Atmos. Meas. Tech. Discuss., 7, C5021–C5053, 2015
www.atmos-meas-tech-discuss.net/7/C5021/2015/

Atmospheric Measurement Techniques
Discussions
Open Access

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.

J. Hoker et al.

hoker@iau.uni-frankfurt.de

Received and published: 4 March 2015

General Remarks:

The authors would like to thank the reviewers for their comments and questions that helped to improve the manuscript and clarified important issues. In the following, the comments of the reviewers are listed followed by our answers additions / changes to the manuscript in blue. Changes to the original manuscript that do not refer implicitly to the reviewers comments:

- added new citations (Watson2011 (doi: 10.1100/2011/430616)) in the introduction.
- p. 12334, l. 11: deleted the sentence “Further the mass accuracy is sufficient to unambiguously distinguish ions as listed in Table 3.” because Table 3 has no relation to mass accuracy.
- In the meantime another reproducibility experiment with a preconcentration volume of 1L was conducted and we recalculated the measurement precisions, no significant chances are observed. Table 6 (now Table 7; see below) has been updated to include all relevant results:

Table 1. The reproducibility (REP) for the QP MS and the TOF MS as a mean value of two measurement series with 20 measurements each and a preconcentration volume of 1.00 L. The given errors are one sigma standard deviation over two reproducibility experiments.

substance	formula	REP QP [%]	REP TOF [%]
CFC-12	CCl_2F_2	0.22 ±0.10	0.23 ±0.09
CFC-11	CCl_3F	0.14 ±0.03	0.16 ±0.00
Halon-1211	$CBrClF_2$	0.60 ±0.05	0.55 ±0.21
Iodomethane	CH_3I	1.31 ±0.23	0.99 ±0.30

Reply to Eliot Atlas:

1. My first suggestion is to change the title to “Comparison of GC/Time-of-Flight-MS with GC/Quadrupole-MS for halocarbon trace gas analysis.” This seems to be the essence of the manuscript. Since only 4 gases are evaluated and discussed, there is really very little in the manuscript that deals with the actual use and application of the TOF-MS. Some discussion of linearity issues are mentioned, but this is mainly in the context of comparison to the QP-MS.

   Changed Title to
   “Comparison of GC/Time-of-Flight-MS with CG/Quadrupole-MS for halocarbon trace gas analysis”

2. 12325, l. 16. One main advantage of the TOF is the full-time, high-sensitivity mass spectral acquisition. A second advantage should be the reduction in background noise by selecting the exact mass (-+ 50 ppm) of a target ion, which should eliminate interferences from those ions with the same unit mass. I think this aspect, esp. in comparison to the QP-MS, deserves more discussion.

   The reviewer is correct. We have rephrased as follows to include this aspect in the introduction:
   TOF MS has only been applied sporadically for measurements of atmospheric trace gases (Kim2012a, Kundel2012, Watson2011, Jordan2009) and in particular not with focus on halocarbons. The main advantage of coupling a TOF MS to a gas chromatograph (GC) over using the QP MS are the intrinsic full mass range acquisition, the better mass resolution and mass accuracy. The identification of unknown peaks is significantly facilitated by these advantages and the use of more narrow mass ranges is expected to reduce interferences and background noise. In addition, much higher data acquisition rates are possible using TOF

MS, which is an advantage for fast chromatography. A TOF MS instrument can measure more than 10000 mass spectra per second. They are added up and averaged over a certain time period to yield the desired time resolution. The possibility of operating the TOF at high data rates is also of high interest for fast chromatography and narrow peaks where the operating frequency of quadrupole instruments (especially when measuring several ions) can be a limiting factor. The maximum time resolution for the TOF MS used in this study is 50 Hz. An increase in the data frequency with lead to decreased Signal to noise levels. The data frequency must therefore be optimised to provide a sufficient number of data points per chromatographic peaks while keeping the Signal to noise level as high as possible. In contrast, a QP MS is a mass filter and will only measure one mass in unit resolution at a time.

3. 12426, l. 8. I would suggest that instrumental drift is a 6th “key parameter”. This can refer to drift in sensitivity or to drift in mass accuracy

   We agree with this suggestion and include a new subsection:
   Section: Experimental: Stability of the Mass Axis and Instrument Sensitivity

   To evaluate the stability of the two mass spectrometers with respect to sensitivity and accuracy of the mass axis, a reproducibility experiment was used. The relative difference between the minimum and maximum detector response of the day and the one sigma standard deviation of all measurements over this day were takens as measures of the drift. For drift in mass accuracy over the day, the mean value and the one sigma standard deviation are given for the main masses for the following four compounds: HFC-134a (CF_3^+, 68.995 u), CFC-12 ($CF_2^{35}Cl^+$, 84.866 u), CFC-11 ($CF^{35}Cl_2^+$, 100.936 u) and Methyliodide (CH_3I^+, 141.928 u). To evaluate the stability of the mass accuracy over a longer time period, the mass accuracy was calculated on measurement days with different time differences since the last mass calibration tune.

Section: Results and Discussion:

A reproducibility experiment was used to evaluate the stability of two detectors over a measurement series (typically 10 hours). For that purpose, the minimum and maximum value of the detector response relative to all recorded responses and the 1-fold-relative standard deviation of all recorded responses were used (see table 4).

