

Interactive comment on “Real-time measurements of gas-phase organic acids using SF₆⁻ chemical ionization mass spectrometry” by Theodora Nah et al.

Anonymous Referee #1

Received and published: 15 March 2018

The manuscript "Real-time measurements of gas-phase organic acids using SF₆-chemical ionization mass spectrometry" by Nah et al. presents a new measurement technique for organic acids and shows results from a field study. Demonstrating that SF₆⁻ is useful for measurements in a humid environment is an important new finding that may expand the capabilities of CIMS instruments for quantifying atmospheric trace gases, since previous reports had shown this reagent ion to be effective only in very dry locations with moderate ozone levels (like the Arctic). The subject matter is appropriate for AMT if the recommendations below are addressed, and the writing is easy to understand. Many experimental details and clarifications are needed to explain and justify this new technique. The discussion of the contribution of these organic

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acid contributions to WSOC and the many figures that detail organic acid mixing ratios should be pared down, since the species identification here are speculative, and there may be many interferences that have not been adequately considered. Specific recommendations are detailed below.

Previous reports have noted that SF6⁻ is a viable reagent ion only for dewpoints below -20 C. The flow tube is at lower pressure here, and that is said to minimize interferences with water vapor (line 167). This needs to be explained much more thoroughly. The very high dilution with dry nitrogen likely does much more to reduce the water vapor interferences, but this is never discussed. This high dilution must reduce sensitivity. Please discuss the trade-off between reduced sensitivity and increased selectivity. The flows as shown don't make sense, and volume flow and mass flow don't appear to be correctly distinguished. Accurately describing and discussing the flows is critical, since it is the altered gas flows that have made SF6⁻ viable in a humid environment. Line 154 gives the sampled air flow as a volume flow, but the orifice is said to maintain a constant mass flow. A 220 l/min scroll pump is used to pump a very small flow of 4 L/min through the flow tube, as shown in Figure 1. I suspect that the N2 flow should be written as 3.7 slpm, rather than L/min. But even that doesn't make sense, since it would be ~300 L/min volume flow, and greater than the pump speed. The instrument is said to be similar to Liao et al 2011, but the flows are very different, and these should be discussed completely. Does the high dilution compromise time response, since there is a very small flow of ambient air into the flow tube? Does the large flow of N2 through the ion source increase reagent ion signal?

Many fundamental measurement characteristics are not discussed. Please state and demonstrate time response, and preferably show a calibration and a zero. Detection limits are given for 2.5 min. I don't understand the relation between the 2.5 min background and the 0.04 s duty cycle for each mass (line 946). Please describe the measurement frequency - how often is a measurement made? I'm confused as to whether these are 0.04 s measurements, 2.5 min measurements, or 1 hr measurements (as

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used in the figures). And please be specific about the integration time for the mixing ratios. For example, are the range of mixing ratios in the abstract (line 22) for 1 hr averages? Detection limits and abundances in the figures are written in ppb, but for most cases, ppt would be a more appropriate unit and much easier to read.

Giving sensitivities relative to $^{34}\text{SO}_2$ is confusing and seems unnecessary, especially since that is a different ion-molecule reaction than all the organic acid reactions studied here and it has a water dependence. Providing absolute sensitivities will be much more useful for anyone who wants to compare this ion chemistry with others. And please discuss how these sensitivities compare to other techniques.

Please discuss the many possible interferences to the organic acids listed. The discussion of calibrations for many compounds was valuable, but then compounds for which calibrations weren't successful (pyruvic, for example) were dismissed. It appears arbitrary to ignore compounds if the calibration didn't work. Those other compounds almost certainly contribute to the signals and make the calculations of WSOC fraction extremely unreliable. For example, the signals at oxalic likely are dominated by or include contributions from lactic acid (both mass 90), butyric includes contributions from pyruvic (both mass 88), propionic includes contributions from glyoxylic acid (both mass 74). The authors correctly note that the mass assignments are speculative. It is OK to speculate, but from then on it would be appropriate to report mixing ratios only as upper limits for that compound and then forego calculations that rely on quantifying abundance. The sensitivities of the reported compounds span a wide range (over an order of magnitude). Thus, if the signal at one of the reported masses comes instead from an isomer with a much higher or lower sensitivity, the organic acid abundance would be drastically over or under estimated. There needs to be considerably more work to justify the WSOC contributions. I don't understand the count rates and normalization shown in figures 6-8. How do the count rates get to be small fractions of 1 Hz? Please use a unit that is more accurate and describe how the values are determined.

I don't understand the reagent ion signal and the use of sulfur isotopes. $^{34}\text{SF}_6^-$ is

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said to be the reagent ion (line 338). Is isotopically labeled SF₆ used? Why do the magnitudes of the peaks at mass 145 and 147 appear to be similar in Figure 2? Please clearly state the magnitude of the reagent ion signal. From figure 2, it appears that the reagent ion signal is approx 400 kHz, and similar in magnitude to SF₅⁻, CO₃⁻. Wouldn't ion chemistry from those other ions also contribute to the reactions? A more thorough description of the reagent ion is necessary to understand how the ion chemistry can be dominated by SF₆⁻. Figure 2 makes it appear that other ions could be substantial contributors to the ion chemistry.

Since the major measurement technique advance here is using SF₆ in high water and ozone environments, there should be greater discussion of water and ozone mixing ratios in the main text, and the necessary modifications to make the ion chemistry work in this environment. Although the supplement shows some ozone and water data, simpler discussion of the range of ozone and water mixing ratios and the effect on the ion chemistry should be included in the manuscript. Please show how formic or acetic sensitivity varies with ozone and water - this will make a much more convincing case for a valuable technique than showing F₂SO₂ versus water in the supplement. One overlooked feature in the results is the differing diurnal variations of acetic and formic acids in figures 3-4. Rather than focus on organic acid budgets that rely on speculative assignments and suffer from unexamined interferences, a study of the diurnal variability of acetic and formic acids could prove interesting.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-46, 2018.

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