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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.

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The reviewer’s primary concerns revolve around his/her sense that we overstate the breadth of the presented data and oversimplify what is required for extending the use of this instrument for the measurement of molecules other than formic acid. We appreciate the message and many of the specific comments, and will make changes accordingly. Simultaneously, we feel there is some confusion about the intent of the paper. In the response that follows, we address specific concerns and attempt to clarify the scope of the paper.

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A large fraction of the review takes issue with the lack of discussion of high resolution TOFMS analysis. In fact, we neither made, nor present any effort to perform high resolution analysis. Because we present only unit resolution data, the review questions “whether or not all this (supposed) resolving power is available in practical situations, like field measurement.” Further, he/she writes that the omission of high resolution and high accuracy data “amplify the feeling in the community that this instrument . . . is just not ready for the extensive ambient measurements in the high-resolution mode.” These would seem to be serious criticisms, but critically, the manuscript does not describe a high-resolution mass spectrometer. Instead, the work uses a high sensitivity, compact TOF mass analyzer (with a demonstrated in-field mass resolving power of 900 Th Th⁻¹). We believe the reviewer was confused on this point, and we therefore consider many of these comments to be irrelevant. Questions and comments related to mass accuracy and mass resolutions are addressed to the extent possible.

Below we respond to each of the reviewer’s general comments:

General comments on the term measurement: The reviewer makes the statement that “When we think of the term ‘measurement’ we think of a systematic demonstration of: 1) sensitivity to an analyte, 2) the ability to calibrate the instrument for the analyte, 3) the ability to measure the system background, and 4) an understanding of the behavior of the analyte on inlet surfaces and perhaps other interference issues. This paper does not manage to do this, even for formic acid.” As we state at the end of the introduction, the intent of the submitted manuscript is to “demonstrate that CI-TOFMS has the sensitivity, accuracy, and precision required to make atmospheric observations from a wide array of measurement platforms.” In the manuscript we assess the performance of the CI-TOFMS, through discussion of the instrument’s response to formic acid. It is not the intent of the manuscript to discuss inlet transmission issues, but rather focus generally on the utility of TOF mass analyzers for chemical ionization instruments and demonstrate the efficient coupling of a well-known CI source design with a TOFMS. As a result, the instrument performance is decoupled from the inlet performance, as the

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impact of inlet transmission and inlet response time is highly platform dependent.

In response to the reviewers general comments regarding the term measurement, we have systematically demonstrated that the CI-TOFMS is 1) sensitive, 2) accurate (able to be calibrated), and 3) able to measure the background for formic acid. Each of which is discussed in great detail. We do not address point 4, as we argue that is beyond the scope of this paper and that this has already been demonstrated previously with QMS based instruments (e.g., Veres et al).

General comment on the applicability of the instrument to acids other than formic acid: The reviewer is correct that we do not specifically demonstrate that the system is capable of detecting other organic/inorganic acids as we focus our discussion on formic acid due to the availability of an accurate calibration standard. It was never our intent to suggest that we had optimized or characterized the instrument for a broad range of acid, and we will modify the title (see below) to make sure that this impression is not given. However, having demonstrated the coupling of acetate reagent chemistry to the mass spectrometer, it is a logical expectation that the instrument has the capability to measure other acids as well, as demonstrated by Veres et al., and Roberts et al. We consider it appropriate to bring this possibility to the attention of the reader. In the revised manuscript we will explicitly state that the demonstrated figures of merit are for formic acid and provide reference of how similar ion chemistry can be (and has been) used in the detection of other organic and inorganic acids. This reference will include Roberts 2010, as suggested by the reviewer.

General comments on mass resolution: The reviewer makes the statement that “this system has the potential for mass resolution that could be truly revolutionary” . . . and later proposes various “interesting, important resolution problems that are related to measuring acid anions” and wonders why we do not approach them. The TOF analyzer used in the described instrument is optimized for compactness and sensitivity, not resolution. In section 2.5 we specifically state that the mass resolving power of the CI-TOFMS with the employed compact TOF is 900 Th Th-1 during the presented field

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measurements and up to 1100 Th Th-1 with careful tuning in the lab. For reference, the high resolution PTR-TOFMS from Ionicon achieves resolving power greater than 6000 Th Th-1 (Jordan, 2009). In the described CI-TOFMS configuration the carbon-13 isotopologue of formic acid and nitrous acid (HONO) are not separable. Further, we never argue that mass resolution is the novel advance of this instrument, but rather that the CI-TOFMS, as configured with a compact TOF, is sensitive, accurate, precise, and capable of measuring complete mass spectra (10–200 Th) at sample rates faster than 2 Hz.

Following this discussion, the reviewer states that “it would be nice to know whether or not all of this (supposed) resolving power is available in practical situations, like field measurements”. For relevant examples of high resolution TOFMS analysis using Tofwerk hardware, see DeCarlo et al, 2006; 2009; Jordan et al 2008; Aiken et al, 2008; 2009; Junninen et al., 2010.

