

Interactive comment on “Application of GC/Time-of-Flight-MS for halocarbon trace gas analysis and comparison with GC/Quadrupole-MS” by J. Hoker et al.

Anonymous Referee #2

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New instrumental approaches often push science forward in quantum leaps. This paper explores the use of time-of-flight mass spectrometry (TOF-MS) for trace-gas analysis of ambient air. Some advantages and disadvantages of this technique over the commonly used technique (quadrupole MS) are discussed, and I believe this topic is highly relevant for consideration by AMT.

The results and discussion provided by the authors provide good information related to the pros and cons of using the TOF-MS compared to the QP-MS. Some information is overly simplistic. But for atmospheric analytical chemists interested in potentially using TOF-MS as a replacement for QP-MS, some additional information would be relevant

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to consider.

The authors understand well that the QP-MS has a limitation associated with "dwell times". Longer dwell times lead to improved signal to noise owing to signals being averaged over this period. Unfortunately longer dwell times result in fewer points being obtained across each chromatographic peak and a reduced capability to monitor multiple ions within a specific retention time window of the chromatogram. In my lab dwell times are limited not by the number of ions I want to measure (usually it is just 1 ion, so I typically operate the MS in the mode described as the "optimized mode" despite the text on p. 12336 suggesting that this isn't typical; it all depends on the resolution power of the column in use), but by the chromatographic peak width and the need to characterize that peak accurately with some minimum number of points in time (typically >15). Although this point isn't mentioned, more significantly, no discussion of this issue is provided for the TOF-MS. It is mentioned that the cycling of ion pulses in the TOF-MS ("spectra extraction rate" of 4 Hz) has been set by the authors to match that of the QP-MS. How rapidly can pulses of ions be sent down the accelerator drift tube of the TOF-MS? Does this frequency affect the S/N of the TOF-MS result? Are ions accumulated between pulses somehow (as in an ion-trap-type source)? Would chromatographic peaks (especially narrow ones) be more accurately characterized by the TOF with higher sensitivity than by the QP-MS? Such details are highly relevant to the main points of the paper but aren't currently considered.

There is a possibility that using air from one tank in the experiment (as a reference and "sample") underestimates true precision as the stability in response could be less for ion currents much different than the reference. Consider some additional measurements to test for this effect.

Details that could be improved. In abstract: non-linearity is better quoted not as a single percentage, but as a percent per mixing ratio difference (or something similar) to convey the degree of non-linearity as a function of differences in response. This is essential for the reader to understand the magnitude of these influences.

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p. 12325, line 12. The UCI group (Salzman and Aydin) have used high resolution GCMS for the analysis of halocarbons in ice; this would seem useful to mention also.

Line 13, even the QP MS doesn't monitor ions simultaneously, consider better wording here. Lines 17-20. It would seem there are other potential advantages of using a TOF-MS worth mentioning here even though the particular TOF-MS used in this study may not be able to achieve all of them (given its resolution capability), e.g., discrimination against ions with equivalent nominal masses (and, therefore, more selective analyses), and potentially frequency of data acquisition (see main comments).

It would seem that the split ratio would be difficult to measure well. Was output from the split device switched at some point to allow the quantification of its value accurately?

p. 12330, line 17. Resolution is somewhat adjustable in a QP-MS. Provide an actual number here (you do elsewhere), and indicate that it is typically fairly constant throughout a broad mass range.

Section 3.3 Does mass stability depend on the number of amu between a reference mass and the analyte ion mass? No mention of the reference masses used here are given. And what are the matrix effects (line 11, p. 12331) mentioned? Are they likely to be minimal in most air analyses?

LOD discussion, The metric used for quantifying the noise magnitude (peak-to-peak, or 1 s.d., or something else) isn't mentioned.

Table 3, I don't see $n(\text{sub } \sigma)$ defined in the caption or in the main text.

Table 6, repeat in the notes to the table what this measurement precision represents. It is expressed as the mean (median, 90th percentile?) standard deviation determined for the sample/reference pairs? Or something else? Also, convince the reader that these values aren't different from those in Table 5 just because they are the result of a single reproducibility experiment (as opposed to 5). Does one theoretically expect a ~ 4 times improvement in precision based on the improvement in S/N for the peaks

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obtained from the different sampled volumes?

p. 12337, line 15, it would be useful to indicate the capabilities of the A/D converter in use to understand if this important limitation could be easily addressed with some upgraded electronics or not.

p. 12338, line 15. Linearity was noted for the QP MS for all 35 gases; please specify the range in response relative to the reference (e.g., from 10% to 5 times?). And for the TOF MS it would be useful to specify the degree of non-linearity observed for the worst to best analyte.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 12323, 2014.

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