



**An automated
GC-TOFMS for
halocarbon analysis
in air**

F. Obersteiner et al.

**An automated gas chromatography
time-of-flight mass spectrometry
instrument for the quantitative analysis of
halocarbons in air**

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Received: 16 July 2015 – Accepted: 21 August 2015 – Published: 14 September 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

We present the characterization and application of a new gas chromatography-time-of-flight mass spectrometry instrument (GC-TOFMS) for the quantitative analysis of halocarbons in air samples. The setup comprises three fundamental enhancements compared to our earlier work (Hoker et al., 2015): (1) full automation, (2) a mass resolving power $R = m/\Delta m$ of the TOFMS (Tofwerk AG, Switzerland) increased up to 4000 Th/Th and (3) a fully accessible data format of the mass spectrometric data. Automation in combination with the accessible data allowed an in-depth characterization of the instrument. Mass accuracy was found around 5 ppm after automatic recalibration of the mass axis in each measurement. A TOFMS configuration giving $R = 3500$ was chosen to provide an R -to-sensitivity ratio suitable for our purpose. Calculated detection limits were as low as a few femtograms as mass traces could be made highly specific for selected molecule fragments with the accurate mass information. The precision for substance quantification was 0.15 % at the best for an individual measurement and in general mainly determined by the signal-to-noise ratio of the chromatographic peak. The TOFMS was found to be linear within a concentration range from about 1 pg to 1 ng of analyte per Liter of air. At higher concentrations, non-linearities of a few percent were observed (precision level: 0.2 %) but could be attributed to a potential source within the detection system. A straight-forward correction for those non-linearities was applied in data processing, again by exploiting the accurate mass information. Based on the overall characterization results, the GC-TOFMS instrument was found to be very well-suited for the task of quantitative halocarbon trace gas observation and a big step forward compared to scanning, low resolution quadrupole MS and a TOFMS technique reported to be non-linear and restricted by a small dynamical range.

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1 Introduction

The history of environmentally harmful airborne halocarbons and the need for monitoring them in the atmosphere goes back to the 1950s with the introduction of chlorofluorocarbons (CFCs) synthesized and promoted by Thomas Midgley (Midgley, 1937). The production of CFCs was banned by the Montreal Protocol in 1987 after highly rising emissions of CFCs and the following discovery of the catalytic destruction of stratospheric ozone (Molina and Rowland, 1974) and the ozone hole (Farman et al., 1985). CFCs were replaced by partly halogenated hydrochlorofluorocarbons (HCFCs) and are nowadays replaced by a variety of hydrofluorocarbons (HFCs). HFCs do not destroy stratospheric ozone significantly (Ravishankara et al., 1994); nevertheless most of them are strong greenhouse gases with global warming potentials much larger than CO₂ (Velders et al., 2005). The ongoing introduction of new compounds and their release to the atmosphere (e.g. Arnold et al., 2012; Vollmer et al., 2011) constitutes the need not only to monitor known compounds but also to identify new compounds. In the attempt to extend site measurements to emission surveillance, promising approaches have been made by combining measurement data with inverse modelling (e.g. Keller et al., 2011; Lunt et al., 2015; Maione et al., 2008; Simmonds et al., 2015; Stohl et al., 2010).

In the early days of halocarbon measurement, the electron capture detector was the instrument of choice (Clemons and Altshuller, 1966). This choice moved to mass spectrometers later on as an additional dimension of information is added: molecule-specific fragmentation. Today, the most sophisticated instrumentation for the task is probably the Medusa GC-MS of the AGAGE network described by Miller et al. (2008) with a quadrupole mass filter for detection. The Medusa systems have been applied for many investigations from perfluorocarbons (Mühle et al., 2010), hydrocarbons (Grant et al., 2011) and nitrogen trifluoride (Arnold et al., 2012) to emerging HFCs just recently by Vollmer et al. (2015). Especially quadrupole MS has been used by many others for halocarbon analysis (e.g. Grimsrud and Rasmussen, 1975; Sala et al., 2014;

AMTD

8, 9455–9502, 2015

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Simmonds et al., 1995) and sometimes also sector-field MS (e.g. Laube et al., 2012; Lee et al., 1995). In contrast, TOFMS is much more wide-spread in other fields of research such as aerosol composition analysis (e.g. DeCarlo et al., 2006), measurements of volatile organic compounds (e.g. Graus et al., 2010) and proteomics (e.g. Bonk and Humeny, 2001). The big advantage of TOFMS over quadrupole MS and sector field MS is the intrinsic full mass range data acquisition without spectral skew. However, there were also two significant limitations to quantitative analysis with TOFMS observed in the past: limited dynamic range and non-linearity, e.g. described by Emteborg et al. (2000), Rowland and Holcombe (2009) as well as Hoker et al. (2015) for the field of application of this work.

In this work, we go one step further from our first application of TOFMS for halocarbon analysis described in Hoker et al. (2015) using a BenchTOF-dx (Markes International GmbH). A new GC-TOFMS system was set up including fully automated sample preconcentration and a Tofwerk EI-TOF model mass spectrometer giving significantly higher-than-nominal mass resolving power data in a fully accessible data format. Technical descriptions regarding sample preparation, gas chromatography, mass spectrometry and data treatment are given in Sect. 2 of this manuscript. The presentation and discussion of characterization experiments and selected applications can be found in Sect. 3. The section is structured to go from the very basic parameters like mass accuracy (Sect. 3.1) over detection limits (Sect. 3.2) and measurement precision (Sect. 3.3) to non-linearities (Sect. 3.4) for which most aspects discussed before have to be considered.

2 Technical description

This section gives a technical overview of the GC-TOFMS discussed in this work. Figure 1 shows a schematic drawing of the instrument. It can be divided into three basic components (i) stream selection and sample preconcentration, (ii) gas chromatograph

and (iii) mass spectrometer. Explanations are given in the following Sect. 2.1 to 2.3. Section 2.4 gives information on instrument control and data processing.

2.1 Stream selection and sample preconcentration unit

The setup described in this work allows for the attachment of five different air samples, a calibration gas and a blank gas. Gas stream selection is realized by solenoid valves (Fluid Automation Systems, Switzerland) that allow for sample pressures up to 5 bars absolute; i.e. a pressure reducer has to be used for high-pressure flasks. All tubing (1/8" stainless steel with Swagelok compression fittings, about 500 mm length) is heated to > 100 °C to reduce accumulation of water and other sample components on tubing walls. All samples with tropospheric water content were dried prior to preconcentration using magnesia perchlorate which was heated to 80 °C.

The very low mixing ratio range of the targeted analytes in the parts per trillion (ppt) to parts per quadrillion (ppq) mole fraction constitutes the requirement for a preconcentration before analysis with GC-MS. The usage of adsorptive material for that purpose is a wide-spread procedure in instrumental analytics. Cooling the adsorption material shifts the steady state of the adsorption-desorption process towards adsorption and is referred to as "cryotrapping" or "cryofocustion". The combination of cryofocustion-thermodesorption, i.e. rapidly heating the formerly cooled material for sample preconcentration and injection into an analytical instrument, is also quite common since nearly 20 years; see e.g. Simmonds et al. (1995), Kerwin et al. (1996) or Bassford et al. (1998) for the field of application related to this work.

A Sunpower CryoTel CT free piston Stirling cooler (FPSC; Ametek Inc., USA) is used for cooling. On top of the cooler's cold tip, an anodized Aluminum coldhead is placed which contains the sample loop, a 1/16" outer diameter and 1 mm inner diameter stainless steel tube. It is filled with HayeSep[®]D adsorption material (Vici Valco Inc., USA) over a distance of about 100 mm with a mesh size of 80/100 and a mass of about 20 mg adsorption material.

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The adsorption temperature is set to about -80°C to quantitatively trap the lowest-boiling substance separated by the GC column from CO_2 (HFC-23, CHF_3 , boiling point: -82.1°C). For all measurements, a constant sample preconcentration flow rate of 100 mL min^{-1} is set by a mass flow controller (MFC; EL-FLOW F-201CM, Bronkhorst, the Netherlands) mounted directly downstream of the sample loop. The MFC can also be used for sample volume determination (ΔV). All components of the sample air which are not trapped on the adsorption material are collected in a 2 L stainless steel flask (“reference volume”) equipped with a pressure sensor (Baratron 626, 0–1000 mbar, accuracy incl. non-linearity 0.25 % of reading, MKS Instruments, Germany) for sample volume determination (Δp). Tubing and reference volume are evacuated with a Vacuubrand MD-1 vario-SP membrane pump (Vacuubrand GmbH & Co. KG, Germany) before each preconcentration step. For desorption, the sample loop is heated to about 220°C and flushed with carrier gas for 3 min to transport formerly trapped analytes onto the GC column. A similar sample preconcentration setup was described by Sala et al. (2014) and Hoker et al. (2015).

2.2 Gas chromatograph

An Agilent Technologies 7890B gas chromatograph is used to separate analytes before detection. A 0.32 mm ID Gas Pro PLOT column of 30 m length is used for chromatographic separation with purified Helium 6.0 as carrier gas (Praxair Technologies Inc., German supplier. Purification System: Vici Valco HP2). The column is divided into a backwards flushable 7.5 m precolumn and a 22.5 m main column. Column head pressure was adjusted so that at maximum flow (lowest column temperature), the ionizer pressure of the TOFMS is suitable ($< 5 \times 10^{-5}$ mbar) and that on the other hand chromatographic peaks are kept sharp at minimum flow (highest column temperature). The head pressure of the carrier gas flow in line with the MS is kept constant at all times.

The gas chromatographic runtime is 16 min, with an additional 3 min cooldown before the next run, which results in a total of 19 min per measurement. The initial oven temperature is 45°C , which is held for 2.3 min and ramped linearly afterwards with 25°C

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per minute to 200 °C and held until 16 min. The precolumn is set to backflush position after the analyte with highest retention time t_R has reached the main column after 11 min to keep the gas chromatographic system free of contaminations with higher boiling compounds. The main column is connected to the MS with a 0.1 mm ID fused silica transfer line (length: about 350 mm) inside the GC oven. The capillary feedthrough into the ionizer of the MS is kept at 210 °C at all times.