Table 2. *

Table 4: The difference of the minimal (Min) and maximal (Max) values in % in one reproducibility experiments for the relative response are shown with a 1 sigma relative standard deviation (RSD) over all measurements (20) on this day and in the comment line the trend of the calibration gas over the day is given.

Mass Sectrometer	Substance	Max-Min [%]	RSD [%]	Comment
TOF-MS	CFC-12	4	1.41	linear
QP-MS	CFC-12	4	1.28	linear
TOF-MS	CFC-11	5	1.32	linear
QP-MS	CFC-11	5	1.38	linear
TOF-MS	Halon-1211	7	1.97	linear
QP-MS	Halon-1211	1	0.63	linear
TOF-MS	Iodomethane	10	3.73	scatter
QP-MS	Iodomethane	5	1.92	scatter

For the substances CFC-11 and CFC-12 the drift of the sensitivity of the TOF MS and QP MS are on the same level. For the low concentrated substances, the drift of the TOF MS is higher than that of the QP MS.

For evaluating in the stability of the mass axis, the drift over a day was calculated

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

as mean accuracy and standard deviation (one sigma). The stability over a long time period was observed over different days away from a mass accuracy tune. As shown in section 4.2 the mass accuracy of the Bench TOF-dx was observed to be on the order of 50-170 ppm. Within this uncertainty no drift of the mass axis with time could be observed for periods of up to 19 days after the mass axis calibration. The stability and absolute accuracy in the determination of the exact mass is thus not a significant additional limitation in the ability of the Bench TOF-dx to separate different ions (see section 4.1).

4. 12326, l. 22. Suggest removing "cryofocusation" and change to "sample enrichment on cooled adsorptive material..."

5. 12326, l. 25. Please provide length and i.d. of 1/16" tube.

6. 12327, l. 1. Please provide mg of Hayesep used in trap. Also, change "cryofocusation" to "enrichment". What was the sample introduction flow rate, and how was it controlled?

   We changed the word to "preconcentration" in subsection Preconcentration (2.1) and added the requested information:
   A 1/16 inch stainless steel tube (sample loop, ID = 1 mm, length = 15 cm) packed with HayeSep D 10 mg adsorption material was cooled to a temperature of -80°C for sample preconcentration. The sample flow during preconcentration was adjusted to 50 mL/minute controlled by a needle-valve.

7. 12328, l. 3. How was this split determined? Calculators available to me suggest that the split ratio is theoretically 55% TOF/45% QP. It seems to me that the uneven split between TOF and QP is a major problem in the experimental design. Since some of the properties depend on the absolute amount of mass reaching the detector, comparison of different mass amounts (which may be off by my calculation) biases the results. At a minimum, some of the tests should

be repeated with the splitters reversed. This would add confidence to the split ratio calculation and to any potential biases due to mass differences reaching the detector.

Due to the mechanical setup of the system a reversal of the transfer lines is unfortunately not possible (different length required). Also, we noted that there was a mistake in the quoted lengths of the transfer lines. The correct lengths are QP MS: 0.7 m and TOF MS: 2.1 m. We corrected this in the revised manuscript and added more information on the determination of the split ratio:

We changed in the subsection Gas Chromatograph (subsection 2.2)) and added the requested information::
The gas chromatographic column was connected to the QP MS and the TOF MS using a Valco three port union and two fused silica transfer lines. The transfer line to the QP MS had a total length of 0.70 m with an inner diameter of 0.1 mm, the transfer line to the TOF MS had a total length of 2.10 m with an inner diameter of 0.15 mm. Based on the length, temperatures and inner diameters of the transfer lines a split ratio of 63:37 (TOF MS:QP MS) was calculated. Using the ratios of the peak areas of the quadrupole when receiving the entire sample (TOF transfer line plugged) to those obtained in the split-mode a spilt ratio of 66:34 was calculated. We have adapted this latter value as it is based on actual measurements rather than calculations.

8. 12328, l. 26. Why set the MS scan to 500? For this test, maximum mass is 142. Presumably some improvement in S/N could be obtained by the QP by scanning a smaller mass range. A scan range of 100 amu could increase S/N by a factor of 2

The reviewer is correct in pointing this out. We set this scan range for direct comparison with the TOF-MS. When using a reduced scan range the LODs are indeed better (see table) for a scan range from 50-200 amu. This is however expected to be true for both mass spectrometers.

We changed in section Results and Discussion, subsection Limits of Detection:

The SCAN mode of the QP MS was chosen for a direct comparison with the TOF MS (scan range from 45 u to 500 u) and is shown in Table 4 (1). Higher and lower m/z ratios were discarded. Reducing the scan range will result in better detection limits for the QP MS and theoretically also for the TOF MS as long as no significant amounts of ions heavier than the chosen upper scan limit are produced in the ion source. Remaining ions in the TOF MS flight tube from a preceding extraction would result in unambiguous detector signals.

Table 3. *

LOD QP-MS SCAN rate 50-200 amu

Substance	ppq	pg
CFC-12	70	1.21
CFC-11	85	1.95
H-1211	64	1.75
Methyliodide	31	0.17

9. 12329, l. 11. Change to “regular”. How often is “regular”? How often were mass calibrations done on the TOF? Were any manual adjustments done to alter the autotune voltages? In my experience the autotune voltages can be manually adjusted to improve S/N. Though clearly good performance characteristics were found in these experiments, I wonder if additional improvement could come from manual adjustments of source or detector voltages.

