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A versatile, refrigerant-free cryofocusing-thermodesorption unit for preconcentration of traces gases in air

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Abstract. We present a compact and versatile cryofocusing-thermodesorption unit, which we developed for quantitative analysis of halogenated trace gases in ambient air. Possible applications include aircraft-based in-situ measurements, in-situ monitoring and laboratory operation for the preconcentration of analytes from flask samples. Analytes are trapped on adsorptive material cooled by a Stirling cooler to low temperatures (e.g. −80 °C) and desorbed subsequently by rapid heating of the adsorptive material (e.g. +200 °C). The setup neither involves exchange of adsorption tubes nor any further condensation or refocusation steps. No moving parts are used that would require vacuum insulation. This allows a simple and robust single-stage design. Reliable operation is ensured by the Stirling cooler, which does not require refilling of a liquid refrigerant while allowing significantly lower adsorption temperatures compared to commonly used Peltier elements. We use gas chromatography - mass spectrometry for separation and detection of the preconcentrated analytes after splitless injection. A substance boiling point range of approximately −80 °C to +150 °C and a substance mixing ratio range of less than 1 ppt (pmol mol^{-1}) to more than 500 ppt in preconcentrated sample volumes of 0.1 to 10 L of ambient air is covered, depending on the application and its analytical demands. We present the instrumental design of the preconcentration unit and demonstrate capabilities and performance through the examination of injection quality, analyte breakthrough and analyte residues in blank tests. Application examples are given by the analysis of flask samples collected at Mace Head Atmospheric Research Station in Ireland using our laboratory GC-TOFMS instrument and by data obtained during a research flight with our in-situ aircraft instrument GhOST-MS.

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1 Introduction

Atmospheric trace gases introduced to or elevated in concentration in the environment by human activities often show adverse environmental impacts. Prominent examples are chlorofluorocarbons (CFCs) and their intermediate replacements, hydrochlorofluorocarbons (HCFCs), which deplete stratospheric ozone (Farman et al., 1985; Molina and Rowland, 1974; Montzka et al., 2011; Solomon, 1999). Present-day CFC-replacements, namely hydrofluorocarbons (HFCs), have zero ozone depletion potentials (ODPs) but are still potent greenhouse gases like CFCs and HCFCs (Hodnebrog et al., 2013; Velders et al., 2009). Another example are non-methane hydrocarbons (NMHCs), which produce harmful tropospheric ozone in the presence of nitrogen oxides (Haagen-Smit and Fox, 1956; Marenco et al., 1994; Monks et al., 2015).

Many of the species found in the compound classes named above show atmospheric concentrations too low for direct detection and quantification by means of instrumental analytics. Therefore, a preconcentration step is required. The method of cryofocusing-thermodesorption is a common technique for that purpose (e.g. Aragón et al., 2000; Demeestere et al., 2007; Dettmer and Engewald, 2003; Eyer et al., 2016; Hou et al., 2006). In principal, an ambient air sample from either a sample flask or continuous flow for online measurement is preconcentrated on adsorptive material at a specific adsorption temperature, T_A. If T_A is significantly below ambient temperature, this step is referred to as “cryofocusing” or “cryotrapping”. Trapped analytes are re-mobilized subsequently by heating the adsorptive material to a desorption temperature T_D and flushed e.g. onto a gas chromatographic column with a carrier gas and detected with a suitable detector.

The primary motivation for the development of the instrumentation described in this manuscript was halocarbon analysis in ambient air. More specifically, there were no commercial instruments available which met the requirements of remote in-situ and aircraft operation: compact (as small as possible), lightweight (<5 kg), safe containment of working fluids and preferentially cryogen-free, pure electrical operation. Liquid cooling agents like liquid nitrogen (LN_2) or argon (LAr) (e.g. Apel et al., 2003; Farwell et al., 1979; Helmig and Greenberg, 1994) offer large cooling capacity but are difficult to operate on board of an aircraft due to safety restrictions and supply demand, e.g. when operating the aircraft from remote airports. Compression coolers (e.g. Miller et al., 2008; O'Doherty et al., 1993; Saito et al., 2010) offer less cooling capacity in terms of heat lift compared to liquid cooling agents and are relatively