General comments on mass accuracy: The reviewer makes the statement “... there is only a vague allusion to a mass calibration. Isn't drift in the mass scale one of the central problems limiting the analysis of true high-resolution data?” We specifically state in section 2.5 how the mass accuracy was determined, and that the relative mass accuracy was 0.1 mTh Th-1 across the course of the CalNex campaign. It is true that the calibration relating ion time of flight to ion mass-to-charge ratio can drift slowly due to environmental factors such as temperature. However, our software tracks this drift in real time and, more importantly, we save all data in a raw format that allows mass calibration in post processing based on the many known peaks in the spectra (e.g., acetate ion and acetate clusters). Section 2.2 includes a detailed description of the saved data format and mentions the possibility for mass calibration during post processing. Further discussion of high-resolution TOF data analysis is beyond the scope of the paper, which reports unit mass resolution results.

General comments on financial support: We thank the reviewer for pointing out that funding sources were not detailed in the acknowledgments. This was an unfortunate

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oversight for which we apologize. THB used start-up funds from the University of California, San Diego to purchase the CI-TOFMS and to fund associated research and development. Development efforts at ARI were supported by DOE and NOAA, grants DE-SC0004577 and NA09AR4310125, respectively. The reviewer writes “It is clear from the author list that the work had substantial support from Aerodyne and probably ToFwerk ...” and suggests that the nature of this support be disclosed. Development of the CI-TOFMS hardware was a collaborative effort, which, of course, drew on the resources of multiple organizations, as indicated by the author list. It would be unusual for academic, government, or industrial scientists to thank research institutions for normal use of facilities. With the addition of the funding sources listed above, acknowledgments are thorough and consistent with standard practice.

Below we respond to each of the reviewer’s specific comments:

1. Title and abstract: To clarify the major theme of the paper, we propose to shorten the title to “A field-deployable, chemical ionization time-of-flight mass spectrometer”. In the revised abstract, metrics of instrument performance will be prefaced as being determined for formic acid. We choose not to include “formic acid” in the title, as suggested by the reviewer, because much of the characterization of the instrument has relevance beyond the detection of formic acid.
2. H₃O⁺ chemistry: The reviewer is correct that most PTR-MS instruments use a hollow-cathode source and low pressure drift tube. However, this is not universally true. For example, Renbaum and Smith (2011), among others, flow H₂O through a ²¹⁰Po source to make H₃O⁺, while keeping the ion-molecule reaction at 40 torr.
3. Thomson unit: The unit will be clearly defined on first use in the revised text. Strictly speaking, m/Q should be negative (as the reviewer points out). We like the suggestion and will revise the figures accordingly.
4. MCP detector, dead-band after large peaks: For a TOFMS, four possible undesirable effects related to large peaks come to mind: (i) time-to-digital converter (TDC) dead

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times in ion counting experiments, (ii) signal ringing caused by electronic impedance mismatch, (iii) peak tails caused by ion scattering on residual gas and grids, and (iv) saturation of the MCP detector. None of these effects are important here. As explained in section 2.2, the CI-TOFMS uses an ADC because the count rates of this instrument make ion counting impractical, thus factor (i) is not relevant here. Detrimental ringing is not observed following the reagent ion peak at 59 Th. While the signal from this peak does have a measurable falling edge tail (scattered ions), it does not prevent us from observing ions at 60 Th. This is noted on line 26 of section 2.4, “The baseline count rate at 60 Th, calculated from the tail of the reagent ion peak at 59 Th (which peaks at 3×10^7 ions s^{-1}), was less than 1000 ions s^{-1} , indicating that electronic or chemical noise associated with high reagent ion count rates has little impact on detection at adjacent masses.” An MCP is said to “saturate” at large output currents which can reduce effective gain. Signal levels here simply are not high enough to produce significant saturation effects (compare, for example, Drewnick et al, 2005). The time required for the MCP to be replenished and return to the constant gain is sometimes termed the “dead time” (although the gain remains non-zero). Typical dead times are on the order of 1 to 10 ms, 2 to 3 orders of magnitude longer than a single TOF measurement (extraction). Therefore, the effect would not manifest in a band after the large peak, rather the effect would be total reduction of sensitivity in the measurement.

5. Clustering reaction: A specific reference to Graul (1990) will be added in the revised text.

6. Collisional dissociation energy: We will add a sentence specifically stating that collisional dissociation energies scale as E/N to support our statement of the location of collisional dissociation in our instrument.

7. Inlet time response: The characterization of the full inlet time response is beyond the scope of this paper; however, we will include a value for the e-folding time for the response of the CI-TOFMS instrument without an ambient inlet.

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8. Normalization of count rate: The normalized count rate used for the Allan variance calculation is the same as discussed in line 6, page 1974. This will be made clear in the revised text.

9. Figures 2 and 3: External ticks will be added to each figure, and the split axis will be used for figure 3, as suggested.

10. Peak Asymmetry: These tails are features of the peak shape of the instrument, as tuned, not overlapping ion peaks. With more careful tuning, spectral peaks can be made narrower and far more symmetric. Because data were only being interpreted with unit resolution, peak shape was not optimized.

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