Changed in section Experimental, subsection Measurement procedure:
To ensure measurement quality, both MS were tuned in regular intervals (autotune by operating software) at least every two month but especially before sample measurements and/or characterisation experiments. Autotune options of both mass spectrometers were used without further manual adjustments. To increase the sensitivity and linearity of the TOF MS, its detector voltage was increased by 30 V, as described in chapter 4.5.

10. 12330, l. 11. Define “u”.

    Deleted unit [u] as it was misleading and not necessary anyway.

11. 12331, l. 6. Change “the according” to “each” (if I understand the meaning).

    Done.

12. 12331, l. 11. Please elaborate about “well-equilibrated” conditions. What are the matrix effects that are seen? How do you know if the system is well-equilibrated? Plus, I did not see a discussion later that described the mass accuracy over multiple runs, and the mean mass accuracy of the target masses.

    The reference to the matrix effects was removed as it was misleading. Instead we precised as follows in section Experimental, subsection Mass Accuracy:
    Only measurements taken under well equilibrated conditions were used for this analysis. As the first two measurements of a measurement day often show enhanced variability they were excluded from the analysis of the mass accuracy.

13. 12331, Limits of Detection. Calculation and definition of instrumental limits of detection are often confusing and sometimes arbitrary. One definition is that

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

used by the authors (e.g LOD = 3 x noise). However, it is critical how and where the noise is calculated, and how the baseline is drawn. I would suggest showing actual examples of the noise calculation for TOF and QP, esp. for the lowest level analyte, CH3I. In fact, the LOD will change over time due to various instrumental factors, so the determination and comparison is only marginally useful for "optimum" conditions. Furthermore, this determination might be significantly affected by the sample split sent to the different MS. Another approach that is being used to characterize instrument performance is the Instrument Detection Limit (IDL). Noise measurement can be quite variable, depending on the location and the width of the calculated noise segment, especially in low noise detectors. The IDL is based on 3x the standard deviation of a compound measured at approximately 5 x the estimated LOD. This statistical approach seems to give a more meaningful evaluation of instrument performance. It would be helpful to have this information to compare for at least one of the analytes.

We agree that the IDL as described above is in principal more informational than the LOD, although it will also change with various instrumental factors and will also be affected by the split ratio. In addition, to derive the IDL you are required to find substances which meet the 5x LOD criteria. As the main purpose of this paper is the comparison of the mass spectrometers the main point is that both instruments are treated in a similar manner. We therefore decided to stay with the LOD as one can easily derive it for all measured substances (with known concentration) and added a description (see Comment No 20) on how noise was calculated.

14. 12332, l. 7. Could you please explain the choice of 0.28 L sample size, when apparently 1.0 L is the normal sample volume (I assume then that the QP run alone would normally get 0.33 L and the TOF run alone would get 0.66 L?)

The choice was based on the range of the pressure sensor used to determine the preconcentration volume. In the meantime, the reference volume was increased and 1L is now the default preconcentration volume.

15. 12332, l. 22-25. This repeats an earlier description and can be deleted.

    Deleted.

16. 12333, Mass Resolution. I found this whole section not very relevant. If the mass resolution of the TOF somehow improves performance, this should be shown with practical examples rather than some theoretical discussion. Can you demonstrate that the ability to separate the halocarbon fragments from a hydrocarbon fragment improves the halocarbon analysis? Is there any co-elution of fragments in the sample? Is there improvement in the baseline noise due to exact mass selectivity? Please provide some specific applications of the impact of mass resolution on the actual analysis of a real sample

    The reason why this discussion stays theoretical is that we do not have the possibility to work with the full-resolution data from the TOF-MS due to the proprietary data format of the manufacturer. As stated in the manuscript, only 1 amu centroid data (exported as netcdf) could be used for the evaluation. This allows to calculate a mass accuracy but does not give access to the actual signal distribution on the mass axis. Despite this limitation we believe it is important to discuss the issue of mass resolution.

    In order to relate the discussion more closely to our instrument the following was added in section Results and Discussion, subsection Mass Resolution: An example of a mass spectrum centered around 85 u is shown in Figure 1 for a chromatogram of a typical ambient air sample at a retention time of 11.35

minutes. Two mass peaks, one centered at 84.943 u ($CH^{35}Cl^{37}Cl^{+}$), a fragment of the Trichloromethane ($CHCl_3$ molecule and one with a mass sligtly above unit mass can be clearly distinguished. The higher mass is the result of an unidentified hydrocarbon peak eluting shortly before the Trichloromethane peak.

figure-1.jpg

Fig. 1. So called 0.01 u mass spectrum of the substance Trichloromethane. Two mass peaks are shown. The higher one by mass 84.9 u, identified as the molecule fragment ($CH^{35}Cl^{37}Cl^{+}$) and the other one by mass 85.1 u as an unidentified hydrocarbon peak.

The resulting chromatogram centered at 11.3 minutes is shown in Figure 2. Three different mass ranges were extracted from the raw data, the nominal mass range from 84.5 u to 85.5 u, the lower mass range from 84.7 u to 85.0 u and the higher mass range from 85.0 u to 85.3 u. When extracting the information centered around the unit mass range a double peak is observed. An extraction of the lower mass range of the 85 u signal yields a much lower signal in the earlier eluting peak yet the signal cannot be reduced to baseline level. An extraction of the higher mass range of the signal gives a larger signal for the earlier eluting peak but again, the signal does not drop to baseline level.