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large in size and weight compared to widespread Peltier type cooling options (Peltier elements; e.g. de Blas et al., 2011; Simmonds et al., 1995; commercial thermodesorbers available from e.g. Markes or PerkinElmer). Peltier elements have the advantage of being very small and requiring only electrical power for cooling. However, their cooling capacity and minimum temperature cannot compete with compression- and refrigerant-based coolers. Stirling coolers pose an in-between solution, well-suited for maintenance-free remote operation: like Peltier coolers, they only require electrical power, do not contain any potentially dangerous working fluids (only helium) or cryogens but have a significantly higher cooling capacity. While not being as powerful as refrigerant-based coolers (LN_2, LAr), they still have comparable minimum temperatures. To our knowledge, the use of Stirling coolers for similar purposes like the one described here is rare with few published exceptions like the preconcentration of methane by Eyer et al. (2016) or the trapping of CO_2 as a carbon capture technology by Song et al. (2012).

The principal design of the cryofocusing-thermodesorption unit in description was developed for the airborne in-situ instrument GhOST-MS (Gas chromatograph for the Observation of Tracers – coupled with a Mass Spectrometer, Sala et al., 2014) and successfully used during three research campaigns up to now – 2011: SHIVA (carrier aircraft: DLR FALCON), 2013: TACTS (carrier aircraft: DLR HALO), 2015/2016: PGS (carrier aircraft: DLR HALO). To extend the substance range, we then developed similar cryofocusing-thermodesorption units for our other GC-MS instruments (Hoker et al., 2015; Obersteiner et al., 2016), which are currently operated in the laboratory. Both detailed description and characterisation of the preconcentration unit were not discussed in the publications Hoker et al. (2015), Obersteiner et al. (2016) (laboratory setups) and Sala et al. (2014) (aircraft instrument). Within this manuscript, a general instrumental description is given in section 2, which is applicable for all the named setups. Characterisation results discussed in section 3 are based on the latest version of the laboratory setup (Obersteiner et al., 2016). To demonstrate the versatility and reliability of the setup, application examples are given in section 4 for sample analysis in the laboratory as well as in-situ aircraft operation. Results are summarized and conclusions are drawn in section 5.

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2 Instrumentation

This section gives a description of principal components of the sample preconcentration unit and is valid for all our analytical setups presented in Sala et al. (2014), Hoker et al. (2015) and Obersteiner et al. (2016). The following section 2.1 outlines the general measurement procedure and gas flow as well as its integration into a chromatographic detection system. Sections 2.2 and 2.3 describe the implementation of the main operations of the unit; cooling ("trapping", i.e. preconcentration of analytes) and heating (desorption of analytes). A preconcentration system can always only be as good as the analytical set-up behind it. The preconcentration system described here has been designed for the coupling with a chromatographic system but in principle could also be adapted for coupling with other techniques. Specific technical components of the instrumentation used in this work to characterise the preconcentration unit will be listed in section 3.

2.1 Measurement procedure and gas flow in GC application

For the preconcentration of analytes, the sample is flushed through a micro packed column of cooled adsorptive material. Analytes are "trapped" on the adsorptive material as the steady state of adsorption and desorption is strongly shifted towards adsorption by the low temperature of the adsorptive material. By subsequent rapid heating of the adsorptive material, the steady state is instantaneously shifted towards desorption ("thermodesorption"). Formerly trapped analytes are flushed backwards onto the warm chromatographic column with a carrier gas. There is no further refocusing or separation step, except for higher-boiling compounds on the GC column itself. **Figure 1** shows a flow scheme of the setup. The outflow of the sample loop during preconcentration ("stripped air"; mainly nitrogen and oxygen) is collected in a previously evacuated reference volume for analyte quantification (2 L electro-polished stainless steel flask; volume determination by pressure difference). A mass flow controller (MFC) is mounted between sample loop and reference volume for sample flow control. The MFC can also be used for sample volume determination e.g. for sample volumes larger than the reference volume. Hardware control is implemented with a LabVIEW cRIO assembly (compact, reconfigurable input output; National Instruments Inc., USA) using self-written control software. It operates the preconcentration unit automatically, i.e. controls system parameters like sample loop temperature by cooling and heating concomitant with system states like preconcentration, desorption etc.