Gas flow switching (backflush, inject etc.) is implemented with two Valco 1/16" 6-port/2-position valves (Vici Valco Inc., USA) which are kept at 180 °C outside the GC oven. Valco stainless steel 1/16" connectors with Valcon T ferrules are used for fused silica tubing (Vici Valco Inc., USA). Carrier gas flow, as determined by the Agilent Technologies flow calculator, is 4.0 mL min⁻¹ at the beginning and 2.3 mL min⁻¹ at the end of the run. However, actual flow rates should lie slightly lower, as the calculation did only include column and transfer line to the MS but no additional restrictions in the flow path like e.g. two Valco 2-position valves, the sample loop and column connectors.

Within the chromatographic runtime of 16 min, a total of 68 substances were detected and identified (most of them halocarbons) in different air samples. The substance with the shortest retention time is HFC-23 (CHF₃, t_R = 3 min), the latest detectable substance is CH₂I₂ at t_R = 15 min.

2.3 Time-of-Flight Mass Spectrometer

The mass spectrometer used in this work is a ToFwerk EI-TOF instrument (model EI-003, ToFwerk AG, Switzerland); an orthogonal extraction, single reflectron TOF MS with an electron ionization (EI) ion source, a quadrupole high-pass filter and a Photonis multichannel plate (MCP) electron multiplier (Photonis, USA). The PCIe data acquisition card records 1.6 GSs⁻¹ with a 14 bit S⁻¹ ADC (analog-to-digital converter) using an on-board averaging firmware. Ions are extracted orthogonally with a rate of 22 kHz into the flight chamber; about 5500 resulting waveforms are averaged to form one mass spectrum that is transferred to the PC and saved to the hard disk. Extraction frequency and number of averaged waveforms give a full spectra rate of 4 Hz. A mass range of up

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to 600 Th (Thomson; $1 \text{ Th} = 1u/e$; u : unified atomic mass unit, e : atomic charge unit) is recorded, which corresponds to a maximum flight time of about $40 \mu\text{s}$ at the given dimensions of the flight tube, acceleration voltage etc.

The choice of spectra rate is a compromise between chromatographic signal integration demands and minimum noise levels. For the described gas chromatographic setup, chromatographic signals typically have a minimum width of about 4 s (± 2 sigma assuming Gaussian peak shape). As TOFMS in contrast to the quadrupole MS is not a scanning technique, the intensity of the chromatographic peak is sampled by the extraction rate (22 kHz in this case) and is therefore not subject to spectral skew. A spectra rate of 4 Hz giving roughly 15 data points per chromatographic peak was chosen for comparability with our other GC-MS systems. For the TOFMS, a lower spectra rate should be possible due to the lack of spectral skew. However, the identification of the lowest possible and of the optimal spectra rate is beyond the scope of this work.

The current data acquisition hardware of the TOFMS theoretically allows for spectra rates of up to 1 kHz (PCIe x4 port). However, as the extraction rate is constant (22 kHz in this case) and determined by the flight time of the heaviest ion produced in the ion source, a higher extraction rate causes less individual waveforms to be averaged which in consequence increases the noise level, assuming a relative error of mean of the counting events given as $1/\sqrt{n}$, with n being the number of waveforms in a spectrum.

The ionizer temperature was kept at 240°C . Ionization energy was 70 eV with an emission current of 0.5 mA. Ionizer pressure varied depending on GC runtime between 2.4×10^{-5} and 4.2×10^{-5} mbar, the flight chamber pressure correspondingly varied from 5.2×10^{-7} to 8.4×10^{-7} mbar. The quadrupole high-pass filter was adjusted to attenuate N_2^+ and O_2^+ signals and completely exclude ions lighter than 15 Th.

The MS is equipped with a calibrant pulser valve (Tofwerk AG, Switzerland) which can be programmed to release a few ng of a calibration substance (Perfluorophenanthrene, $\text{C}_{14}\text{F}_{24}$, CAS 306-91-2) into the ionization chamber. To ensure mass axis stability, calibrant pulses were triggered at the beginning of each chromatogram, prior to

the elution of any compound. By this procedure, the mass axis can be recalibrated in each chromatogram as part of data processing.

2.4 Automation and data processing

The analytical system can run a fully automated sequence of measurements. The automation is based on a LabVIEW cRIO system (National Instruments Inc., USA) which controls the system state (preconcentration, desorption etc.) and can start GC and MS to record the chromatogram.

The analysis of high-resolution mass spectrometric data is performed in the IDL programming environment (Exelis Inc., USA) using asymmetric Lorentzian fits on mass peaks to determine peak width for mass resolving power and peak center for mass accuracy.

Chromatographic mass traces are generated by summing specified intervals of the mass axis in every mass spectrum. For nominal masses, an interval of ± 0.3 Th around the nominal mass is used. For accurate masses, an interval of ± 0.025 Th around the exact mass value is used unless noted otherwise.

Determination of noise levels and integration of chromatographic signals is done in IDL with a custom written, widget-based software named IAU_Chrom. Previous versions of this software were used by Sala et al. (2014) and Hoker et al. (2015). IAU_Chrom was extended to include import and processing tools as well as viewing functionality for the HDF5 file format of the Tofwerk MS data. Noise levels on chromatographic mass traces are calculated as the 3-fold standard deviation of the residuals between data points and a 2nd degree polynomial fit through these data points. This calculation is performed routinely for all quantifier masses on baseline sections with a typical length of 25 s which includes 100 data points in the calculation. Chromatographic peaks are integrated with a custom routine using the IDL “gaussfit” function. Signal heights used in signal-to-noise ratio calculation are also taken from this Gaussian fit.

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Mixing ratios in the measured samples are determined by a relative calibration scheme assuming a linear relation of the substance signal in the sample measurement with the substance signal in the calibration gas measurement, a high-pressure flask sample of ambient air with known mixing ratios. This procedure requires that no significant non-linearities are induced by the sample preconcentration, the chromatography and the detector (see Sect. 3.4).

3 Characterization

Four aspects of the instrument are described in this section to give the reader an impression of the system's capabilities: mass accuracy and mass resolving power (Sect. 3.1), sensitivity and limits of detection (Sect. 3.2), measurement precision and reproducibility (Sect. 3.3) and non-linearity (Sect. 3.4). All results are based on GC-MS data with recalibrated mass axis using signals from the calibrant pulser described in Sect. 2.3.

3.1 Mass accuracy and resolving power

Mass accuracy as used here refers to mass measurement accuracy, i.e. the accuracy of a measured mass-to-charge ratio m_{ac}/Q ("accurate m/Q ") compared to the corresponding calculated mass-to-charge ratio m_x/Q ("exact m/Q "). The relative mass error E_{mac} is calculated as $E_{mac} = \frac{m_{ac} - m_x}{m_x}$; multiplication by 10^6 gives E_{mac} in ppm, which is the quantity that is referred to by *mass accuracy*. The term *mass* is used synonymous to m/Q with $Q = 1$ while *mass trace* is used to refer to the intensity vector for a specific m/Q recorded during a chromatographic run. The term *mass resolving power* is used according to the full width at half maximum (FWHM) definition of IUPAC (2014) as $R = \frac{m}{\Delta m} = \frac{m_{ac}}{FWHM(m_{ac})}$.

Mass accuracy and resolving power are both core parameters of the MS. They are the basic determinants (in addition to sensitivity, see Sect. 3.2) of data quality with re-

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spect to measurement precision from a chromatographic point of view and the benefits from having accurate mass information for chemical identification. From an application point of view, mass resolving power determines, if neighboring signals from ions of different m/Q can be separated and mass accuracy describes the uncertainty of the measured m/Q . Insufficient mass accuracy cannot be compensated by high mass resolving power and vice versa. In fact, low mass accuracy can render a high mass resolving power “unexploitable” to some extent as it represents the uncertainty of a found accurate m/Q .

Data from five different measurement series was analyzed to answer the questions what the achievable calibration quality is and how it varies over time, i.e. during one measurement series and between different measurement series. Different configurations of the TOFMS giving different average mass resolving powers were tested to assess the question how mass accuracy, mass resolving power and signal intensity are correlated.

3.1.1 Mass accuracy

Experimental values for the mass accuracy of calibrant masses (28 to 555 Th) were found to be $E_{\text{mac}} = 4 \pm 0.3$ ppm as the arithmetic mean ± 1 -fold standard deviation derived from five measurement series (186 measurements in total). Target substance masses (51 to 174 Th) within those measurement series showed a mean E_{mac} of 8 ± 0.8 ppm. Exemplary results for individual masses are shown in Fig. 2.

The variation of mass accuracies over the mass range is quite large relative to the mean value but generally not worse than 20 ppm, which is the manufacturer specification given as an absolute mass error of ± 0.002 Th at 100 Th. This specification can be considered as a worst-case estimate, especially when signals are very small. The underlying mass axis calibration model was chosen to yield best results over the whole mass range and gives a systematic and reproducible distribution of mass accuracies over the whole mass range. Different models might be better suited for individual sections of the mass axis.

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For the target masses from analytes, only a slightly elevated E_{mac} was found compared to mass accuracies of calibrant masses used for mass axis calibration curve fitting. Mass accuracy also did not change significantly over the chromatographic run-time. Furthermore, mass accuracy was found to be stable over time, i.e. no significant trend over one measurement series or on average over different measurement series within a time span of multiple months as long as the same MS tuning was used. However, the instrument was found to be very sensitive towards changes of ambient air temperature between individual chromatographic runs, probably due to changes in material elongation. Without recalibration of the mass axis, changes of around 100 ppm were observed. The routinely executed recalibration of the mass axis in each chromatogram can compensate the effect of such temperature changes but might not fully extinguish it, especially during a field campaign where temperature fluctuations are potentially larger than in the laboratory.

