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Interactive comment on “A field-deployable, chemical ionization time-of-flight mass spectrometer: application to the measurement of gas-phase organic and inorganic acids” by T. H. Bertram et al.

Anonymous Referee #2

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This paper presents the development and characterization of a chemical ionization time-of-flight mass spectrometer (CI-TOFMS) for the measurement of trace gases in the atmosphere. The focus of the paper is on the determination of instrument sensitivity, detection limits and mass accuracy with respect to the measurement of formic acid aboard the R/V Atlantis. The combination of a high ion-duty cycle, high sensitivity, and low limits of detection make this technique ideal for the application to ambient flux measurements. While coupling CI techniques to TOF systems is not entirely new this paper represents the first attempt at using TOF technology for the measurements of

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gas phase acids. The characterization of this instrument is extremely thorough and well presented, however, it is somewhat limited in scope and largely specific to the particular instrument and methods being employed during the CalNex measurements. Previous work has detailed the achievable detection limits, instrument responses and background determination using this acetate chemistry (Veres et al. 2008). The clear advantage over the previous work is the application to a TOF mass spectrometer (with the high mass resolving power and duty cycle) while maintaining the high sensitivity of the previous quadrupole systems. It is in my opinion that additional discussion on the field performance of this particular CI source (instrument intercomparisons?) and the benefits of the high mass resolving capabilities of the TOF would be largely beneficial and necessary to establish this technique as a new and preferable alternative to the CIMS techniques currently available. The content is well suited for publication in AMT and as such i recommend this for publication after the following general comments and suggestions have been addressed.

General Comments

In the abstract as well as throughout the paper, a sensitivity (300 ions/s-pptv) and detection limit (4 pptv) are stated. It is not clear, particularly in the abstract, that these values apply to the detection of formic acid. It is necessary to explicitly state this as it is beyond the scope of this work to comment on these values for other compounds. It is suggested that the authors either explicitly state this in the text when quoting these values or modify the title to indicate a sole focus on formic acid.

Two key points immediately brought up in the introduction are the advantages of TOFMS versus quadrupole MS. More specifically the introduction discusses the improved ability of the TOFMS to acquire full mass spectra improving the duty cycle as well as briefly mentioning the improved mass resolution. These two selling points are highly underrepresented in this manuscript. It seems more apparent that the goals of this manuscript are to “demonstrate that the newly developed CI-TOFMS has the sensitivity, accuracy, and precision required for atmospheric observations from a wide array

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of measurement platforms." The paper nicely shows that the detection limit and sensitivity of the CI-TOFMS towards the measurement of formic acid make this technique ideal for ambient measurements of formic acid. It does not however provide enough evidence to comment on the accuracy of the measurements. It would be beneficial to this work to include an instrument intercomparison using the CalNex data, a comparison to previously reported formic acid measurements, or even a time series plot of formic acid measurements made during CalNex.

pg. 1970 In section 2.2, the authors state that the entire manuscript is presented with "unit mass resolution" data. This choice is a curious one considering that the high mass resolution is a significant factor to utilizing a TOF. With this acetate CI method the mass resolution could be used to separate several overlapping compounds such as butyric and pyruvic acid among others. This choice should be explained here as it is a significant driver for the content of this entire manuscript.

Pg. 1971 A suggestion to make the written form of the clusters similar, i.e. the use of $\text{CH}_3\text{C}(\text{O})\text{O}^-$ (HX) versus $[\text{CH}_3\text{C}(\text{O})\text{O}^-]\text{-}[HX]$.

pg. 1971 The ion chemistry section of this manuscript presents an argument concluding that the reaction of acetate with an acid proceeds primarily via the formation of an adduct. This is new information regarding this chemistry and is of importance. While it is not necessary, it may be advantageous to discuss this conclusion in a bit more detail. It seems also likely that at low fields, i.e. a high occurrence of the acetate-acetic acid cluster ions, the reaction would proceed via the reaction of HX with the first acetate cluster to form X- which could subsequently form a cluster ion.

pg. 1974 The estimated 20% error on the permeation source, is this based on a gravimetric analysis done in lab or the error reported from the supplier (Kin-Tec)

pg. 1974 It would be useful to discuss the sensitivity a little bit more with respect to the values previously reported. Specifically what is the primary ion count rate to which the 338 ions/s-pptv is normalized. Veres et al. 2008 have normalized to 1e6 ions

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and reported a value of 21 ions/s-pptv at a flow tube pressure of 32 torr. Assuming a primary ion count rate in this work of 30e6 and normalizing for pressure and primary ions, the TOF sensitivity is 6 ions/s-pptv as a first order approximation. It may be useful to walk through a comparison such as this to bring this 338 ions/s-pptv into perspective and at the very least the primary ion signal the sensitivity is reported should be explicitly stated.

Pg. 1975 How were background measurements performed? Please explicitly state what methods were used to zero the instrument, i.e. catalyst, denuders.

Figure 2. Tick marks are present on the top graph however not the lower graph and would be helpful.

Figure 3. The inset graph is shown using higher than unit mass resolution data. This is confusing since the paper specifically denotes unit mass resolution was used.

Figure 4. It would be useful to make the markers smaller or transparent to see the error bars at lower concentrations. It would also help to distinguish the point at the origin as either a zero or a calibration point, which is unclear.

On all figures that present mass spectrum data it would be useful to present the data in logarithmic scale or a split log axis to highlight the baseline noise. As a large focus of this paper is on the determinations of background levels and detection limits it would seem necessary.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 4, 1963, 2011.

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