Fig. 2. 5 A chromatogram of an unidentified hydrocarbon peak (smaller one) eluting slightly earlier as the higher Trichloromethan peak. The nominal mass 85 u (black) shows a double peak. By chosen the lower mass range (84.7 u to 85.0 u; red) a lower signal for the unidentified hydrocarbon peak is observed and by chosen the higher mass range (85.0 u to 85.3 u, blue) a lower signal for the Trichloromethane peak is observed.

This shows that the mass resolution of the Bench TOF-dx is sufficient to qualitatively show that two different fragments are present but that the resolution does not allow to separate these fragments in a way sufficient for quantifications. For a quantitative separation as defined above, the mass resolution of the Bench TOF-dx is not sufficient without further data processing steps like a peak deconvolution.

17. 12335, Mass Accuracy. I have the same comments about mass accuracy. A 50 - 100 ppm mass error may exclude some hydrocarbon fragments (though there is no indication that these fragments cause a problem), but this mass error does not exclude potentially other mass fragments of different elemental composition. Mass accuracy of <5 ppm or so would be a more relevant standard for discriminating ion fragments. Also, it would be helpful to understand how the

mass accuracy drifted or varied over the different runs.

We agree with this comment; unfortunately the mass accuracy of the Bench TOF-dx is only about 50-170ppm. Therefore we believe that it is important to state this fact and to show this limitation, given that other TOF instruments are quoted to have much higher mass accuracies. We also added a discussion on the drift of the mass axis in the new section on drift, based on your suggestions.

We include in the section Experimental, subsection Mass Accuracy:
Mass accuracy was calculated for four different ion masses of four different substances: HFC-134a (CF_3^+, 68.995 u), CFC-12 ($CF_2^{35}Cl^+$, 84.866 u), CFC-11 ($CF^{35}Cl_2^+$, 100.936 u,) and Methyliodide (CH_3I^+, 141.928 u) which cover most of the mass range of the substance peaks in our chromatogram. Individual values for the mass accuracy were taken at the maximum of each chromatographic peak. Data from reproducibility experiments (see subsection 3.5) as well as regular sample measurements were analysed to gain information about mass accuracy for the four exemplary ion masses. Only measurements taken under well equilibrated conditions were used for this analysis. As the first two measurements of a measurement day often show enhanced variability there were excluded from the analysis of the mass accuracy.

And in the Section Results and Discussion, subsection Mass Accuracy:
The mass accuracy for the Bench TOF-dx was found to be in a range of 50 to 170ppm for a mass range from 69 u to 142 u. Mass accuracies for the analysed target masses were determined as follows: (100±60) ppm for mass 68.995 u, for 84.966 u a mass accuracy of (80±50) ppm, for 100.936 u a mass accuracy of (120±50) ppm and for 141.928 u a mass accuracy of (130±40) ppm. A correlation between the displayed masses is observed: If the accuracy of one mass is decreased, the others are, too. There is no correlation given by

the proximity of target masses to tuning compound (PFTBA, e.g. 68.995 u) masses. A suspected reason for the instability of the mass axis is the instrument temperature and resulting changes in material elongation. This is however speculation.

18. 12335, Limits of detection. I believe there are some mistakes in the description of dwell time effects. The number of ions that reach the detector are not influenced by the dwell time. Lower dwell times do not reduce signal intensity (at least on the MS systems I use), but rather increase the noise level. Longer dwell times improve S/N by averaging the signal.

    The reviewer is indeed right that the count rates do not depend on the dwell time. As the ion source is continuous, the number of ions reaching the detector is dependent on the filter settings and the time that these filter settings are applied i.e. the dwell time. The analog output of the EMT is digitalized and in the case of the Agilent QP normalized by the according dwell time value to give comparable numbers. This means the output signal of the Agilent QP is proportional to “ion counts per time” and not to “ion counts” directly. However, shorter dwell times lead to lower ion count statistics and this also explains why noise levels are higher for shorter dwell times. As noted by Elliot Atlas the signal to noise level in the data decreases.

    We have changed the wording to make this clearer by discussing the signal to noise instead of the number of ions, section Result, subsection LOD:
    For the QP MS, the signal to noise level of a certain m/z depends on the concentration and dwell time. The dwell time represents the time interval in which the quadrupole mass filter is tuned to the specific mass-to-charge ratio (m/z) before switching to the next mass setting. Lower dwell times will decrease sensitivity but allow for more different mass filter settings per scan, resulting in

more different m/z monitored per time.

19. 12336, LOD. The increased LOD of the QP-MS in operational mode can be mitigated somewhat to use short dwell times for more abundant ions and longer dwell times for low concentration species. Further, one can often do without qualifier ions, and thus allow more dwell time for small peaks.

    We already used this method, so we include a sentence in the manuscript (Results and Discussion, subsection LOD):
    In measurements of ambient air, several m/z are usually monitored simultaneously (operational SIM mode (3)). The dwell times are optimised for the different substances. For substances with high concentration shorter dwell times are chosen, while the dwell time is increased for substances with low concentrations in order to increase the sensitivity. Only one ion is measured for most species in order to reach optimum sensitivity.