3.1.2 Mass resolving power

In TOFMS, mass resolving power is inversely proportional to sensitivity to a certain extent. Assuming an optimal ion beam focusing, higher sensitivity would require more ions of equal m/Q to reach the detector – which in turn would cause a higher arrival time distribution per m/Q (Guilhaus, 1995). To optimize sensitivity at the given spectra rate and sample volume, a configuration giving an average of $R = 3500 \text{ Th Th}^{-1}$ over the whole mass range was chosen. For further discussion of the effect of changes in mass resolving power on sensitivity, see Sect. 3.2.

Mass resolving power in general showed a stable behavior over time, i.e. no significant trend during a measurement series or over multiple measurement series conducted with the same settings. Figure 3 shows the distribution of mass resolving power along the mass axis. Resolution for lighter ions is reduced compared to the average resolution. This effect is known in TOFMS (e.g. Coles and Guilhaus, 1994) and caused by a lower arrival time distribution of lighter ions at the detector. The single ion signal width is however finite and determined by the detection system bandwidth. Therefore,

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the increase in overall ion signal width is relatively larger for lighter ions compared to heavier ions. When a higher mass resolving power is enforced by instrument tuning, the reduction in resolution at lower m/Q becomes more pronounced as ion arrival time distributions become lower overall. From an application point of view, this aspect has to be considered when very light ions ($m/Q < 30$ Th) are the focus of the analysis.

Based on an analysis of the mass axis calibration masses in routine measurement data (default resolution setting $R = 3500$ Th Th⁻¹), a slight negative correlation of mass resolving power and ion signal height was found with a Spearman rank correlation coefficient of $\rho = -0.4$ ($\rho < 0.05$) in mean over the five analyzed measurement series. The correlation between mass accuracy and ion signal height was found to be $\rho = +0.2$ but with very high ρ values > 0.1 and therefore of low significance. The correlation was more pronounced with $\rho = -0.8$ (resolving power) and $\rho = +0.8$ (mass accuracy) for the target ions from analyte molecules, both correlations with ρ values < 0.01 .

The correlation of mass resolving power and intensity implies that a very small signal has an above-average mass resolution as smaller signals get effectively narrower due to decreased ion velocity disturbance by other ions of equal m/Q . This effect is clearly visible for the target substance ions and also selected calibrant masses displayed in Fig. 3; every m/Q with an elevated mass resolution compared to an interpolated m/Q to R curve in Fig. 3 was found to have below-average signal intensity (calibrant as well as targets). When becoming even smaller, signals are on the other hand be afflicted with below-average mass accuracy as counting statistics quality decreases.

3.1.3 Exemplary identification of HFC-1234yf

The substance HFC-1234yf (CH₂CF₂CF₃, CAS 754-12-1) has been introduced as a replacement for HFC-134a (CH₂FCF₃) in mobile air conditioning systems in 2011 and can already be detected at remote measurement sites as published by Vollmer et al. (2015). The identification of emerging substances like the one used as an example here is often difficult due to an unknown fragmentation. However, the CH₂CF₂CF₃ molecule should form CF₃⁺ (69 Th), CH₂CF⁺ (45 Th), CH₂CF₂⁺ (64 Th), CH₂CF₂CF₃⁺

(114Th) and related ions. The likelihood of the identification can then be significantly increased by using the accurate mass information. Table 1 shows found fragmentation and accurate masses of the four most abundant fragments observed in an air sample with an elevated concentration of HFC-1234yf; the chromatographic peak of HFC-1234yf is shown in Fig. 4. Thanks to the all-time full m/Q range data acquisition of the TOFMS, no dedicated mass filter settings are necessary for identification like it would be with a quadrupole MS.

3.2 Sensitivity and limits of detection

To characterize the analytical system in respect to its sensitivity, the lowest detectable amount of a substance (limit of detection, LOD) is the quantity of interest. Due to the general applicability to all signals caused by substances with known mixing ratios in the sample, a signal-to-noise ratio (S/N ; signal represented by the signal height) of 2 : 1 was chosen as detection limit in accordance with IUPAC (1998).

As the instrument discussed here offers the possibility to increase sensitivity by trading off mass resolving power (see also Sect. 3.1), changes in sensitivity were analyzed relative to different mass resolving power settings of the MS. Furthermore, the detector is not independent of the chromatographic system; its effects on noise levels are therefore discussed based on the analysis of different baseline sections from a sample measurement series. To answer the question, where the actual limits of detection lie, a practical example is given for the substance Halon-1202 (CF_2Br_2) which was detected at $S/N \approx 2$. Additional LOD for different substances were derived from measurements of different ambient air samples to include possible sample matrix effects on LOD. A description of the applied noise level and signal height determination was given in Sect. 2.4.

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3.2.1 Sensitivity and its interdependence on mass resolving power

As pointed out before, an increase in sensitivity of the TOFMS goes along with reduced mass resolving power (see Sect. 3.1). The task for the user is to choose a resolution setting which gives optimum sensitivity and data density for the desired application and spectra rate.

Table 2 shows a comparison of three different mass resolving power settings and the resulting changes in sensitivity, represented by a change in S/N relative to the default setting. While mass resolving power changed by approximately $\pm 25\%$ relative to the commonly used setting $R = 3500 \text{ ThTh}^{-1}$, the changes in S/N are more pronounced with $+38$ and -64% . This implies that the correlation between resolution and sensitivity is not linear and has an optimum. Column four of Table 2 gives a more practical view on the experiment: the number of integrable substance signals substantially decreases with increasing mass resolving power. However, the change in number of integrable substances does not totally reflect the change in S/N . This can be related to the integration method and/or individual properties of the chosen substances.

3.2.2 Dependence on chromatographic effects

The key parameter in the discussion of sensitivity is the noise level. A special property of a chromatographic system is that noise levels can change over the chromatographic runtime with changing column temperature and pressure due to increased mobility of high-boiling compounds, column bleeding etc. In most cases, column temperature and noise level are positively correlated. Furthermore, the correlation strength also depends on ion mass.

For the GC-MS system discussed here, Table 3 shows a comparison of three different ion masses typically formed by halocarbons and their change of noise level depending on the baseline section where noise is calculated. It has to be pointed out that noise levels change by factors of around 3 depending on the position in the chromatogram. Limits of detection based on S/N are therefore dependent on the retention time and

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qualifier/quantifier ion of the substance of interest. The detection limits of substances with ion masses displayed in Table 3 seem to be limited by the chromatographic system (and not the MS) towards higher retention times as noise levels tend to increase over the chromatographic runtime.

To illustrate the benefit of the use of accurate masses on noise levels, a comparison for mass 69 Th (e.g. CF_3^+ , 68.9947 Th exact mass) is shown in Table 4. This ion mass is known to be quite noisy compared to other ion masses, especially later in the chromatogram as demonstrated in Table 3 (column 3 vs. column 2).

Two things can be observed: first of all, noise levels are significantly reduced by around 70 % in all samples when using the accurate mass instead of the nominal mass. Second, the relative comparison of the noisiest sample (S_01) shows that the elevation in noise level, compared to the other samples, is strongly reduced when the accurate mass is used (70 % elevation on nominal mass trace vs. 12 % elevation on accurate mass trace). The analytical system gains independence from sample matrix effects by the usage of accurate mass traces.

3.2.3 Detection limits derived from quantified substances

To demonstrate detection limits from a practical point of view, Fig. 5 shows the integrated signal of Halon-1202 (CBr_2F_2) which was detected and integrated at a signal-to-noise ratio of around 2.

A mixing ratio of 0.035 ± 0.006 ppt was determined for the sample shown here (calibration scale of Halon-1202: UEA-2009). For a 1 L air sample, the calculation gives a LOD of 0.016 ± 0.003 ppt. With the ideal gas law, one can convert this mixing ratio LOD to a mass LOD of 0.138 ± 0.024 pg L^{-1} air at standard pressure and temperature.

LOD were found in the sub-ppt and sub-pg range for all analyzed substances and even go down to the low ppq or fg range for some species. The benefit from going from detection on nominal m/Q to detection on accurate m/Q yields LOD improvements by factors of 5 and more. Table 5 shows an excerpt from calculated LOD for six different substances roughly covering the mass and retention time range of the chromatogram.

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LOD were calculated as arithmetic means of five different samples measured five times each during one measurement series as well as the calibration gas to include sample matrix effects on detection limits.

From Table 5 it can be observed that the compounds Halon-1301 (CBrF_3) and HCFC-22 (CHClF_2), both detected on fluorinated fragments, show less improvement in LOD on accurate m/Q compared to the other three compounds. An explanation could be that the noise on nominal m/Q 51 and 69 Th is caused mainly by the CHF_2^+ and CF_3^+ fragments, especially for the corresponding relatively early baseline sections (see also Table 4). In comparison, the $\text{CH}_2^{35}\text{Cl}_2^+$ and $\text{CH}_2^{79}\text{Br}^{81}\text{Br}^+$ from Dichloromethane (CH_2Cl_2) and Dibromomethane (CH_2Br_2) show much more pronounced improvements as most of the noise is potentially not produced by those fragments and both exact m/Q lie further off the nominal m/Q .

In general, it is hard to say, how much sensitivity will be gained for which ion mass. A strong positive correlation was found between retention time and m/Q over the full substance range with $r = 0.70$ ($p < 10^{-7}$). It is therefore very difficult to disentangle, if there also is e.g. a significant correlation between gain in S/N and m/Q (attributing the effect to the MS) or gain in S/N and t_R (attributing the effect to the chromatographic system).

3.3 Precision and reproducibility of quantification

In order to quantify small trends of long-lived species like CFC-12, CFC-11 or CFC-113 (Carpenter et al., 2014) with only a few individual measurements, a high measurement precision is necessary. Additionally, high measurement precision is a prerequisite to analyze systematic effects and potential systematic errors like system non-linearities in measurement data. Note that measurement precision and reproducibility in this paper refer to precision of analyte quantification and not e.g. mass measurement precision.

