

are some newly detected fully halogenated species (Laube et al., 2014). Also, many fluorocarbons which do not destroy stratospheric ozone and are thus not regulated under the Protocol show increasing trends in the atmosphere (Laube et al., 2012; Ivy et al., 2012; Vollmer et al., 2011). Although these fluorocarbons do not destroy ozone, many of them are strong greenhouse gases with long atmospheric lifetimes, resulting in increased radiative forcing of the troposphere. Therefore, the need persists for continuous measurements to identify new compounds in the atmosphere and monitor and document their atmospheric trends. The mass spectrometric instrument type commonly used for halocarbon analysis is the quadrupole mass spectrometer (QP MS) (Cooke et al., 2001; Miller et al., 2008; Sala et al., 2014). Besides the QP MS, the use of high mass resolving and extremely sensitive sector field MS has also been reported (Lee et al., 1995; Laube et al., 2014). Both sector field and QP MS generally only measure one mass or a few selected masses at a time despite having scanning capabilities. Nevertheless, TOF MS has only been applied sporadically for measurements of atmospheric trace gases (Kim and Kim, 2012; Kundel et al., 2012; Jordan et al., 2009) and in particular not for halocarbons. The main advantage of coupling a TOF MS to a gas chromatograph (GC) over using the QP MS is the intrinsic full mass range acquisition which constitutes, desirably in combination with a high mass resolution and mass accuracy, an advantage for unambiguous substance identification. In contrast, a QP MS is a mass filter and will only measure one mass at a time. It needs to scan many individual masses sequentially to register a full mass spectrum. To achieve high sensitivity, QP MS are therefore often operated in single ion monitoring (SIM) mode where the instrument is tuned to only one or a few selected ion masses and all other ions do not pass the quadrupole mass filter. 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.

In this paper, a comparison of a state-of-the-art QP MS and a TOF MS is presented, with both mass spectrometers being coupled to the same gas chromatographic system. The instrumental setup is described in Sect. 2. The GC QP MS system was charac-

12325

terised and used before for studies by (Laube and Engel, 2008; Brinckmann et al., 2012) and showed consistent results in the international comparison IHALACE (International Halocarbons in Air Comparison Experiment) with the NOAA (National Oceanic and Atmospheric Administration) network (Hall et al., 2013). We discuss the use of TOF MS in atmospheric trace gas measurements, in particular for the detection and quantification of halocarbons, focusing on four substances: CFC-11, CFC-12, Halon-1211 and iodomethane. These four substances cover the boiling point and typical concentration range of a total of 35 substances analysed. The five key parameters for atmospheric trace gas measurements discussed in this paper are (1) mass resolution and (2) mass accuracy of the detectors, (3) detector sensitivity represented by the limits of detection (LOD), (4) reproducibility of the measurement procedure and (5) the linearity of the detectors for varying amounts of analyte. The underlying experiments are described in Sect. 3 and their results are discussed in Sect. 4. Section 5 summarises the results of this work.

2 Instrumental

An overview of the analytical system used in this work is displayed in Fig. 1. Explanations regarding the individual components are given in the following subsections.

2.1 Preconcentration unit

Atmospheric mixing ratios (mole fraction) of halocarbons are very low, i.e. in the parts per trillion (ppt) to parts per quadrillion range (ppq). To achieve signals clearly distinguished from noise in GC MS analysis, a sample preconcentration procedure is required. In this work, the method of sample cryofocussation on adsorptive material followed by thermodesorption prior to gas chromatographic separation was used. Figure 2 shows a schematic of the preconcentration unit; explanations are given in the following. A similar setup was described by (Sala et al., 2014). A 1/16 inch stainless

12326

steel tube (sample loop) packed with HayeSep D adsorption material was cooled to a temperature of -80°C for cryofocusing. For cooling, a Stirling cooler was used (Global Cooling, Inc., model M150). The sample loop was placed inside a cooled aluminium cylinder (cooling head) and was thermally and electrically isolated with two layers of glass silk and one layer of Teflon shrinking hose. The cooling head was thermally isolated towards ambient air with two layers of Aeroflex-HF material. All sample components which were not trapped on the adsorption material were collected in a 2 L stainless steel flask equipped with a pressure sensor (P) (see Fig. 1). The pressure difference between beginning and end of the preconcentration phase was recorded to calculate the preconcentration volume. After the preconcentration phase, the sample loop was heated resistively to $+172^{\circ}\text{C}$ in a few seconds for instantaneous injection of the trapped analyte fraction onto the GC column. Desorption temperature was maintained for 4 min to clean the sample loop from all remaining compounds. All tubing (stainless steel) used for sample transfer between sample flask and preconcentration unit as well as preconcentration unit and GC was heated to 80°C to avoid loss of analytes to the tubing wall.

