

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

Anonymous Referee #2

Received and published: 16 March 2018

Nah et al. describe the extension of SF₆⁻ ion chemistry for the selective detection of organic acids. The paper describes both laboratory and field characterization of the technique and highlights challenges specific to the ion chemistry that need to be accounted for when making ambient measurements. The paper is well suited for publication in AMT following the author's response to the comments raised here.

General Comments:

The authors make a strong statement (line 95) that new techniques for the real-time measurement of gas-phase organic acids are needed due to deficiencies in existing CIMS based ion chemistry (acetate and iodide CIMS). The authors cite issues with acetate

C1

CIMS in the detection of acetic acid and the wide range of sensitivities to different organic acids in iodide CIMS. After reading this paper it was not clear to me that SF₆⁻ has an advantage over these techniques. It was shown that interferences due to O₃ hinder detection of acetic acid and there is an order of magnitude spread in sensitivity to various organic acids in Table 1. I think the authors need to better articulate how this technique is an advance over existing ion chemistry or acknowledge that it is a parallel approach to existing ion chemistry.

Given the focus of the journal, I think more emphasis on the experimental configuration of the CIMS should be given. Direct comparisons to existing measurements are always welcome, but the focus should remain on describing the details of the ion chemistry and or instrument operation.

Specific and technical comments:

Line 46: I would cite Molina et al. (2004), or Vlasenko et al. (2008) for the heterogeneous source of organic acids from the chemical aging of organic aerosol.

Line 166: Please elaborate on how the lower pressure (13 mbar) minimizes interferences in reactions of SF₆⁻ with water vapor.

Line 171: Rather than reporting voltages, it would be better to report electric fields or relative electric fields (E/N).

Line 182: Why was the background measurement period so long (~4 minutes). It would be helpful to show one of these in time. I would have expected that the background measurement period could be significantly shorter and still capture the baseline, unless there are inlet equilibration issues.

Line 183: What was the 1.12 ppm SO₂ standard diluted to? Presumably calibrations were not done at this mixing ratio.

Line 184: Again, it would be more helpful to present as the concentration of FA or AA that is delivered instead of the permeation tube emission rates.

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Line 308: For reactions 1a-c, should one think of these as separate reaction channels governed by ion-molecule kinetics or does every reaction proceed through 1a and the electric field strength of the CDC sets the ratio of the observed products. This may lead to strong deviations in the observed products based on instrument configuration.

Line 334: Can the mass (or molar) dilution constant be reported here instead of the inlet flow? This would help the reader understand how much ambient O₃ and H₂O are reduced by the sampling geometry. Also, perhaps it would be helpful to more explicitly state how a reduction in ion-molecule reaction time is helpful. This would not help in sensitivity (assuming all reactions are at the collision limit), but presumably would help minimize secondary ion chemistry, correct?

Line 335: What is the uncertainty in the IMR and CDC pressure? Are these pressures also controlled?

References:

Molina, M. J., Ivanov, A. V., Trakhtenberg, S., and Molina, L. T.: Atmospheric evolution of organic aerosol, *Geophys Res Lett*, 31, 2004.

Vlasenko, A., George, I. J., and Abbatt, J. P. D.: Formation of volatile organic compounds in the heterogeneous oxidation of condensed-phase organic films by gas-phase OH, *J Phys Chem A*, 112, 1552-1560, 2008.

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