Measurement precision as variability of the measured values around a mean value (random error) is analyzed with so-called precision experiments consisting of up to 50 measurements of the same reference gas with constant sample volume. Within this se-

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ries, a subset of measurements is treated as calibration points and another subset as samples. This gives blocks of repeated sample measurements between bracketing calibration points. Calibration is achieved by linear interpolation between calibration points and referencing the bracketed samples to the calibration, giving a relative response for every sample measurement. An ideal measurement should give a relative response of one; i.e. the spread around one represents the measurement precision. Measurement precision of an individual measurement is then taken to be the mean standard deviation of all sample subsets of the series. In order to gain information about the reproducibility of precision, multiple precision experiments as well as normal sample measurements have been considered. A normal sample measurement is principally the same as a precision experiment with the exception that a real air sample instead of a reference gas is analyzed in a sample block.

3.3.1 Measurement precision

Measurement precision in regard to analyte quantification for a single measurement was found to be better than 1 % for about 15 out of 47 analyzed substances and in good correlation with the signal-to-noise ratio of the respective substances. Best values were achieved for CFC-12 at exact ion mass 84.9651 ($\text{CF}_2^{35}\text{Cl}^+$) with 0.15 % individual measurement precision and 0.08 % error of mean for sample blocks of three subsequent measurements of the same sample (evaluation of accurate mass).

Figure 6 illustrates the precision range of the instrument for 47 analyzed substances (mostly halocarbons, evaluation of signals on nominal mass traces) and their correlation with the signal-to-noise ratio. It can be observed that measurement precision exponentially improves with exponentially increasing signal-to-noise ratio with a good correlation coefficient of $r^2 = 0.86$. The quality of the correlation was underlined during routine measurements by the fact that outliers did indicate “problematic” substances like e.g. Methyl iodide which was found in the system blank; with the stainless steel tubing being the likely source.

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The lower end of precision $> 10\%$ is limited by signal quality, i.e. signals with a signal-to-noise ratio < 3 constitute a problem for the integration routine used to determine signal area. At the high end of precision, a very large increase in S/N seems to be necessary to achieve higher precision, i.e. approximately doubling the sample volume from 0.66 to 1.33 L to improve precision from 0.2 to 0.1 %. A precision experiment with a preconcentration volume of about 1.38 L showed that this theoretical extrapolation of the correlation is not valid. S/N did increase but not linearly and measurement precision was even lower in mean although it was improved for some species, mostly in the lower S/N regime < 100 . These findings implicate that chromatographic effects play an important role and that there is an optimum sample volume if overall measurement precision should be maximized with a given chromatographic setup.

3.3.2 Benefits from accurate mass traces

As the ToFwerk AG mass spectrometer allows the use of the information gained by a significantly higher than nominal mass resolving power, the question arises how signal-to-noise ratios and measurement precision are influenced by the use of accurate mass information for further data processing.

Accurate mass traces comprise mass accuracy as an additional error source if fixed mass intervals are used to generate the chromatographic mass trace. Consequently, the correlation of measurement precision and signal-to-noise ratio is less pronounced ($r^2 = 0.75$) for the same experiment shown in Fig. 6 and overall measurement precision is slightly decreased (10 out of 53 vs. 15 out of 47 better than 1 %), even if it is also increased for some species. Signal-to-noise ratios are increased in almost all cases using accurate mass traces. The changes in both quantities, measurement precision and signal-to-noise, relative to values determined for nominal masses are shown in Fig. 7.

While S/N is mostly increased by factors up to 3 when comparing accurate mass to nominal mass evaluation, a coinciding decrease in measurement precision can be observed (upper right quadrant of Fig. 7). However, this is not strictly true for all ana-

5 lyzed substances; some are improved in both quantities by using the accurate mass information instead of the nominal mass information (lower right quadrant of Fig. 7). A possible explanation is the interference from other ions with matching nominal mass caused by an unknown substance in the specific retention time window. This interference
10 can be compensated by the use of accurate mass traces, if the accurate ion masses from known and unknown compound differ in that case. Only very few substances show better *S/N* and better measurement precision on nominal mass traces (upper left quadrant of Fig. 7) and only one substance exhibits a better measurement precision on the accurate mass trace together with a decreased *S/N* ratio (lower left quadrant of Fig. 7). This substance was identified to be Methylchloroform (CH_3CCl_3) which will be discussed in the following.

Measurement accuracy can also be increased in some cases by using the accurate mass information which can then compensate the coelution of substances with matching nominal mass but deferring accurate mass. An example which was found frequently
15 in routine measurements and also appears as an “outlier” in Fig. 7 is Methylchloroform.

Figure 8 demonstrates that there are cases of coelution and matching nominal mass signals, especially if chromatographic runtime is kept short. In such cases, the accurate mass trace from the GC-TOFMS system is likely to give a mixing ratio much closer to the true value. This again is an argument for using the accurate mass traces for mixing
20 ratio determination (at least in selected cases) instead of the nominal mass traces even though measurement precision could be slightly reduced.

3.3.3 Reproducibility and instrument stability

To demonstrate measurement precision over a longer time period and varying conditions, Table 6 displays mean single measurement precision of ten selected substances
25 derived from five idealized precision experiments and four routine measurement series. For simplification, only values derived from nominal mass evaluation are shown.

The selection and order within Table 6 is based on best average measurement precision within the underlying precision experiments. Measurement precision in routine

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ambient air sample measurement series is subject to a greater variability as sample matrix, water content etc. also varies. This can be observed in column 3 of Table 6, where precision values derived from routine measurement series are shown. Precision values are slightly elevated compared to values derived from idealized experiments as expected. However, all values are in good agreement considering the standard deviation of the estimated single measurement precision of the selected substances.

Column 4 of Table 6 shows maximum-minimum differences for normalized signal areas of calibration measurements for each substance to give information about instrument drift over routine measurement series, which typically took 10–16 h of continuous operation. The Instrument was found to be less stable (10–20 % drift) if highly contaminated (e.g. by hydrocarbons) and/or very moist samples were measured or if measurements were conducted directly after start-up of the MS, e.g. after down-time due to ion source cleaning and filament replacement.

3.4 Non-linearity

With the instrument in discussion, a large substance portfolio is analyzed routinely with a mixing ratio range of less than 1 to more than 500 ppt (about 1 pg to 4.4 ng in 1 L of air). A large short-term variability has to be expected for some substances like HFC-134a or CH₃Cl (e.g. Stemmler et al., 2004; Yokouchi et al., 2000) whereas other substances like HFC-143a or HCFC-22 show strong trends (e.g. Carpenter et al., 2014; Hartmann et al., 2013). For the described field of application, detector non-linearities are therefore relevant in a range from detection limit upwards to about two to three orders of magnitude. Detector saturation is unlikely to appear in that range, especially with the 14 bit ADC of the TOFMS used in this work.

The attribution of a mixing ratio to an unknown air sample with a GC-MS system, as the one discussed in this work, is commonly done relative to the known mixing ratio of a specific calibration or reference gas (e.g. Miller et al., 2008). The integrated detector response over time, the area of the so called chromatographic peak, for a specific substance is proportional to the mixing ratio of the sample, if the estimated peak area is

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normalized with the amount of analyzed air represented by the preconcentrated volume of the sampled gas, i.e. the area-to-volume ratio (A/V). In this procedure, a linear detector response is assumed for calculation of mixing ratios in the sample. If mixing ratios in sample and calibration gas differ and the detector features significant non-linearities within the observed concentration range, measurement accuracy is decreased by the degree of the non-linearity. A correction of non-linearities as a post-processing step is only possible, if non-linearities are systematic or very well understood. In any case, non-linearity correction adds an additional error source and is very time consuming and often complex, because it can be different for every target substance. This is especially important when thinking about retrospective analysis or digital air archiving.

As discussed in the previous section, the instrument shows reproducible, high measurement precision for many analyzed species. This is a prerequisite for non-linearity analysis: e.g. a non-linearity of 0.5 % is unlikely to be detected for a substance, which shows a measurement precision of 3 % or which is affected by other systematic errors like a memory effect or a system blank. For analysis, the results of the non-linearity analysis based on nominal mass traces were used as reference and compared to the results based on accurate mass traces.

To analyze non-linearity effects of the GC-MS setup, volume variation experiments were conducted similar to the precision experiments described in Sect. 3.3 only that different volumes of preconcentrated air were used as “samples”. The reference volume was 0.5 L of ambient air taken from a high pressure flask. Variation volumes of 0.1 to 1.0 L from this reference gas were compared to the 0.5 L calibration points. For volume determination, the MFC installed in the system (see Sect. 2.1) was used. Volumes determined in parallel by the MFC and by the pressure sensor derived from Δp were found to correlate linearly ($r^2 > 0.999998$) According to the description in the second paragraph of this section, all A/V were normalized $n(A/V)$ by dividing them by the drift-corrected calibration A/V . The ratio of any sample $n(A/V)$ to the calibration $n(A/V)$ at that point within the measurement series, which was calculated by linear interpolation of the bracketing calibration $n(A/V)$, should give a relative response of 1 in case of

a linear system. A deviation of up to the 3-fold measurement precision ($3 \times \sigma$) from a relative response of 1 was still considered to be linear behavior.

3.4.1 Concentration-specific non-linearities

To provide a structured overview, three classes of substances were formed by differentiation according to measurement precision and concentration range. Substances with known memory or blank effects were excluded from the analysis.

The first class comprises substances with mixing ratios from around 1 to 5 ppt (1 to 40 pgL^{-1} of air) and measurement precision generally worse than 1%. No non-linearities were found in this class, e.g. Halon-1301 (CF_3Br , 3.4 ppt, 14 pgL^{-1} , quantified on the CF_3^+ ion) was found to be linear within 1.4-fold measurement precision ($\sigma = 3.3\%$) over the sample volume range of 0.1 to 1.0 L. The results for this class were however found to be very sensitive towards integration parameters. Close attention has to be paid to effects like an ascending baseline around the respective substance signal.