2.2 Gas chromatograph

An Agilent Technologies 7890A GC with a Gas Pro PLOT column (0.32 mm inner diameter) was used for separation of analytes according to their boiling points. The column had a total length of 30 m, divided inside the GC oven into 7.5 m pre-column (backwards flush-able) and 22.5 m main-column. Purified Helium 5.0 (Alphagaz 1, Air Liquide, Inc.) was used as carrier gas. The GC was operated with constant carrier gas pressure on both pre- and main column. The temperature program of the GC consisted of five phases. (1) For the first two minutes, the temperature was kept at 50°C . (2) Then the oven was heated with a rate of $15^{\circ}\text{C}\text{minute}^{-1}$ up to 95°C , (3) from thereon $10^{\circ}\text{C}\text{minute}^{-1}$ up to 135°C and (4) with a rate of $22^{\circ}\text{C}\text{minute}^{-1}$ up to 200°C . (5) The final temperature of 200°C was kept for 2.95 min. The resulting runtime was 17.95 min. The pre-column was flushed backwards with carrier gas after 12.6 min to avoid contam-

12327

ination with high-boiling substances. 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 split ratio of the gas flow after the GC was $\approx 34\%$ into the QP MS and $\approx 66\%$ into the TOF MS. The transfer line to the QP MS had a total length of 0.60 m with an inner diameter of 0.1 mm, the transfer line to the TOF MS had a total length of 2.54 m with an inner diameter of 0.15 mm. All parts of the transfer lines outside the GC oven were heated to 200°C .

2.3 Mass spectrometer

The two mass spectrometers in comparison were (1) an Agilent Technologies 5975C QP MS and (2) a Markes International (former ALMSCO) Bench TOF-dx E-24 MS. Both MS were operated in electron ionisation (EI) mode with an ionisation energy of 70 eV and ioniser temperatures of 230°C . The QP MS was operated in SIM and SCAN mode (see Table 2 for more information). As the GC was operated in constant pressure mode, i. e. the head pressure of the columns were kept constant, the carrier gas flow into the two MS therefore varied according to the temperature ramp during each gas chromatographic run. Pressures inside the ion flight tubes of the MS therefore also varied; the TOF MS had a pressure range from 1.8×10^{-6} to 1.6×10^{-6} hPa and the QP MS had a pressure range from 2.1×10^{-5} to 1.8×10^{-5} hPa. 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, G. Horner and P. Schanen, personal communication, 2014). The MS was set up to detect mass ranges from 45 to 500 m/z ; higher and lower m/z were discarded. The reason to discard ions with m/z ratio below 45 was to eliminate a large part of the CO_2 which is trapped by our preconcentration method and can lead to saturation of the detector. A schematic of

12328

strument property. In this work, so called 1 amu centroid mass spectra are used to calculate mass accuracy. The exact mass hereby is taken as the maximum intensity of the mass spectrum within a certain window (± 0.5 u) around the nominal mass. Mass accuracy was calculated for four different ion masses (68.995, 84.966, 100.936, 150.933 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 the according chromatographic peak. Data from reproducibility experiments (see Sect. 3.5) as well as regular sample measurements were analysed to gain information about (1) mass accuracy over multiple chromatographic runs and (2) mean mass accuracy over multiple measurement series for four exemplary ion masses. Only measurements taken under well equilibrated conditions were used for this analysis to minimise matrix effects.