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2.2 Cryofocusing: sample loop and cooling technique

A stainless steel tube with 1/16" outer diameter (OD) and 1 mm inner diameter (ID) is used as sample loop. The tube is packed with adsorptive material and placed inside an aluminium cuboid ("coldhead") which is cooled continuously to maintain a specific adsorption temperature. **Figure 2** shows a technical drawing of sample loop and coldhead. The coldhead can contain two sample loops; in this case one of them is an empty stainless steel tube with 1/16 inch OD and 1 mm ID to characterize the sample loop heater. For that purpose, a thin temperature sensor is inserted into the empty tube. To save space and avoid mechanical, moving parts, the sample loop is not removed from the coldhead during desorption. It is insulated and thereby isolated electrically by two layers of glass silk and four layers of Teflon shrinking hose. The insulation is a variable parameter which determines the rate at which heat is exchanged between sample loop and coldhead. Consequently, it determines coldhead warm-up rate during desorption and sample loop cool-down rate after desorption. More insulation would result in longer cool-down time after desorption but also to less heat flowing into the cold head, thus to lower possible temperature of the cold head. The insulation used represents a compromise that works well for the application presented here but could potentially be improved by e.g. using a ceramic insulator. The coldhead itself is insulated towards surrounding air with 45 mm of Aeroflex HF material (Aeroflex Europe GmbH, Germany).

The Stirling cooler used for cooling offers the advantage of requiring only electrical power while providing a relatively large cooling capacity at very low minimum temperatures. The latter are comparable to liquid nitrogen in case of Sunpower CryoTel MT, CT and GT Stirling coolers, with maximum heat lifts of 5 W to 16 W at −196 °C according to the manufacturer. Heat that is removed from the coldhead by the Stirling cooler has to be released to the surrounding air; either directly by an air-fin heat rejection or indirectly by a water coolant system mounted to the cooler's warm side. The cooler should maintain a defined adsorption temperature T_A of the sample loop over the series of measurements. However, during thermodesorption, a certain amount of heat is transferred to the coldhead as the sample loop is kept directly inside with only a small amount of insulation. Excess heat has to be removed by the Stirling cooler to regain T_A for the preconcentration of the next sample. The preconcentration unit is attached to a gas chromatograph; therefore, the gas chromatographic runtime allows coldhead and sample loop to cool down after thermodesorption and return to T_A before preconcentrating the next sample.

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Besides chromatographic runtime, various factors determine the minimum cycle time (i.e. sample measurement frequency) including:

- targeted adsorption temperature T_A
- Stirling cooler's cooling capacity (i.e. heat lift around T_A) and coldhead insulation as well as ambient temperature
- thermodesorption duration and T_D as well as insulation of the sample loop
- volume of the sample to preconcentrate and preconcentration flow

To give a practical example, **Table 1** shows cycle times derived from routine operation data. With the laboratory setup, a total time per measurement of 18.6 minutes is necessary if $T_A = -120$ °C and $T_D \approx 200$ °C is desired – mainly determined by the time needed to compensate the warm-up of the coldhead during desorption. This minimum time interval significantly shortens to 8.5 minutes if T_A is increased to −80 °C (same T_D). Data from the in-situ setup shown in **Table 1** demonstrates that even shorter cycle times of 4.1 minutes are possible with a decreased preconcentration volume (100 mL instead of 500 mL; requiring a detector that is sensitive enough) and a slightly higher T_A. General measures to increase the number of measurements per time would be to increase the preconcentration flow, reduce the sample size (see in-situ setup), improve the coldhead and sample loop insulation and increase the cooling capacity.