The second class goes towards higher mixing ratios from 5 to about 150 ppt (0.1 to 1.1 ngL^{-1} of air) and measurement precision around 1%. Again, no significant non-linearities were found within this class, e.g. Dichloromethane (CH_2Cl_2 , 84.5 ppt, 592 pgL^{-1} , quantified on the $\text{CH}_2^{35}\text{Cl}_2^+$ ion) was found to be linear within 1.7-fold measurement precision ($\sigma = 0.66\%$) over the analyzed sample volume range. On average, the deviation from a relative response of one was found to lay around 1σ .

All higher concentrated substances are summed in the third class, going from 150 to 500 ppt and more, or 0.6 ngL^{-1} to 4.4 (and more) ng L^{-1} of air expressed in mass. Measurement precision was found to be significantly below 1% within this class. Large systematic deviations of up to 18σ from linearity were found for all substances within this class; the most dominant example, CFC-12, is shown in Fig. 9.

It can be observed that the concentration in smaller sample volumes is systematically underestimated while the concentration in large volumes is systematically overestimated. This clear systematic behavior was found for all substances within the high-concentration class, although it was most pronounced for CFC-12.

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3.4.2 Source and correction of non-linearities

The source of this effect can possibly be assigned to a potentially instrument-specific signal reflection at high intensities, presumably in the high-frequency line between MCP and pre-amplifier or also within the pre-amplifier itself. An illustration is given in Fig. 10.

As signals were summed up over an interval of $\pm 0.3 \text{ Th}$ around the integer mass, the area of the artificial “shoulder” was included in the nominal mass trace, creating an offset which increases with the number of total ions reaching the detector per time (i.e. sample volume). Consequently, larger sample volumes are overestimated and smaller sample volumes are underestimated as the comparison was done relative to a sample volume somewhere in the middle, at 0.5 L . The fact that no non-linearities were found in substance classes one and two suggests that the offset becomes insignificant below a certain ion count.

When the ion signal that was used to generate the chromatographic mass trace was limited to a narrow interval around the accurate ion mass (here: $84.965 \pm 0.0175 \text{ Th}$), the non-linearity was effectively suppressed as shown in Fig. 11.

The suppression by accurate mass intervals did work for all substances of the high-concentration class without a significant decrease in measurement precision. Too narrow intervals were clearly indicated by a drop in measurement precision. Therefore, if mass resolving power is set too low, it might not be possible to set mass intervals small enough to compensate non-linearity without seriously reducing measurement precision. Based on the results shown, it is unlikely that the peak shape deformation (Fig. 10) is caused by an actual spread of ion velocities, i.e. reduced ion beam focusing for large amounts of ions. Note that this artificial signal elevation might be specific for the instrument in description.

From a practical point of view, an emerging compound is not affected by the found detector induced non-linearities until it reaches a relatively high concentration level of 100 ppt and more. Despite rising trends, this is still a long way to go for many compounds. However, non-linearities might become relevant in case of large daily varia-

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tions in concentration found in tropospheric samples (e.g. HFC-134a) or when stratospheric samples or historic samples are analyzed. In any case, the open data format of the used MS does offer many options to correct the non-linearity by exploiting the accurate mass information. Narrow mass intervals is just one straight-forward approach and other procedures like a mass peak fitting using prescribed peak shapes would also be possible.

4 Summary and conclusion

In this work, a newly developed GC-TOFMS system designed for the quantitative analysis of halogenated trace gases was characterized. Besides a state-of-the-art GC and TOFMS, the setup comprises a self-built sample preconcentration unit. It is routinely operated with an adsorption temperature of -80°C , but allows -120°C (tested) and depending on the cycle time of cooling and heating even lower adsorption temperatures, without needing a cooling agent like liquid nitrogen. The thermodesorption of the preconcentrated sample directly onto the warm GC column together with a cool-down time back to adsorption temperature of less than 60 s allows a high cycle time. The combination of automated sample selection, preconcentration and measurement sequencing, as well as the fully accessible data format of the TOFMS, enabled us to gain in-depth understanding of the analytical instrument with focus on the mass spectrometer.

The medium-level mass resolving power of around 4000 Th Th^{-1} allows the quantitative separation of e.g. many hydrocarbon fragments from halogenated fragments. This makes the analysis more independent from sample matrix effects and can therefore increase accuracy of quantification. The latter is mandatory for high precision quantitative measurements, as needed for many atmospheric halocarbon analyses. It also gives the instrument an advantage over quadrupole mass spectrometers in chemical identification, although it cannot compete with instruments built specifically for this task with mass resolving powers of multiple tens of thousands. Mass accuracy determined

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for the characterized instrument was found to support the benefits from the mass resolving power of the instrument in respect to unambiguous fragment identification. The calibrant pulser of the TOFMS was found to be a very valuable innovation as it offers the option to establish automated recalibration of the mass axis.

5 The mass spectrometer was also found to be very sensitive, especially when using the accurate mass information. This allows for relatively small and easy-to-handle sample sizes of 0.5 to 1.0 L and also the early detection of emerging compounds with very low atmospheric mixing ratios in the range of a few ppt to ppq. At the upper end of the concentration range, no saturation effect of the detector was observed for any of the
10 analyzed species; the largest preconcentration volume tested was 2.5 L corresponding to about 10 ng (ca. 2.5 ppb) of the highest concentrated halocarbon CFC-12.

A measure for the measurement precision needed for atmospheric trace gas analysis, here mainly halocarbons, is the capability of resolving atmospheric variability and trends. One of the most challenging tasks is the attribution of atmospheric trends of major long-lived halocarbons, at least on yearly base. The instrument is capable of classifying most sample mixing ratios into the yearly trend of the respective substances (Carpenter et al., 2014) based on a single measurement. There are only a few exceptions of substances with very small trends, e.g. CFC-114 with $-0.2\% \text{ yr}^{-1}$ ($-0.01 \text{ ppt yr}^{-1}$).
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Instrument non-linearities were found to be negligible for the low and medium concentration range (up to about 1 ng L^{-1} or 150 ppt). At higher concentration levels, significant non-linearities were found. These non-linearities could be removed by setting narrow mass intervals around the affected mass signals and thereby excluding the artificially elevated signal. At this time, it is not clear, if this issue is specific to our instrument or affects a series of EI-TOFMS. A hardware solution is ongoing work at
20 Tofwerk and also in cooperation with us to fully understand and solve the problem.

Overall, the instrument was found to be very well-suited for the quantitative analysis of halocarbons in air and a big step forward compared to common quadrupole and TOFMS with low resolving power $\leq 1000 \text{ Th Th}^{-1}$. The availability of accurate mass information at medium mass resolution has proven to be very valuable due to the sim-
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plified substance identification, the gain in sample matrix independence and measurement accuracy and also in respect to the exclusion of non-linearities induced by the detection system of the MS. Within the described field of application, both the general limitations being low dynamic range and non-linearity of TOFMS seem to be overcome by the Tofwerk instrument. Together with the always present, high-sensitivity full mass range, these aspects make TOFMS in general an ideally suited method for digital air archiving. This work is only focused on halocarbons in atmospheric air samples but in principle, there are much more information in the chromatograms recorded with full mass range. We just started to look into other substance classes like hydrocarbons and the GC-TOFMS data looks very promising for future (re-)analysis of many more substances than discussed here.

Acknowledgements. The authors would like to thank the Deutsche Forschungsgemeinschaft (DFG) for funding the project under research grant EN367/12-1, L. Merkel and the workshop of the institute for technical drawings as well as component construction and M. Vollmer (Laboratory for Air Pollution/Environmental Technology of the Swiss EMPA) for providing substance identification samples. Finally our thanks go to Tofwerk AG, especially Y. Papadopoulos for support with the TOFMS and M. Gonin for proof-reading the manuscript.

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Table 1. Experimentally determined fragmentation and accurate m/Q of fragments from HFC-1234yf in an air sample from a parking lot. No calibration gas mixing ratio was available for this substance; a comparison with HFC-134a and Halon-1301 gave a crude estimate of 3–4 ppt. For identification, the maximum intensity spectrum was chosen within the chromatographic peak.

| Fragment | CF_3^+ | $C_2H_2F_2^+$ | $C_3H_2F_4^+$ | $C_3H_2F_3^+$ |
|------------------------------|----------|---------------|---------------|---------------|
| Calculated m_x/Q [Th] | 68.9947 | 64.0119 | 114.0087 | 95.0103 |
| Experimental m_{ac}/Q [Th] | 68.9958 | 64.0116 | 114.0091 | 95.0126 |
| E_{mac} [ppm] | 16 | 5 | 3 | 24 |
| Experimental rel. Abundance | 1 | 0.78 | 0.64 | 0.40 |

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Table 2. Comparison of different resolution settings with regard to changes in sensitivity. Values based on 10 measurements per setting and 37 calibration m/Q for resolution calculation (avg. R , ΔR). Changes in S/N ($\Delta S/N$) determined as the mean relative change in S/N for 39 substances. From the total of 68 identified substances, a variable fraction could be integrated depending on the resolution setting as shown in the last column (n subst. integrated). All calculations executed on accurate mass traces.

| avg. R | ΔR | $\Delta S/N$ | n subst. integrated |
|----------|------------|--------------|-----------------------|
| 2577 | −27% | +38% | 59 (+9%) |
| 3545 | 100% | 100% | 54 |
| 4477 | +26% | −64% | 39 (−28%) |

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Table 3. Intra-sample comparison of noise levels on three typical halocarbon ion masses. For each ion mass, two baseline sections were chosen for noise calculation, at the beginning and towards the end of the chromatogram. Noise levels and according 1σ standard deviations were determined over 40 chromatograms measuring the same reference gas and constant sample volume of 0.66 L. The Δ Noise row shows noise on late baseline section divided by noise on early baseline section.