3.4 Limits of detection

The lowest amount of a substance that can reliably be proven is considered to be its limit of detection (LOD) and serves as a measure for the sensitivity of the analytical system. Based on the assumption that a molecule fragment f can be detected when its detector signal height H_{f_i} is equal to or higher than three times the signal noise N_{f_i} on the adjacent baseline (signal-to-noise level (S/N) > 3), a limit of detection (LOD) for a fragment f_i from an analyte substance S_i with a mass m_{S_i} in the injected sample can be calculated as:

$$\text{LOD}_{S_i} = \frac{3 \cdot N_{f_i} \cdot m_{S_i}}{H_{f_i}} \quad (3)$$

For comparison with the QP MS, the LOD of both instruments were calculated from calibration gas measurements by linear down scaling. Possible detector non-linearities were omitted in this case. The LOD error was considered to be the standard deviation of 10 calculated Limits of Detection. Different settings of the QP MS (SCAN mode (1), optimised (opti.) SIM mode (2) and operational (oper.) SIM mode (3)) were applied.

12331

In the SCAN mode (1), the Quadrupole MS scanned from 50 to 500 u (comparable to the mass range of the TOF MS) with a dwell time of ≈ 3.7 ms ion⁻¹ and a scan rate of 1.66 scans per second. In the optimised SIM mode (2), the Quadrupole MS measured only one ion with a dwell time of 310 ms with ≈ 3 scans per second. In the operational SIM mode (3) the Quadrupole MS measured several masses (up to six) in one scan with individual dwell times given in Table 2 and ≈ 3 scans per second.

The LOD in pg and ppq were calculated for 0.28 L sample volume with respect to the split ratio (see Sect. 2.2) and then extrapolated to 1 L of ambient air.

3.5 Reproducibility and measurement precision

The measurement precision describes the repeatability of a measurement. We determine the precision from the reproducibility (i.e. the standard deviation) of the measurements. The mean reproducibility is derived from dedicated multiple experiments designed to assess measurement precision (reproducibility experiment). Reproducibility was analysed over five measurement series, conducted on five different days, to give the mean measurement precision. Every experiment followed the procedure described in Sect. 3.1, with a total of 19 evaluated measurements of the same ambient air sample. A subset of the samples was treated as standard, the other part as unknown samples (two samples bracketed by two standards. Every individual measurement of these five series was conducted with a preconcentration volume of 0.28 L of the reference gas. An additional reproducibility experiment was conducted with a higher preconcentration volume of 1 L to assess the possible dependence of the reproducibility on the preconcentrated sample volume. The bracketing calibration points were interpolated point to point giving a calculated calibration value for every sample. The quotient of sample and calculated calibration value gives the relative detector response for the respective sample. For each sample pair, a standard deviation of the relative response was calculated, summed up over all pairs and divided by the number of pairs to form the sample pair measurement reproducibility of that measurement series. The described procedure was applied to all analysed substances and five reproducibility experiments.

12332

a reproducibility experiment with a larger preconcentration volume of 1 L was performed. The results are shown in Table 6.

The increase of the preconcentration volume to 1 L yields a significant improvement of the measurement precision. The high signal to noise species CFC-12 and CFC-11 now show reproducibilities below 0.3 % for the QP and for the TOF. For the low signal to noise species Halon-1211 and CH₃I the reproducibilities are improved by a factor of up to four for the TOF MS and by a factor of up to three for the QP MS, with the TOF instrument showing better reproducibilities. As for the TOF MS, the detector itself was found to be a limitation to higher preconcentration volumes as it showed saturation effects for some analysed ions already at 0.5 L preconcentrated sample. E.g. CFC-12 had to be evaluated on mass 87 u (relative abundance: 32.6 %) and CFC-11 on mass 103 u (relative abundance: 65.7 %) (NIST, 2014) as both main quantifier ion masses (85 and 101 u) showed saturation in the respective retention time windows. This is a specific problem of the Bench TOF dx used here due to the limited dynamic range of the Analogue to Digital converter.