20. 12336. Reproducibility. Please include some detailed discussion of the method of peak integration. To get sub % precision requires some very reproducible methods for peak integration (esp. for the low abundance peaks). It would be valuable to know specifically how the different data were processed

    We added this paragraph on section Measurement procedure and data evaluation:

    Chromatographic peaks were integrated with a custom designed software, written in the programming language IDL. The peak integration is not based on a standard baseline integration method commonly used in chromatographic applications but on a peak fitting algorithm. For the results shown here Gaussian fits were used for peak integration. This software was also used for data processing by Sala2014 and described there. Noise calculation was performed on baseline sections of the ion mass traces of interest. The noise level was determined as the 3-fold standard deviation of the residuals between data points and a second degree polynomial fit through these data points. This approach accounts for a drifting non-linear baseline. Otherwise, a non-linear baseline would cause an overestimation of the noise level.

21. 12337, l. 13. I do not think the linearity issue is specific to the model of TOF used. All TOF suffer from less linear range compared to QP MS.

    As we only performed experiments to characterize the Bench TOF we have to limit our results to this specific mass spectrometer. Non-Linearity might be an issue for other TOF-MS but we cannot make any statements with respect to this.

    We rephrased our statement as follows for additional clarity (section Result and Discussion, subsection Reproducibility):
    This saturation shows the limited dynamic range of the Analog to Digital converter (memory of 8 bits) used in the Bench TOF dx.

22. 12337, l. 24. I do not see how it is possible to quantitatively measure any substance retrospectively if a standard reference was not run at the same time. At best, retrospective analysis is only semi-quantitative

    A retrospective, quantitative analysis would require two things: 1) the substance of interest was also present in the calibration gas and 2) a sample of the calibration gas (or a gas which was cross-calibrated to this calibration gas) is still available for absolute calibration. Of course one would have to estimate an error for substance drift in the flask etc. If the substance was not present in measurable amounts in the calibration gas, the retrospective analysis would indeed be semi-quantitative at best, e.g. relative to other substances with known mixing ratio. As this is an issue of more general character, we decided to add a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

brief discussion of this in the introduction.

We added the following statement in the introduction:
...Regardless of these limitations of the QP MS, it is widely used in analytical chemistry due to its stability, ease of operation, high degree of linearity, good reproducibility as well as sensitivity. Especially for atmospheric monitoring the advantage of obtaining the full mass information from the TOF instrument might allow retrospective quantifications of species which were not target at the time of the measurement. For this purpose the TOF MS must be well characterised (in particular with respect to linearity) and the calibration gas used during the measurements must contain measurable amounts of the retrospective substances and be traceable to an absolute scale.

23. 12338, l. 3. Delete “exemplary”

    Deleted.

24. 12338. Linearity. Though it may be the subject for another manuscript, it would be interesting to know if the authors have examined the non-linear response as a function of ion-intensity. While the author′s discuss the impact of detector saturation on linearity (but also on mass accuracy), it is unclear why the low level samples demonstrate lower responses. This could be related to lower detector efficiency at low ion counts, or might it be related to some other baseline attribution issue (i.e. choosing a baseline that eliminates some response due to compound). Also, do the authors note the same functional behavior for all “non-linear” compounds in the group of 35, or is the shape of the response curve different?

    We agree with the reviewer that it would be very interesting to understand the reasons for the non-linearity and have indeed given this some thoughts.

However this is very speculative and is beyond the scope of this paper.

We added the following to discuss this issue in subsection linearity:
The non-linearity of the TOF-MS was highest for the low preconcentration volume (33%, 0.09 L) with deviations of -10% to +20% compared to a standard preconcentration volume of 100% (0.28 L). For most substances the non-linearity showed a similar behavior as observed for CFC-11 (decreased sensitivity for low amounts of analyte) while some species showed an opposite behavior (increased sensitivity with decreasing amount of analyte). The reason for these non-linearities need to be investigated in more detail in the future.

25. 12339, l. 6-7. Change deferring to different, and suggest including parentheses around ...(for example ... 0.136).

    Done.

26. 12340, conclusions. A brief mention of current relative costs of a QP vs TOF might be another useful comparison.

    We added the following statement in the conclusion:
    With reduced non-linearities, TOF MS could well be the technology of the future for the analysis of halogenated trace gases in the atmosphere, despite the significantly higher costs of the TOF MS in comparison to QP MS instruments.

27. General. It would have been interesting to see a demonstration of the ability of a TOF to identify new compounds. For example, could the authors show the signal for one of the emerging or low concentration perfluorocarbons with TOF? This would be unlikely to be detected with a QP-MS in scan mode.

    This demonstration will potentially be part of a future publication. Due to the fact that Methyliodide was not detectable in scan mode in the QP-MS even though noise levels are comparably low on its masses, the low concentrated emerging hydro- and perfluorocarbons are most likely to be undetectable, too.

28. Table 3. Typo? I calculate 96.961 for the C2H3Cl2 fragment. The listed fragment must be with one Cl-35 and one Cl-37.

    Typo corrected.

29. Table 4. Caption. Delete “used”. Define the error (2 sd?,3 sd?) . Also for Table 5.

    Table 4. ....The given errors are one sigma standard deviation.
    Table 5. ....The given errors are one sigma standard deviation.

30. Figure 1. This is not a particularly revealing diagram. Could more detail be provided about the preconcentration unit, and also show the splitter inside the oven (as described in the text). In the caption change “splitted by a 3-way split” to just “split”.

    The Figure has been deleted.

31. Figure 4. As noted above, I was not crazy about the discussion of mass resolution, and this theoretical plot does little to help. If something like this is to be shown, please use data from your instrument.