| m/Q | 69 Th nominal | | 85 Th nominal | | 101 Th nominal | |
|---|----------------|--------------|----------------|----------------|------------------|----------------|
| Baseline section [s] | 200–225 | 930–950 | 200–225 | 930–950 | 200–225 | 800–825 |
| (Noise $\pm 1\sigma$) $\times 10^{-3}$ | 4.5 ± 0.50 | 17 ± 2.0 | 1.5 ± 0.13 | 4.1 ± 0.35 | 0.96 ± 0.076 | 3.2 ± 0.21 |
| Δ Noise (late/early) | 3.7 | | 2.7 | | 3.3 | |

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Table 4. Inter-sample comparison of noise levels on nominal mass 69 Th and corresponding accurate mass 68.9947 Th (CF_3^+) for four different samples. Noise levels were calculated as means over five measurements per sample on a baseline section from 870 to 895 s chromatographic time. Errors given as the corresponding 1-fold standard deviations. All samples were measured in one measurement series with constant sample volume and the same MS settings.

| Sample | S_01 | S_02 | S_03 | S_04 |
|---|----------------|----------------|----------------|----------------|
| 69 Th: (noise $\pm 1\sigma$) $\times 10^{-3}$ | 32 ± 0.7 | 19 ± 1.3 | 19 ± 1.7 | 17 ± 0.9 |
| 68.9947 Th: (noise $\pm 1\sigma$) $\times 10^{-3}$ | 7.2 ± 0.32 | 6.4 ± 0.20 | 6.8 ± 0.75 | 6.3 ± 0.32 |
| Noise ratio, nominal/accurate | 4.4 | 3.0 | 2.8 | 2.7 |

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Table 5. Limits of detection for six different species with different retention times and fragment m/Q . Values derived from the analysis of five different air samples as well as the calibration gas (mean LOD shown). Sample volume was extrapolated from approximately 490 mL to 1 L. LOD were calculated based on an evaluation of the respective (1) nominal and (2) accurate mass traces. Errors were derived from mean errors of noise and height calculation for each sample. The ratio of nominal m/Q LOD to accurate m/Q LOD is shown in the last column.

| Substance | t_R [s] | Fragment | m_x [Th] | (1) nominal | | (2) accurate | | nom./acc. |
|-----------------|--------------|--|---------------|------------------|------------------|------------------|------------------|-----------|
| | | | | LOD [ppt] | LOD [pg] | LOD [ppt] | LOD [pg] | |
| Halon-1301 | 232 | CF ₃ ⁺ | 68.9947 | 0.107 ±0.0076 | 0.644 ±0.0453 | 0.105 ±0.0071 | 0.631 ±0.0428 | 1.0 |
| HCFC-22 | 313 | CHF ₂ ⁺ | 51.0041 | 0.079 ±0.0040 | 0.277 ±0.0138 | 0.066 ±0.0043 | 0.230 ±0.0150 | 1.2 |
| Halon-1211 | 379 | CF ₂ ³⁵ Cl ⁺ | 84.9651 | 0.078 ±0.0346 | 0.517 ±0.2306 | 0.054 ±0.0038 | 0.357 ±0.0253 | 1.4 |
| Dichloromethane | 491 | CH ₂ ³⁵ Cl ₂ ⁺ | 83.9528 | 0.123 ±0.0039 | 0.421 ±0.0132 | 0.022 ±0.0018 | 0.075 ±0.0063 | 5.6 |
| Halon-2402 | 516 | C ₂ F ₄ ⁷⁹ Br ⁺ | 178.9114 | 0.008 ±0.0003 | 0.086 ±0.0029 | 0.003 ±0.0003 | 0.034 ±0.0028 | 2.5 |
| Dibromomethane | 606 | CH ₂ ⁷⁹ Br ⁸¹ Br ⁺ | 173.8497 | 0.018 ±0.0011 | 0.128 ±0.0078 | 0.004 ±0.0004 | 0.030 ±0.0027 | 4.3 |

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Table 6. Mean single measurement precision and relative drift in calibration of ten selected substances which were chosen according to a precision of generally better than 1 %. Data based on five different precision experiments using different reference gases and sample volumes from 0.49 to 1.38 L as well as four routine measurement series including four to five samples per series. Precision values were calculated as the arithmetic mean of all sample blocks per measurement series. Drift calculated as minimum to maximum range of normalized signal areas of calibration measurements within the routine measurement series. Errors displayed as the 1-fold standard deviation over all values used per substance.

| Substance | Single measurement precision, idealized experiments | Single measurement precision, routine measurements | Drift in calibration, routine measurements |
|--------------------|---|--|--|
| CFC-12 | $(0.22 \pm 0.06) \%$ | $(0.30 \pm 0.09) \%$ | $(5.49 \pm 4.24) \%$ |
| Chloromethane | $(0.28 \pm 0.08) \%$ | $(0.45 \pm 0.20) \%$ | $(6.01 \pm 3.56) \%$ |
| CFC-11 | $(0.28 \pm 0.08) \%$ | $(0.29 \pm 0.04) \%$ | $(5.62 \pm 4.37) \%$ |
| HCFC-22 | $(0.30 \pm 0.06) \%$ | $(0.49 \pm 0.22) \%$ | $(5.23 \pm 3.82) \%$ |
| Carbonylsulfide | $(0.42 \pm 0.10) \%$ | $(0.39 \pm 0.17) \%$ | $(8.47 \pm 7.99) \%$ |
| Dichloromethane | $(0.52 \pm 0.10) \%$ | $(0.48 \pm 0.24) \%$ | $(8.07 \pm 3.35) \%$ |
| HFC-134a | $(0.54 \pm 0.23) \%$ | $(0.55 \pm 0.15) \%$ | $(6.05 \pm 5.15) \%$ |
| CFC-113 | $(0.55 \pm 0.08) \%$ | $(0.39 \pm 0.11) \%$ | $(6.48 \pm 3.99) \%$ |
| HCFC-142b | $(0.67 \pm 0.15) \%$ | $(0.83 \pm 0.06) \%$ | $(5.54 \pm 5.23) \%$ |
| Tetrachloromethane | $(0.68 \pm 0.21) \%$ | $(0.65 \pm 0.09) \%$ | $(6.31 \pm 4.77) \%$ |

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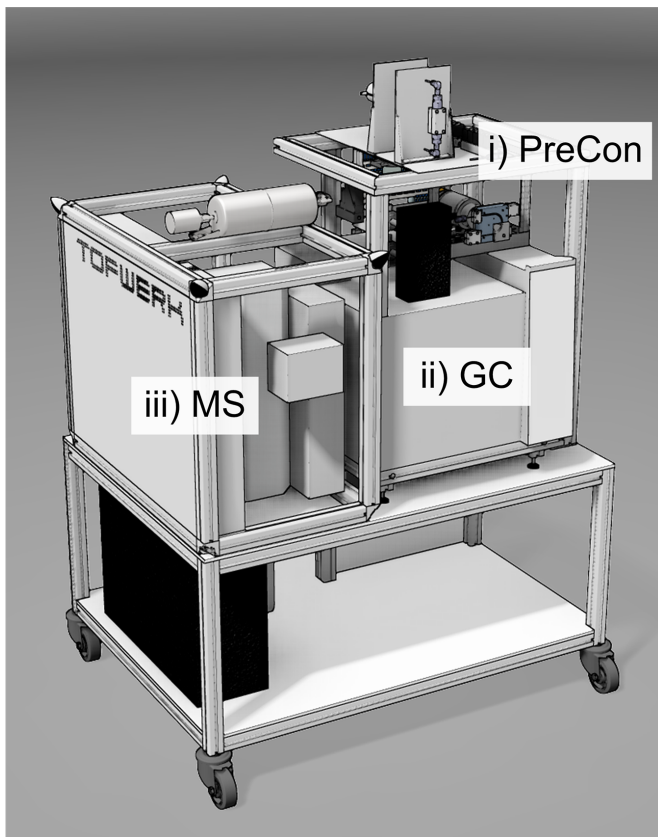


Figure 1. Schematic drawing of the GC-MS instrument. The sample preconcentration unit (i) is placed on top of the GC (ii), which is placed adjacent to the MS (iii). The whole setup is placed on a movable frame; data acquisition PC and power supplies are mounted below the instrument.

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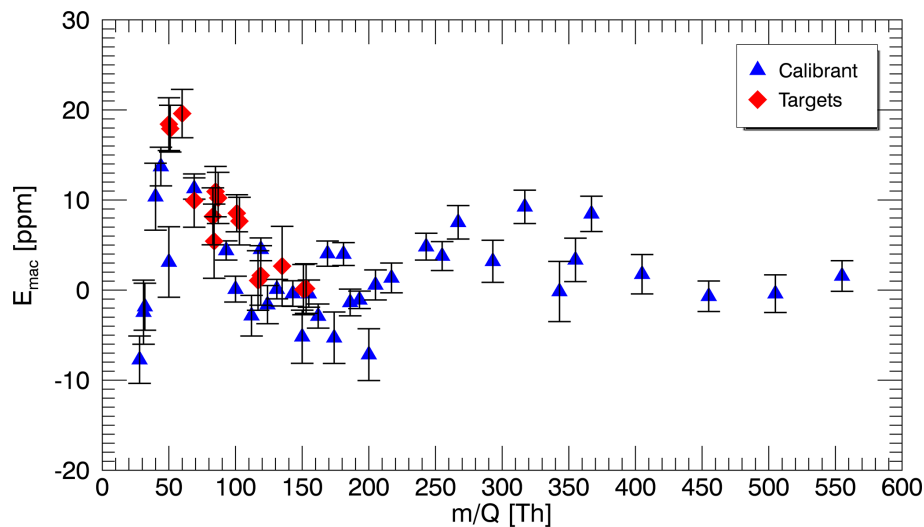


Figure 2. Mass accuracy (E_{mac}) in ppm over the whole mass range as determined for calibrant masses and masses of target substances during a measurement series. Error bars: one-fold standard deviation from 44 individual measurements. Arithmetic mean of absolute values: 3.9 ± 3.47 ppm (calibrant), 8.2 ± 6.59 ppm. Mean mass resolving power used in this measurement series: 3500 Th Th^{-1} .