4.5 Linearity

For the calculation of the mixing ratio of a measured substance, its detector signal has to be correlated with the signal of the same substance in a calibration measurement with known mixing ratio. If the detector behaves linearly, this correlation is linear and the calculation of the mixing ratio is straight forward. As mixing ratios in different air samples might vary to a great extent (e.g. diurnal variations of short-lived substances) (Sala et al., 2014; Derwent et al., 2012; Law and Sturges, 2011), a linear detector simplifies data evaluation to a great extent. Furthermore, retrospective analysis of substances that were not identified at the time of measurement is possible without an unknown error due to detector non-linearity. Figures 5 and 6 show linearity plots for the QP MS for the CFC-11 and CFC-12 based on two linearity experiments. The QP MS showed a linear behaviour within the measurement errors (3-fold measurement reproducibility for the respective substance). This linearity test includes possible effects of the pre-

12337

concentration unit (quantitative adsorption and desorption) as well as the determination of the preconcentration volume, the GC and data processing (signal integration). Figures 5 and 6 illustrate exemplary results from the two linearity experiments for the TOF MS. For CFC-11 (Fig. 5) a deviation from linearity for small preconcentration volumes of nearly 10 % is observed, while detector behaviour is close to the ideal value for high preconcentration volumes. The red curve was derived based on the standard detector voltage of -2244.8 V. An decrease of the detector voltage by -30 V brought slight improvements but did not solve the issue. Figure 6 shows a linearity plot for the substance CFC-12. For CFC-12 the detector is considered to be linear within the error bars. Both detectors compared in this work depend on the same sample preparation and separation steps before detection. As measurement reproducibilities of QP MS and TOF MS were not significantly different, the direct comparison is possible without limitations. The examples displayed for the QP MS and the TOF MS are two of 35 substances measured and analysed. The QP MS showed linear behaviour for all substances within the uncertainty range. The TOF MS in contrast showed non-linear behaviour (like CFC-11) for two thirds of all 35 analysed species. Proportionality of detector signal against the amount of analyte in the sample over the given concentration range was thus found for the QP MS but only for some species in the TOF MS. If the detector does not behave linearly, the relationship between the integrated peak area and the atmospheric concentration has to be approximated by a fit function. In order to generate this fit function, additional measurements with varying preconcentration volumes are necessary before each measurement series. This procedure was found to be necessary for the TOF MS. It lengthens measurement series, implies an additional error source and requires additional time for data processing.

5 Conclusions

A Markes International Bench TOF-dx was compared to an Agilent Technologies 5975 QP MS with respect to the measurement of halogenated trace gases in the atmo-

12338

sphere. Both detectors ran in parallel (1 : 2 split) after cryogenic preconcentration and gas chromatographic separation of the air sample. The comparison included the mass resolution, mass accuracy, the limit of detection (LOD), the measurement precision (reproducibility) and the detector linearity. The TOF MS showed a resolution of 1000 and a Δm of 0.071 at mass 219.995 u with a mass accuracy of 50 to 100 ppm. Therefore it is able to qualitatively separate ion signals at differing exact mass but equal unit mass for example the mass 84.966 u from the mass 85.106 u by a Δm of 0.136. This qualitative mass separation of the TOF MS could be sufficient for improved substance identification and is an advantage over the QP MS. The QP MS does not allow for separation of exact masses as the mass resolution of QP MS instruments is generally too low ($R \approx 200$) for that purpose. The analysis of detection limits showed that the TOF MS is generally more sensitive than the QP MS (despite using selected ion monitoring mode). The LOD of the QP in the SCAN mode are up to a factor of 12 higher than the LOD of the TOF MS. LOD of the TOF MS are lower by factors of up to 3 (Table 4) in comparison to the QP MS with operational SIM mode settings used for routine measurements. In the SIM mode with only one quantifier (optimised SIM mode) the TOF MS is similar to the QP MS. In that respect, the TOF MS with its very high sensitivity and full mass range information provides a considerable advantage compared to a QP MS. The reproducibility of both instruments was found to be on an equal level with slightly better reproducibilities of the QP MS at high signal to noise levels and slightly better reproducibilities of the TOF MS for low-concentrated species. Regarding detector linearity, the Bench TOF-dx in its current configuration could not compete with the QP MS. A high degree of linearity is however necessary for high accuracy measurements in trace gas analysis. The encountered non-linearities necessitate a correction which adds an error source, especially if there is a large concentration difference between sample and calibration measurement. It furthermore complicates measurements as well as data evaluation. For other applications where concentration variability is significantly higher than the non-linearity of the detector, the observed detector non-linearities might not be of such high relevance. Concluding, the TOF MS does show advantages

12339

in respect to mass resolution and sensitivity without losing the full mass spectra information. Persisting non-linearities are a big disadvantage but might be conquered in the future by developments in detector electronics. With reduced non-linearities, TOF MS could well be the technology of the future for the analysis of halogenated trace gases in the atmosphere. These conclusions are only valid for the Markes International TOF MS E-24 and atmospheric trace gas measurements and might turn out differently for another field of research or another TOF MS.

