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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions" *by* J. M. Roberts et al.

Anonymous Referee #1

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The manuscript presents a new NI-PT-CIMS technique for inorganic acid (i.e., HONO, HNO3, HCl, and HNCO) detection and demonstrates its potential application in biomass burning experiments. This technique is validated by calibrations with pure acid samples and inter-comparison with OP-FTIR HONO measurements. The reported detection limits are within a few tens of pptv and meet the requirements for ambient measurements.

Generally, the manuscript is well written and within the scope of AMT. This NI-PT-CIMS technique appears to be a versatile method for both organic and inorganic acid mea-

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surements in the atmosphere, which is usually a very challenging work. The author selected acetate anion as the reagent ion for its low gas-phase acidity. Thus any acids with higher acidity can be detected. However, the mass spectra could also be potentially complicated by fragmentations of bigger organic acids, especially if the author wants to utilize this technique in field measurements. Water cluster is another potential issue of this method. Although the CDC can break up water clusters before QMS detection, water clusters can still form inside the reaction tube given the low pressure and long residence time. The fact that no significant RH dependence in instrument sensitivity is reported in the manuscript might be due to the dilution by dry N2 during the sampling process, as shown in Fig. 1. Nevertheless, the results presented in the paper appear to be robust at least in a laboratory setting. I think this is a useful contribution to the field of atmospheric chemistry and to AMT. Thus I recommend this paper for publication in AMT after addressing the following comments.

Specific Comments: 1) The sensitivity of the NI-PT-CIMS is very impressive (6-16 Hz/pptv). However the background level is also very high (about 3300 Hz or roughly 300 pptv), which could raise serious issues regarding the quality of this method. What could be the underline cause of this high background? My major concern is that this high background level is due to not only the dirty reaction tube but some other unknown ion chemistry. I suggest the author conduct “clean” background checks to investigate the origin of background signal. 2) As indicated by the author that the inlet used in this work cannot be used to measure HNO3, I also believe that the reaction tube has a serious memory effect during HNO3 detection (shown in Fig. 5). This problem might be solved by adding NH3 into the reaction chamber to neutralize HNO3 adsorbed on the wall surface. However, NH3 might also interfere with the ion chemistry. The author need to resolve this issue before utilize this technique to measure ambient HNO3.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 301, 2010.