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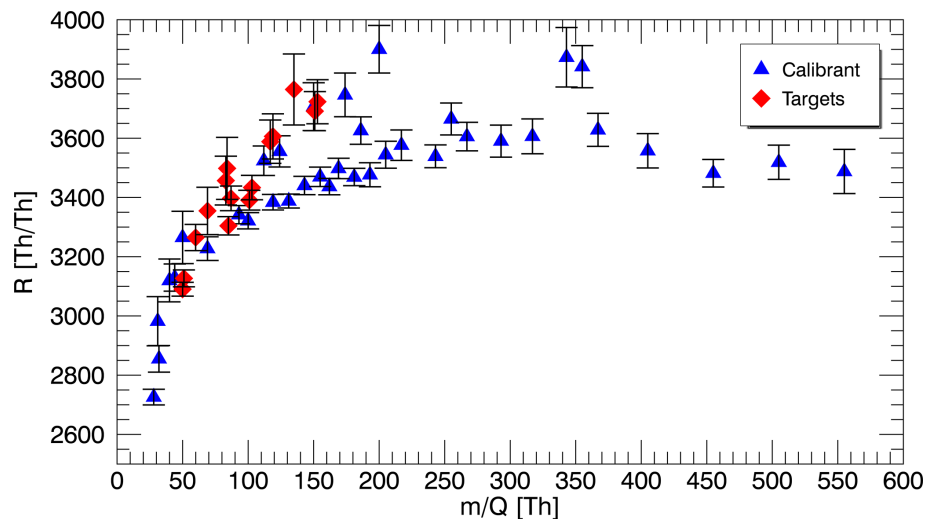


Figure 3. Mass resolving power over the whole mass range as determined for all mass axis calibration masses found in calibrant pulses during a measurement series as well as 15 m/Q targets from analyte molecules. Error bars: one-fold standard deviation of each m/Q over 44 individual measurements.

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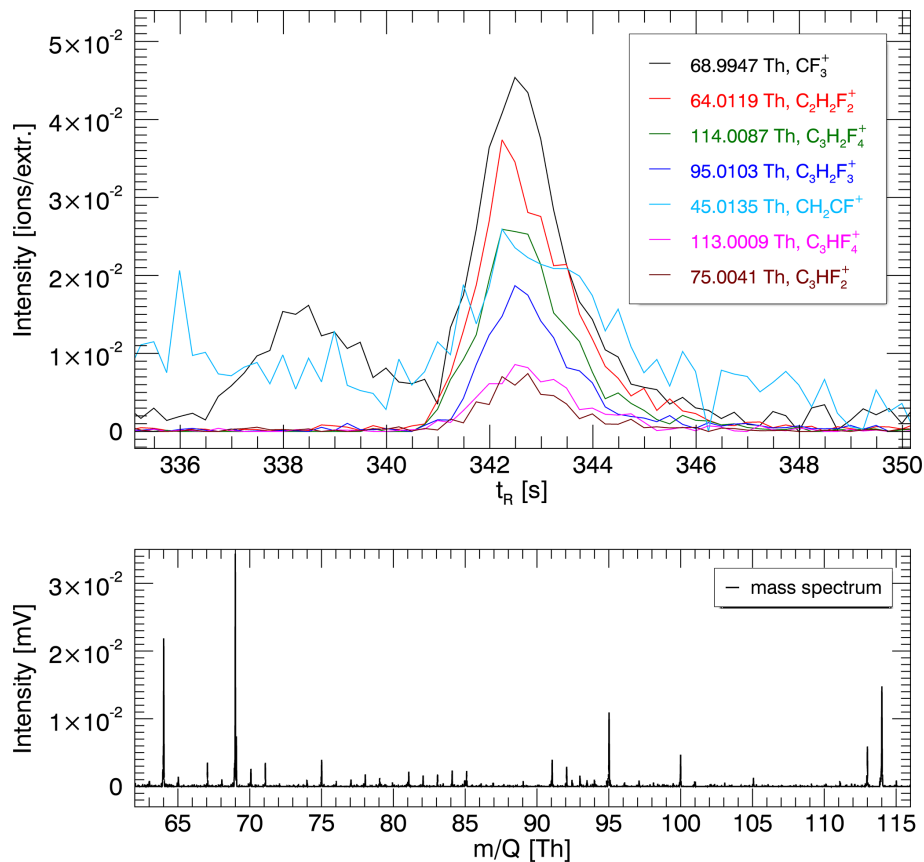


Figure 4. Upper graph: chromatographic signal of HFC-1234yf (CH_2CFCF_3) observed in an air sample from a parking lot. Lower graph: mass spectrum excerpt at the chromatographic peak apex. Y axis unit conversion, lower to upper graph: divide by the number of extractions per spectrum and the signal of a single ion (SiS; determined separately).

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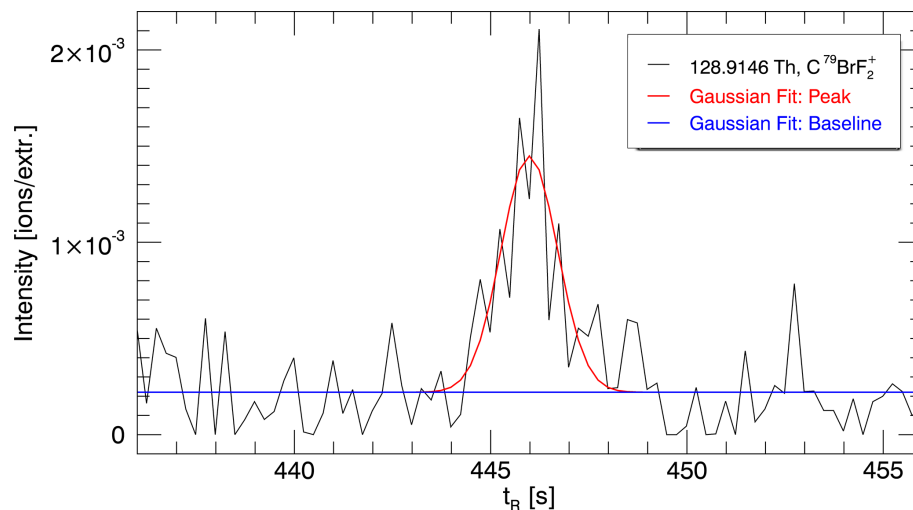


Figure 5. Plot of the integrated signal of Halon-1202 (CF_2Br_2) on m/Q 128.9146 ($\text{C}^{79}\text{BrF}_2^+$ fragment) at a retention time of 446 s. Sample: H-218 flask AGAGE calibration gas, 490 mL preconcentration volume.

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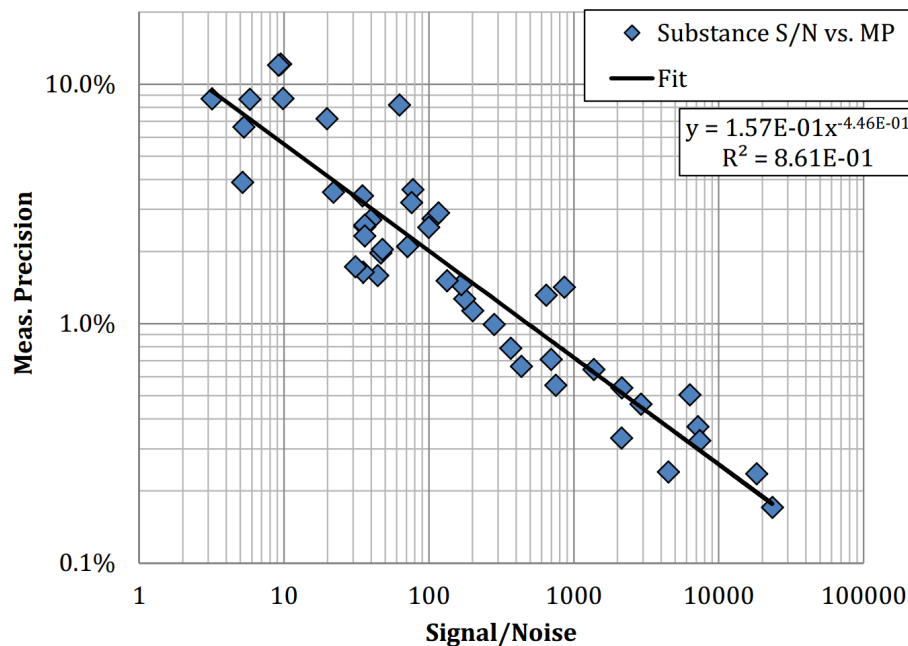


Figure 6. Correlation of measurement precision (y axis, MP) and signal-to-noise ratio (x axis) on a double-logarithmic plot. Data derived from repeated measurements of the same reference gas at constant sample volume of about 0.66 L. Evaluation based on nominal masses.

