

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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In the following response we address both the general and specific comments of anonymous referee #2 and will revise the manuscript accordingly. In cases where referee #2 has made similar remarks to referee #1, we direct the referee to our earlier responses.

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

1) Application of technique beyond formic acid: In our response to reviewer #1, we stated that we do not specifically demonstrate detection of other organic/inorganic

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acids as we focus our discussion on formic acid due to the availability of an accurate calibration standard. The sensitivity and detection limit that is reported is specific to formic acid. 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 (Roberts et al., 2010).

2) Absolute accuracy, intercomparisons, and comparison to previous measurements: In this manuscript, the absolute accuracy of the technique is solely constrained by the accuracy of the permeation source (discussed below). Referee #2 suggests we include an intercomparison, time-series, or comparison to literature values. This is a valuable suggestion. In the revised manuscript, we compare the concentration values reported in Figure 5, for clean marine air (50-100 pptv) and off-shore pollution (650-850 pptv) with the range of values reported in the literature. Specifically, we will reference the collection of observations of HCOOH measurements in urban areas (1-10 ppbv) and remote continental and marine areas (< 1 ppbv) made by both collection/IC and mass spectrometric methods (e.g., Keene et al., 1989, Grosjean et al., 1990, Veres et al., 2008, Keene and Galloway, 1988, Paulot et al., 2011)

3) Mass resolution (pg. 1970 section 2.2): As discussed in our response to referee #1, the TOF analyzer used in the described instrument is optimized for compactness and sensitivity, not resolution. In section 2.5 we state that the mass resolving power of the CI-TOFMS with the employed compact TOF is 900 Th Th⁻¹ during the presented field 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 overlapping compounds such as butyric and pyruvic acid are not separable.

Referees #1 and #2 made similar comments about the surprising lack of high resolution data interpretation, suggesting that the practical consequences of our achieved 900 Th Th⁻¹ resolving power need more emphasis. The revised manuscript will include

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examples of what can and cannot be resolved with this resolving power. We will also emphasize that the described source and interface are compatible with a high resolution TOF (specifically, the ToFwerk HTOF platform), but that when using TOF analyzers there are inherent trade-offs between sensitivity (ion throughput) and mass resolving power.

4) Cluster notation and ion-molecule reaction (pg. 1971): Following the reviewer's suggestion, we will be constant in the cluster notation (e.g., $\text{CH}_3\text{C}(\text{O})\text{O}(\text{HX})$ vs. $[\text{CH}_3\text{C}(\text{O})\text{O}] \cdot [\text{HX}]$) and following the comments of referee #1, we will provide reference to the work of Graul (1990) for details of the clustering reaction.

5) Permeation tube error (pg. 1974): Since submitting the manuscript, we have further assessed the permeation rate of the formic acid tube through collection and subsequent IC analysis. The permeation rate calculated through the collection/IC analysis was within 5% of that quoted by Kin-Tec. Given fluctuations in the temperature and the pressure over the permeation tube during field operations, we estimate a conservative upper limit of 20% for the uncertainty in the permeation rate.

6) Further discussion of sensitivity calculation (pg. 1974): As stated on page 1974, the observed count rate at 45 Th was normalized by the ratio of the reagent ion count rate in the absence of formic acid to that observed at each calibration step. For this specific calibration, the reagent ion count rate was $1.5\text{E}7$ Hz in zero air, and $1.36\text{E}7$ Hz at a volume fraction of formic acid equal to 2.5 ppbv, thus the normalization is a 10% correction at 2.5 ppb and close to a 25% correction at 7 ppbv. In the revised manuscript, the reagent ion count rate in zero air and at formic acid concentration of 2.5 ppb will be included and Figure #4 has been updated to show both the measured and normalized count rate at 45 Th and the reagent ion count rate at 59 Th.

It is unclear to us exactly how referee #2 calculated a sensitivity of 6 ions/(s pptv), and in particular what comparison the referee was attempting to make? If we understand correctly, the referee wants the sensitivity reported in our manuscript and that of Veres

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et al on a more fundamental basis for direct comparison. We instead prefer to compare instruments based on detection limit and short and long term precision, as in the end these are the metrics that matter for making robust measurements. Moreover to make the type of comparison the referee has suggested requires an assumption that the sensitivity of both instruments are linear functions of reagent ion counts and pressure. In our experience, the sensitivity is a complex function of pressure, as our ion transmission is highly non-linear with pressure.

7) Background measurement technique (pg. 1975): Background determinations were made by measuring the instrument response in UHP zero air. This will be noted in the text.

8) Figure 2: Tick marks (that cross the axis) will be added to Figure 2

9) Figure 3: Both Figure 3 and the inset figure show the recorded mass spectrum. The yellow shaded region indicates the UMR integration region. The data is not recorded at UMR, but rather peaks are integrated to yield UMR data.

10) Figure 4: The squares will be made smaller, however we note that the precision of the instrument ($< 1\%$ at count rates greater than $1E6$ Hz) is such that the error bar in the y-dimension is very small.

11) General comment on figures containing mass spectra: A split axis will be used for figure 3, as also suggested by reviewer #1.

References:

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