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12340

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12341

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12342

Table 4. The limit of detection (LOD) in ppq and pg of the substances CFC-12, CFC-11, Halon-1211 and Iodomethane in 1 L of air sample per detector. The used dwell times and settings for the QP MS are given in Table 2.

Substance	LOD TOF [ppq]	LOD TOF [pg]	LOD QP [ppq] SCAN (1)	LOD QP [pg] SCAN (1)	LOD QP [ppq] opti. SIM (2)	LOD QP [pg] opti. SIM (2)	LOD QP [ppq] oper. SIM (3)	LOD QP [pg] oper. SIM (3)
CFC-12	25 ± 2	0.12 ± 0.02	241 ± 19	1.18 ± 0.09	21 ± 3	0.10 ± 0.01	48 ± 6	0.23 ± 0.30
CFC-11	31 ± 2	0.17 ± 0.02	370 ± 19	2.05 ± 0.29	36 ± 1	0.20 ± 0.01	64 ± 9	0.35 ± 0.05
Halon-1211	27 ± 2	0.182 ± 0.004	276 ± 53	1.84 ± 0.13	36.0 ± 0.3	0.240 ± 0.002	43 ± 5	0.29 ± 0.02
Iodomethane	12.00 ± 0.01	0.069 ± 0.001	Not a Number	Not a Number	16 ± 1	0.090 ± 0.003	42 ± 2	0.24 ± 0.05

12347

Table 5. The reproducibility (REP) for the QP MS and the TOF MS as a mean value of five measurement series with 20 measurements each and a preconcentration volume of 0.28 L.

Substance	Formula	REP QP [%]	REP TOF [%]
CFC-12	CCl ₂ F ₂	0.56 ± 0.31	0.56 ± 0.18
CFC-11	CCl ₃ F	0.45 ± 0.26	0.54 ± 0.23
Halon-1211	CBrClF ₂	1.56 ± 0.52	0.94 ± 0.39
Iodomethane	CH ₃ I	3.96 ± 0.72	3.44 ± 1.61

12348

Table 6. Measurement Precision (MP) for the QP MS and the TOF MS based on a single reproducibility experiment with a preconcentration volume of 1.0 L.

Substance	Formula	MP QP [%]	MP TOF [%]
CFC-12	CCl_2F_2	0.27	0.29
CFC-11	CCl_3F	0.12	0.16
Halon-1211	CBrClF_2	0.56	0.40
Iodomethane	CH_3I	1.14	0.78

12349

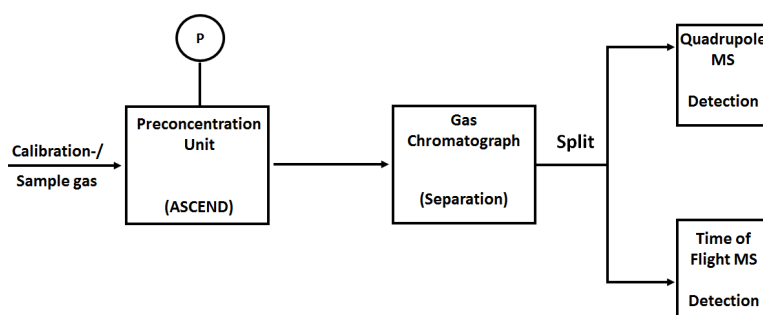


Figure 1. Schematic of the analytical setup, All sample components which cannot be cryofocused are collected in a stainless steel flask equipped with a pressure sensor (P) for sample volume determination. After preconcentration, the sample is thermally desorbed and transported into the GC via the carrier gas flow. After gas chromatography, the flow is splitted by a 3-way-split inside the GC oven into the Quadrupole MS and in the Time of Flight MS for detection of the analytes.

