hydroxyacetaldehyde, hydrogen peroxide, and methyl peroxide in air by chemical ionization mass spectrometry: airborne method development” by Victoria Treadaway et al.

Anonymous Referee #2

Received and published: 4 December 2017

Review Treadaway et al AMTD 2017

This paper describes calibrations, humidity tests, interference tests and initial results for the measurements using the PCIMS instrument on board the NSF/NCAR C130 aircraft during FRAPPE and the NSF/NCAR GV aircraft during DC3. The PCIMS is a chemical ionization quadrupole mass spectrometer using a mix of I- and O₂- as primary ions to detect formic and acetic acid together with hydrogen peroxide and methyl peroxide. Currently the CIMS techniques are developing rapidly with the more commonly available high mass resolution ToF mass spectrometers together with easily adaptable

Printer-friendly version

Discussion paper



ion chemistries and papers such as this one are needed to explain the usefulness of the various versions of the CIMS instruments and used ion chemistries. The PCIMS still uses a quadrupole with unit mass resolution and suffers more from interferences and lower sensitivities than some of the current instruments. Nevertheless, I think this paper could be useful to the community, but clearly needs some improvements in organization and in presentation quality.

Major/broader comments:

- Why use multiple ion chemistries? It is not clear until quite late in the paper why a mixture of primary ions is used in this work and not only I⁻. Especially the abstract says: the focus is on organic acids and hydrogen peroxide and methyl peroxide react with I⁻ as well. Later looking at Figure 3, one would pick O₂⁻ as the primary ion, because it has high sensitivity for all the compounds investigated here. Only on page 11 and 12 it becomes clear that O₂⁻ suffers from interferences and that methyl peroxide sensitivity is very low using I⁻ only. This discussion needs to be moved to early in the paper to motivate the complicated ion chemistry setup.

- Why combined focus on acids and peroxides? In the introduction it should also be discussed why the PCIMS is focused on measuring the small acids and the small peroxides at the same time. Looking at recent literature, especially using I⁻ chemistry a very large number of compounds can be measured. So why not focus on those and use a setup that improves the sensitivity and reduces the humidity dependence and generally simplifies the ion chemistry? Hydrogen peroxide seems to be detectable at sufficient sensitivity, only methyl peroxide will lack in sensitivity. So please give the reasoning for the focus on methyl peroxide, even though it significantly complicates the used ion chemistry.

- What is different in this paper than Heikes and O'Sullivan 2017 papers? There seems to be significant overlap with the Heikes et al and O'Sullivan et al 2017 (although not available yet) papers. Explain in detail what is different and new in this paper compared

Printer-friendly version

Discussion paper



to the two previous ones.

- The ambient data need other results to strengthen the arguments. During field campaigns like DC3 or FRAPPE lots of additional data are available. These data should be used here to strengthen the arguments made about the vertical profiles, identifying the biomass burning plumes, and biogenic influence. For example, do other measurements show the same C-shaped altitude profiles as the small acids? What are the enhancements of CO in the plume that is shown.

- GA calibration The weakest part of the paper is the order of magnitude uncertainty in the glycolaldehyde calibration. Glycolaldehyde is in most atmospheric environments only a minor contributor to the sum compared to acetic acid with biomass burning plumes being the notable exception, but nevertheless the glycolaldehyde sensitivity should be determined more accurately in this manuscript and not to only within a factor of ten. It is understood that producing a stable and accurate calibration source for glycolaldehyde is difficult, but a liquid calibration unit that completely nebulizes the GA/water solution (for example the LCU from Ionicon) or a catalytic conversion of GA to CO₂ and subsequent CO₂ detection (Veres et al 2010) would likely deliver much more accurate results than presented here. If no better calibration can be achieved, I would suggest to change the discussion in the manuscript such that an upper limit of the interference for acetic acid is used. In addition, the chapter of the GA calibration should be moved to the chapter 2.4: Calibration.

Minor/detailed comments:

Abstract: line 19: Add the ions that are used for the detection of HP and MHP.

Abstract: line 20: Already add here, why you are looking at HP and MHP, even though the focus seems to be on the small organic acids.

Page 2 line 58: add the values of the Henry's law constants to the text here.

Page 3 line 95-100: Delete this sentence: it is not relevant to the readers how you

Printer-friendly version

Discussion paper



found out about this interference. It was pretty well known from previous literature.

Page 4 line 139: Please explain what “wetted” surfaces means.

Page 4 line 142: What is a “span check”?

Page 4 line 143: Please give more details on the organic acids and peroxide traps.

Page 5 lines 157-163: Please show how much the sensitivity changed with the inlet pressure.

Chapter 2.4: The uncertainty in the calibration should be added here somewhere.

Page 6 line 203-215: Describe only the trap that you used for FRAPPE and not the ones that did not work.

Figure 2: Figure 2 needs some improvement. First of all, please give the conditions (RH, press, ...) that this mass spectrum was recorded with. I suggest showing the mass spectrum as a stick plot, where all the masses are color coded according to their respective ion chemistry (I⁻ or O₂⁻). Then also label all the individual peaks with their mass and chemical composition.

All Figures: please be consistent with cts/s/ppb or cps/ppb. Just use one or the other, but don't mix them throughout the manuscript. There was also a switch to cps/ppt somewhere in the manuscript.

Figure S1 should be combined with Figure 3 in the main text. The FRAPPE results in Figure 3 are very difficult to distinguish from the rest of the data, please use a different symbol. Add the name of the compound or the ion to the y-axis label of each panel and not only give the mass. The same changes are needed for Figure 4. In general, for Figure 3 you are discussing the variation of the sensitivity caused by the flow of CH₃I, so why is the flow not on the x-axis instead of the humidity. It would much easier to follow the discussion.

Tables 5-7 are all very small and should be combined into one larger Table.

[Printer-friendly version](#)[Discussion paper](#)

Page 8 line 299: How much CH₃I was present and how different was it during DC3 and FRAPPE?

Page 9 line 325-335: If there is a wide range of Henry's law constants in the literature, why did you compare in detail to the Johnson et al values, which are picked because they are the closest to the current measurements. It would me more important to discuss why there is such a wide range in the literature and why you think yours should be used here.

Page 10 line 343: The reasons for the lower sensitivity of the alcohols compared to the acids are very different for the PCIMS and the PTR-MS. I- does not cluster efficiently with alcohols whereas proton transfer from H₃O⁺ causes fragmentation for the alcohols. This should be mentioned here, if you want to compare the two techniques. At this point I would also add that with a high resolution ToF, these compounds can be distinguished.

Page 10 line 346-365: As mentioned above: it would be good to describe the interference as an upper limit here and show how bad the interference could potentially be. Only if you are much more confident with one of the calibration cases, you can describe the interference with that one. The same for the discussion on Page 12.

Page 13 line 453: Also add Yuan et al 2017.

Figure 5: The flight tracks should be on top of a proper map showing the potential sources of the small acids such as urban areas and feed lots, all of which are readily available from FRAPPE.

Figure 7: indicate why there is such a large data gap in the HP data in the biomass burning plume.?

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-344, 2017.

Printer-friendly version

Discussion paper