    The discussion of the mass resolution has been extended significantly. We also added a Figure showing a mass peak of the TOF and the effect of different mass range extractions on the chromatogram. We still believe that this theoretical Figure is useful in explaining the mass resolution required for quantitative and qualitative separation.

Reply to Anonymous Referee:

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 is not 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 is not mentioned, or because 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.

Especially the reviewer required some more specific information on the following issues:

1. 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?

   Ion extraction rates are in principal dependent on the flight distance, the flight velocity (i.e. extraction energy) and the heaviest ion that is produced in the ion source. Typically a TOF-MS measures several thousand to ten thousands of mass spectra per second, which are then averaged to yield the requested time resolution and improve signal to noise ratio. For the Bench TOF dx, the full spectra rate can be set between 2 and 50 Hz. Even higher data rates are possible with special configurations.

We added the following statement in the introduction:
TOF MS has only been applied sporadically for measurements of atmospheric trace gases (Kim2012a, Kundel2012, Watson2011, Jordan2009) and in particular not with focus on halocarbons. The main advantage of coupling a TOF MS to a gas chromatograph (GC) over using the QP MS are the intrinsic full mass range acquisition, the better mass resolution and mass accuracy. The identification of unknown peaks is significantly facilitated by these advantages and the use of more narrow mass ranges is expected to reduce interferences and background noise. In addition, much higher data acquisition rates are possible using TOF MS, which is an advantage for fast chromatography. A TOF MS instrument can measure more than 10000 mass spectra per second. They are added up and averaged over a certain time period to yield the desired time resolution. The possibility of operating the TOF at high data rates is also of high interest for fast chromatography and narrow peaks where the operating frequency of quadrupole instruments (especially when measuring several ions) can be a limiting factor. The maximum time resolution for the TOF MS used in this study is 50 Hz. An increase in the data frequency with lead to decreased Signal to noise levels. The data frequency must therefore be optimised to provide a sufficient number of data points per chromatographic peaks while keeping the Signal to noise level as high as possible. In contrast, a QP MS is a mass filter and will only measure one mass at a time.

2. Are ions accumulated between pulses somehow (as in an ion-trap-type source)?

   They are not accumulated as in an ion trap. However for this particular TOF instrument the ions are extracted directly from the ion source (direct extraction) for each mass spectrum so there is an accumulation between each extraction. Another more common type of TOF-MS, the orthogonal extraction TOF-MS, creates a continuous ion beam from the ion source and accelerates "packages" from this ion beam into the flight chamber, orthogonal to the axis of the ion beam.

   This issue is briefly discussed in section 2.3:
   The Bench TOF-dx uses a direct ion extraction technique with an acceleration voltage of 5 kV. In contrast to many other TOF instruments the ions are accelerated directly from the ion source into the drift tube, instead of extracting them from the ion source and then accelerating them orthogonally to the extraction direction (orthogonal extraction). The direct extraction method in combination with the high acceleration energy orients the instrument towards a high sensitivity, especially for heavier ions (five technologies GmbH, Dr. G. Horner and Dr. P. Schanen, personal communication, 2014)

3. Would chromatographic peaks (especially narrow ones) be more accurately characterized by the TOF with higher sensitivity than by the QP-MS?

   As stated above, higher spectra rates are possible in principal, but also afflicted with higher noise levels. The choice is again somewhat application dependent. For our purposes, the data acquisition rate of 4 Hz is sufficient because the width of the chromatographic peaks is large enough, so that they are determined by more than 15 data points. However, the higher data frequency of the TOF is an advantage for narrow peaks. We added a passage in the

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

introduction, see answer to question 1.).

4. 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.

   This is true. Using air from only one tank to estimate the reproducibility could lead to under- or overestimation of the measurement precision of other air samples with different characteristics, e.g. highly polluted samples or samples with sub-ambient concentrations. However, from our measurements we find, that the reproducibility in a typical atmospheric air sample is similar to that obtained in the calibration gas used for the reproducibility experiment. Therefore we regard the measurement precision estimated from this type of experiments carried out with only one reference tank as representative for atmospheric air samples.

5. 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.

   We changed the graphics (y-axis label) for the linearity plot to a % deviation for better understanding (e.g. see Figure 3). The deviation is of course concentration dependent and cannot be quantified with a single number. Therefore we choose not to change the text but changed the graphics (see Figure 6) in order show the deviation more clearly.

6. p. 12325, line 12. The UCI group (Salzman and Aydin) have used high resolution

figure-3.png

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

GCMS for the analysis of halocarbons in ice; this would seem useful to mention also.

Added citation Aydin, 2002, doi: 10.1029/2002gl014796

7. Line 13, even the QP MS does not monitor ions simultaneously, consider better wording here. Lines 17-20. It would seem there are other potential advantages of using a TOFMS 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 comment).

   Changed structure of the according paragraph in the introduction (see also question 1.)

8. 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?

   This comment is similar to comment No. 7 from E. Atlas; please find our reply there.

9. 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.

As for the used Agilent QP, resolution is not adjustable with the used operating software (Agilent MS Chemstation). To take into account that the absolute mass

resolution is rather independent of the mass for the quadrupole we added as follows section Experimental, subsection Mass Resolution:
The QP MS was operated with MS Chemstation (Agilent Technologies, Inc.) which only processes unit mass resolution, independent of mass range.