12350

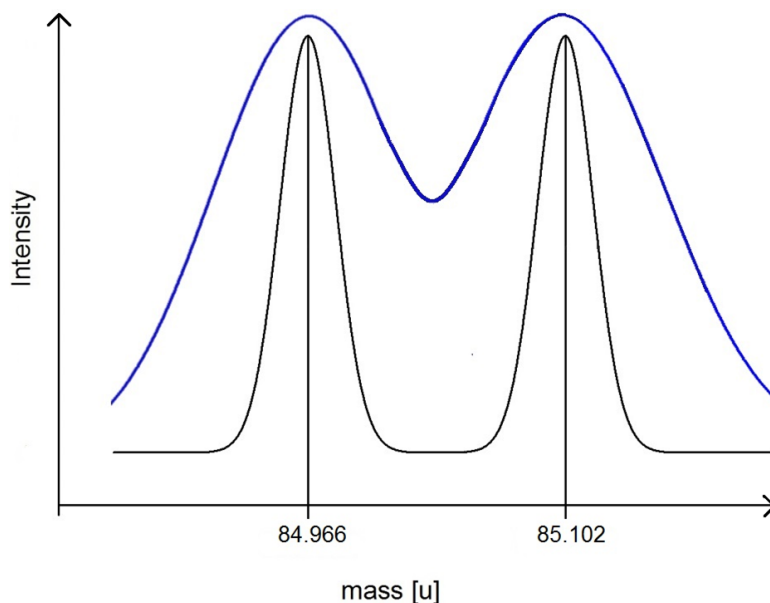


Figure 4. Schematic display of two different mass resolutions (blue and black curve). Two signals on masses 84.966 and 85.102 u with equal intensities demonstrate the mass separation with $R = 600$ (blue curve) and $R = 3700$ (black curve). Assuming Gaussian peak shapes for the signals, $R = 3700$ separates both peak by 8σ (quantitative separation), $R = 600$ separates them by only 2σ (qualitative separation).

12353

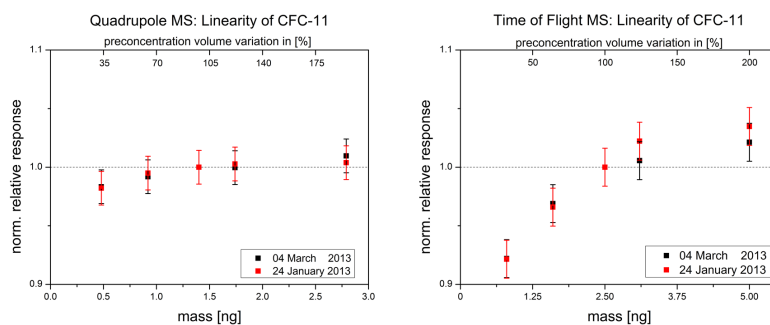


Figure 5. Linearity graphs of CFC-11 (CFCI_2^+ fragment), based on two different linearity experiments (red and black plots in each graph). Primary x axis (lower): mass on column in ng. Secondary x axis (upper): preconcentration volume variation in % vs. a default preconcentration volume of 0.3 L. y axis: relative detector response (vs. the detector response of the default preconcentration volume). For every preconcentration volume, the relative response should be one in case of a linear detector behaviour (dashed line). The errors show the three fold measurement precision. On the left hand side for the QP MS and on the right hand side for the TOF MS. The second linearity experiment (black) of the TOF MS was conducted with a decreased detector voltage (-2274.8 V instead of -2244.8 V).

12354

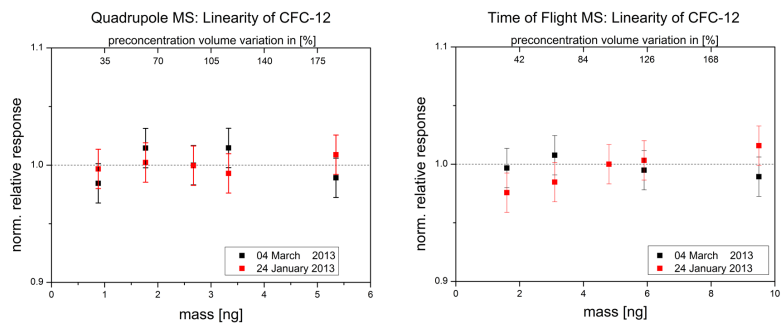


Figure 6. Same figure as Fig. 5 for the substance CFC-12 (CF_2Cl^+ fragment).