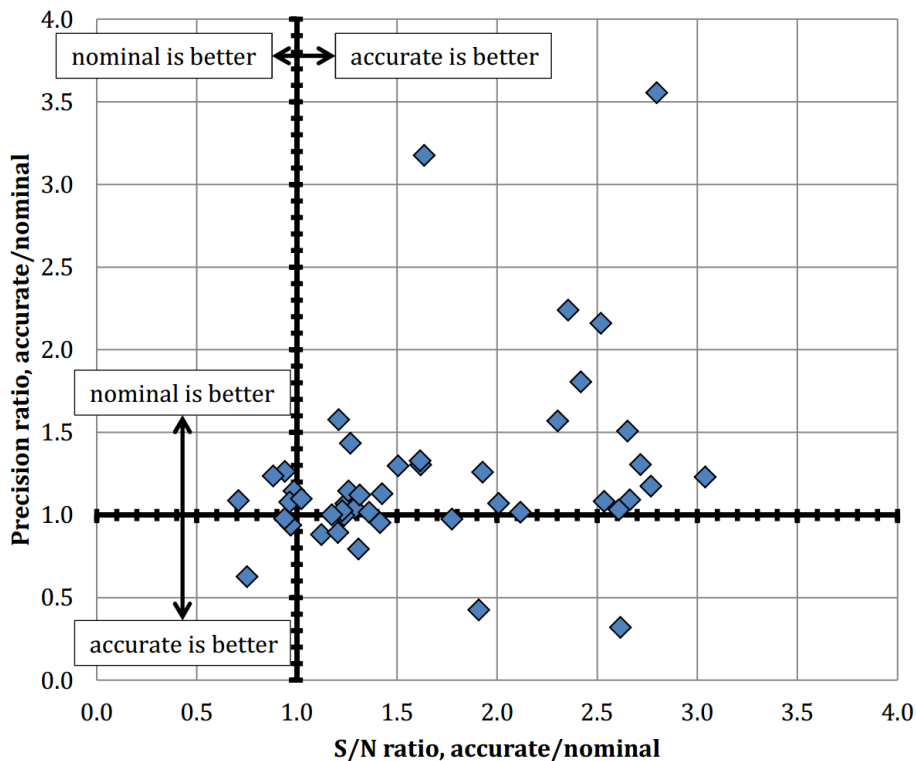


Figure 7. Corresponding ratios of signal-to-noise (x axis) and measurement precision (y axis) of values determined on accurate masses relative to values determined on nominal masses. Each dot represents a substance which was evaluated on both nominal and accurate mass trace. Data based on repeated measurements of the same reference gas at constant sample volume of about 0.66 L, see Fig. 6.

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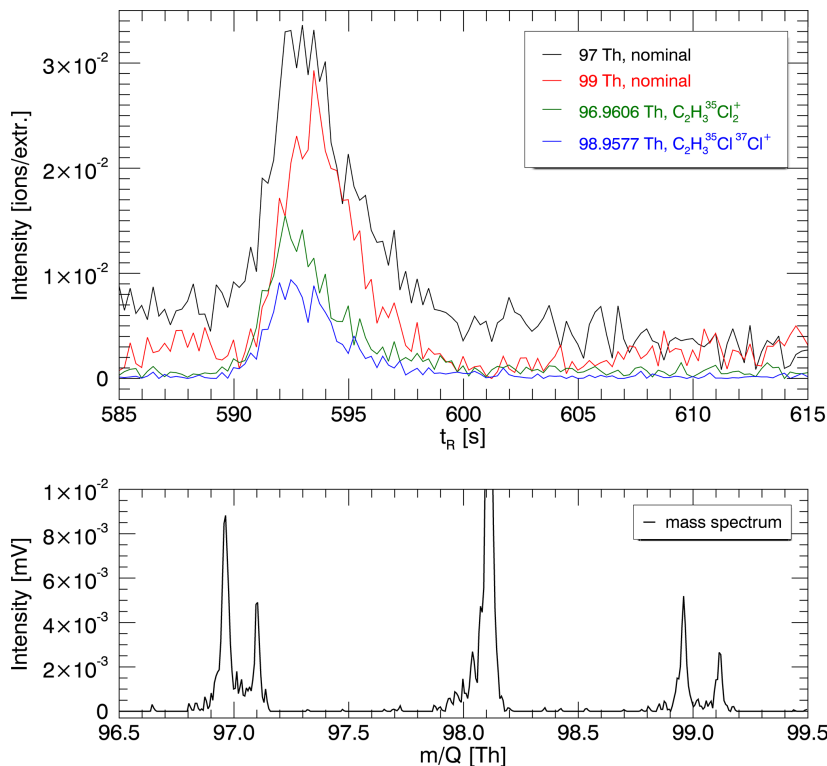


Figure 8. Upper graph: chromatographic signal of Methylchloroform (CH_3CCl_3) on ion masses 97 and 99 Th, nominal mass traces shown in black and red, accurate mass traces shown in green and blue. Lower graph: mass spectrum excerpt at the chromatographic peak apex. A coeluting substance with matching retention time and nominal masses 97 and 99 Th leads to a systematic error in mixing ration determination if the nominal mass trace is used for substance quantification. Unit conversions, y axis of lower to upper graph: see Fig. 4.

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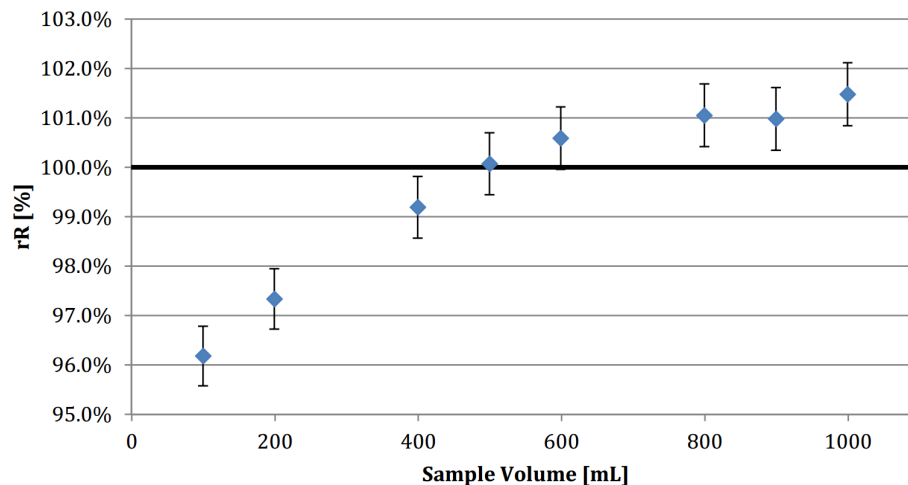
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Figure 9. CFC-12 (CCl_2F_2 , ca. 4.4 ng L^{-1} of air) relative responses (rR) derived from a volume variation experiment. All measurements were conducted with the same reference gas within one measurement series. Relative responses were calculated relative to the response calibration points with a preconcentrated sample volume of 0.5 L. Error bars: 3-fold measurement precision ($1\sigma = 0.22\%$).

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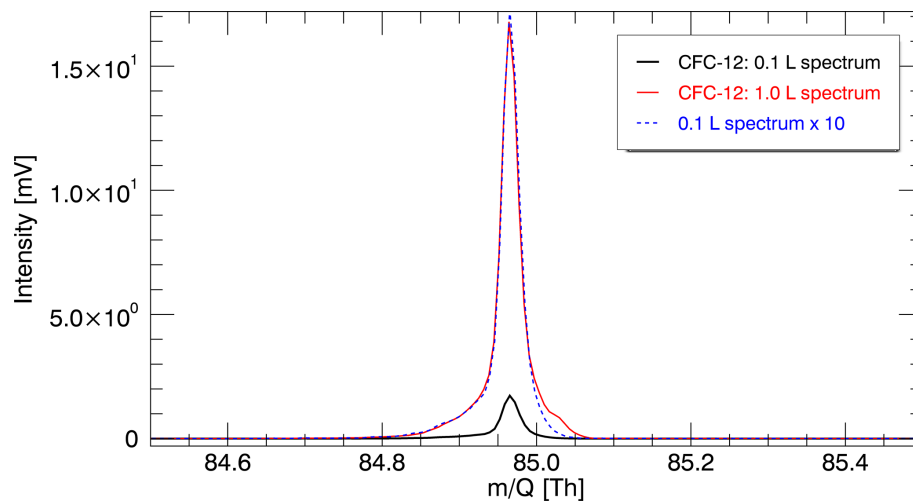


Figure 10. Comparison of $\text{CF}_2^{35}\text{Cl}^+$ mass spectra taken from the chromatographic peak apex of CFC-12. The solid lines in black and red show the intensity of a 0.1 and 1.0 L sample. The blue dashed line shows the 10-fold intensity of the 0.1 L spectrum. Towards high intensities, a “shoulder” appears to the right of the mass peak, which is not detectable at low intensities.

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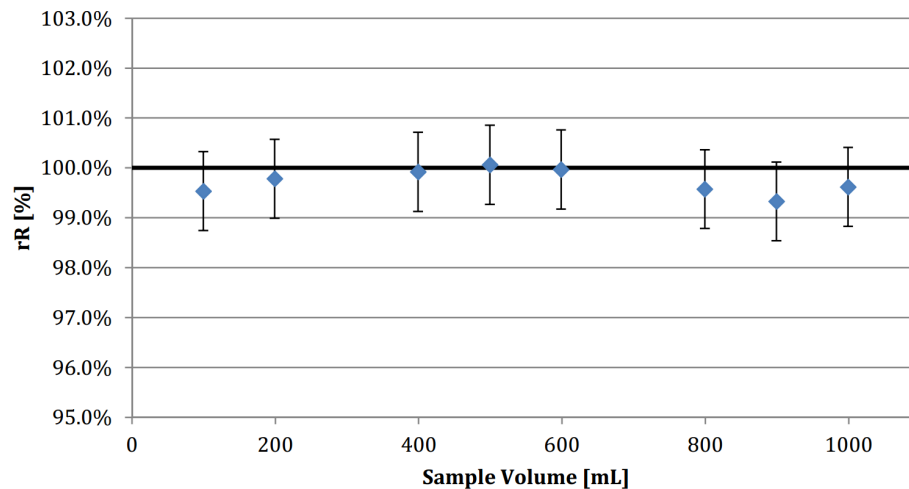


Figure 11. CFC 12 relative responses (rR) derived from a volume variation experiment using the accurate mass information. Data based on the same measurement series as used for Fig. 9. Error bars: 3-fold measurement precision, $1\sigma = 0.26\%$.