10. Section 3.3 Does mass stability depend on the number of amu between a reference mass and the analyte ion mass?

    We added the following paragraph in section Results and Discussion, subsection Mass Accuracy:
    There is no correlation given by the proximity of target masses to tuning compound (PFTBA) masses. A suspected reason for the instability of the mass axis is the instrument temperature and resulting changes in material elongation. This is however speculation.

11. No mention of the reference masses used here are given

    Please see section “Drift” in our reply to comment No. 3 of E. Atlas.

12. And what are the matrix effects (line 11, p. 12331) mentioned? Are they likely to be minimal in most air analyses?

    This comment is similar to comment No. 9 from E. Atlas; please find our reply there.

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

    This comment is similar to comment No. 20 from E. Atlas; please find our reply there.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

14. Table 3, I don′t see n(sub sigma) defined in the caption or in the main text.

    We changed the text of the manuscript as follows:

    For a value of $n_\sigma = 8$, equation 4 gives the quantitative separating resolution, for a value of $n_\sigma = 2$ a qualitative separating resolution.

15. 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 are not 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 obtained from the different sampled volumes?
    In the meantime we conducted another reproducibility experiment with higher sample preconcentration volumes. Therefor we changed the values and caption of Table 6 (see Table below). The re-producibility derived after the second experiment was found to be on the same level as the first one.

Table 4. The reproducibility (REP) for the QP MS and the TOF MS as a mean value of two measurement series with 20 measurements each and a preconcentration volume of 1.00 L. The given errors are one sigma standard deviation over two reproducibility experiments.

substance	formula	REP QP [%]	REP TOF [%]
CFC-12	CCl_2F_2	0.22 ±0.10	0.23 ±0.09
CFC-11	CCl_3F	0.14 ±0.03	0.16 ±0.00
Halon-1211	$CBrClF_2$	0.60 ±0.05	0.55 ±0.21
Iodomethane	CH_3I	1.31 ±0.23	0.99 ±0.30

16. p. 12337, line 15, it would be useful to indicate the capabilities of the A/D con-

verter in use to understand if this important limitation could be easily addressed with some upgraded electronics or not.

The A/D converter of the used mass spectrometer has a 8 bit register for data accumulation. A lager memory can theoretically extend the dynamic range of the instrument. To clarify the limitation of this A/D converter, we include the capability in the section Results and Discussion, subsection Reproducibility:
This saturation shows the limited dynamic range of the Analog to Digital converter (memory of 8 bits) used in the Bench TOF dx.

17. 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.

We found that the QP MS showed linear behavior for all substances within the uncertainty range. Non-linearities for the QP-MS showed a maximum of 5% for some species at the small preconcentration volume (33%) but in this case the measurement precision was also at a 5%-level. The TOF MS in contrast showed non-linear behavior for 25 of all 35 analyzed species, 10 species showed a linear behavior within the error bars. The non-linearity of the TOF-MS was highest for the low preconcentration volume (33%) with deviations of -10% to +20% compared to a standard preconcentration volume of 100% (0.28L).

We changed the discussion regarding the linearity of the TOF MS in respect to the suggestion of E. Atlas, including the above sentence:

The non-linearity of the TOF-MS was highest for the low preconcentration volume

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

(33%, 0.09 L) with deviations of -10% to +20% compared to a standard preconcentration volume of 100% (0.28 L). For most substances the instrument showed a similar behavior as observed for CFC-11 (decreased sensitivity for low amounts of analyte) while some species showed the opposite behavior (increased sensitivity with decreasing amount of analyte). Reasons for this conflicting behavior are still subject to further investigation.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C5021/2015/amtd-7-C5021-2015-supplement.pdf

---

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

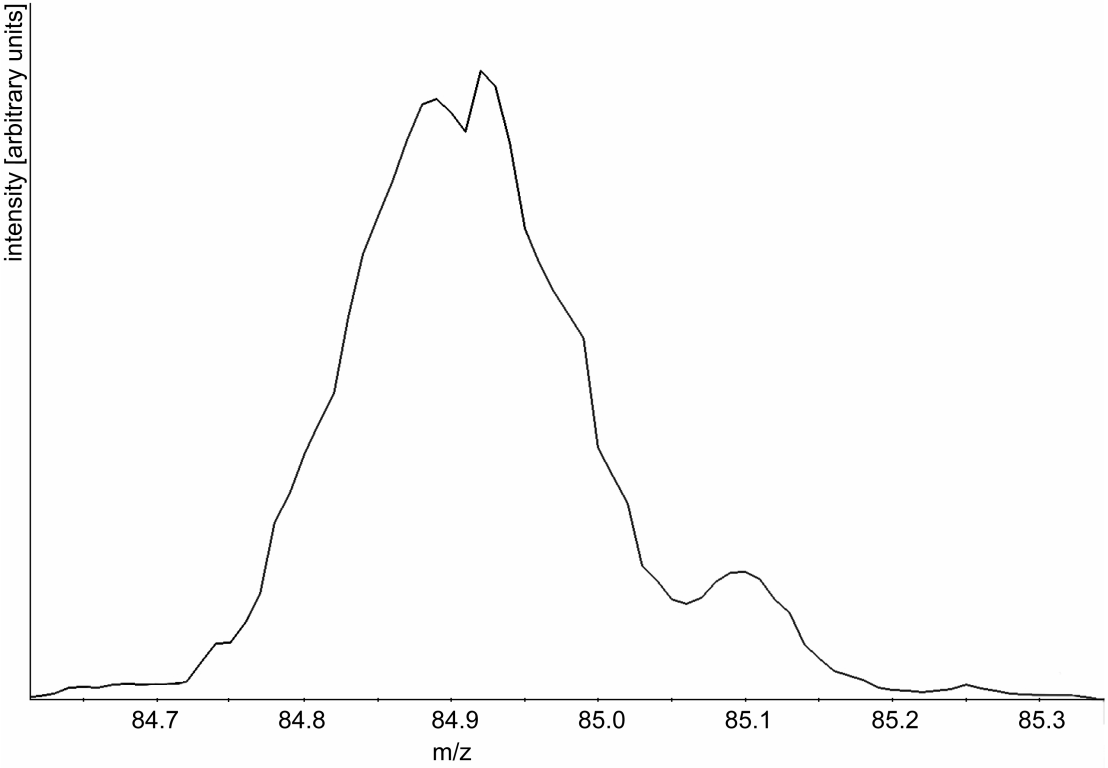


Fig. 4.

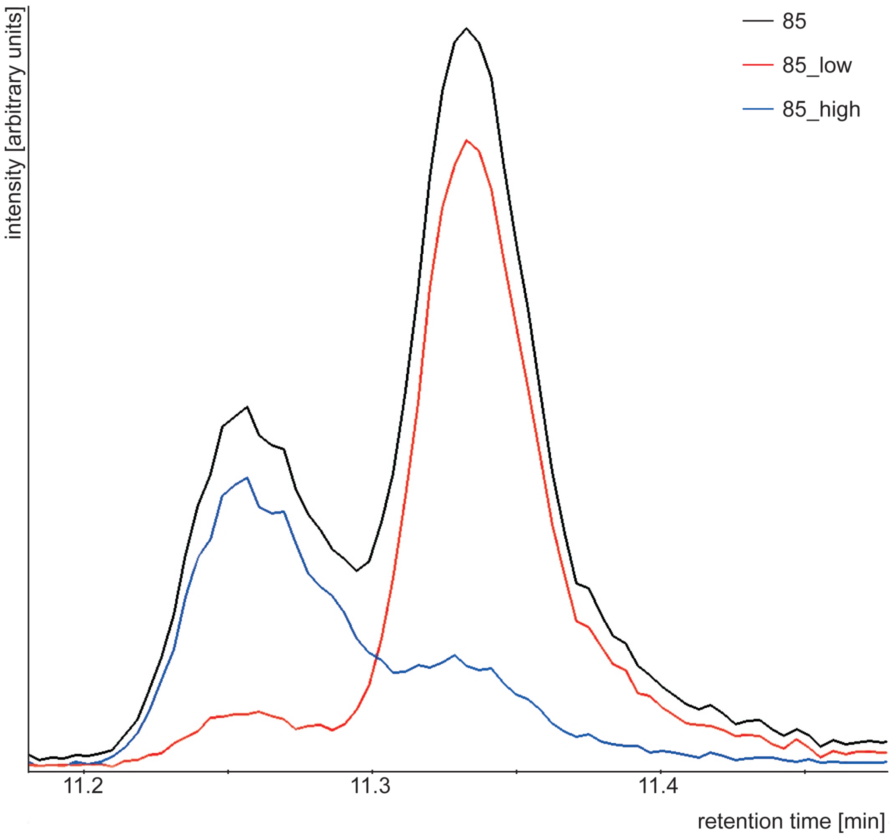
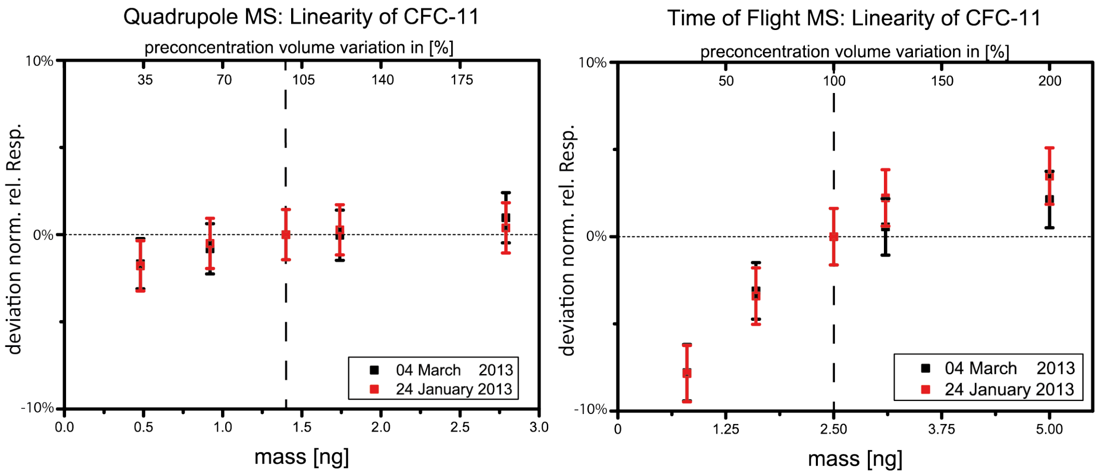


Fig. 5.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper



Quadrupole MS: Linearity of CFC-11

Time of Flight MS: Linearity of CFC-11

Fig. 6.