After desorption, sample loop temperature drops in an exponential decay shaped curve due to the decreasing temperature difference between coldhead and sample loop. After a desorption at $T_D \approx 200$ °C, sample loop and coldhead temperature reached similar temperatures after approximately 30 s cool-down time ($T_A = -80$ °C). The cool-down time increases to about 90 s at −120 °C cold head temperature. Considering the total run times shown in (**Table 1**), sample loop cool-down time is not a limiting factor to the overall cycle time. Consequently, thermal insulation of the sample loop could still be increased, thereby decreasing coldhead warm-up during desorption.

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2.3 Thermodesorption: sample loop heater

Depending on the targeted substance class to analyse and the analytical technique, the requirements for thermodesorption will differ. In case of a gas chromatographic system for analysis of volatile compounds, these requirements are:

- a fast initial increase in temperature to yield a sharp injection of highly volatile analytes onto the GC column,
- no overshooting of a maximum temperature in case of thermally unstable sample compounds or adsorptive material (e.g. HayeSep D, T_D < 290 °C)
- preservation of the desorption temperature over a time period for desorption of analytes with higher boiling points
- good overall repeatability, especially of the injection of highly volatile analytes

Desorption heating is implemented by pulsing a direct current (max. 12 V / 40 A, relay: Celduk Okpac; spec. switching frequency 1 kHz, Celduk Relays, France) directly through the sample loop tubing which has a resistance of ~0.5 Ω. A temperature sensor (Pt100, 1.5 mm OD) was welded to the outside of the sample loop tubing (see also **Figure 2**), for feedback control of the heater temperature. However, mainly due to the thermal mass of the sensor and its proximity to the coldhead (despite the insulation), it was found to give no representative values for temperature inside the sample loop during desorption. Differences of around 100 °C were found in comparison to temperature measured within the sample loop (equilibrium state; after 2-3 minutes of continuous heating). Nevertheless, the temperature sensor can be (after being characterised) used for feedback control as the indicated values are reproducible. As an alternative to feedback control, a deterministic heater with prescribed output settings can be used. For security reason, measured coldhead and sample loop temperature have to be used as heater shutdown triggers in this case.

Figure 3 shows a comparison of temperature sensor data from in- and outside the empty sample loop as well as the coldhead. Very good results were achieved with a two-stage, deterministic heater setup with a fast heat-up, a small overshoot between stage 1 and 2 of the heating phase and preservation of T_D with only a small drift and fluctuation. With the described heater setup, T_D can be reached within a very short time of approximately 3 seconds. Initial heating rates (first second of heat pulse) were calculated to be more than 200 °C s^{-1} depending on the power output setting. As the sample loop is getting warmer, heating rate drops resulting in a mean heating rate of about 80 °C s^{-1} during stage 1.

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If a deterministic heater is used instead of a feedback controlled heater, sample loop temperature becomes directly dependent on coldhead temperature (more precisely: heat flow from the sample loop into the coldhead). Consequently, higher output settings are necessary at lower coldhead temperatures to achieve comparable temperatures. On the other hand, if the coldhead gets warmer, sample loop temperature increases as well. This effect can be observed in **Figure 3** as a slight upward drift of the sample loop temperature (red curve, temperature measured within the sample loop) during stage 2. The absolute temperature differences caused by this drift as well as the oscillation amplitude are small (approximately 20 °C min. to max. and 4 °C standard deviation without trend correction) compared to the temperature difference between coldhead and sample loop during heating (about 300 °C).

Besides the problem of differing inner and outer temperature of the sample loop during heating, temperature was not found to be distributed homogeneously alongside the empty sample loop inside the coldhead. Temperature differences of up to ±30 °C at 200 °C mean temperature were observed with the current setup if measuring temperature at different points within the sample loop, potentially due to (a) difficulties in accurately measuring the inner temperature (wall contact of sensor) and (b) inhomogeneity in sample loop insulation as well as variations in tubing wall width or carbon content leading to an inhomogeneous electrical resistance and thus an inhomogeneous distribution of heat. These temperature variations might be different or ideally negligible in the sample loop packed with adsorptive material. However, the finding underlines the importance of an insulation as homogeneous as possible and suggests that “cold points” (possibility of insufficient desorption) as well as “hot points” (possibility of adsorptive material or analyte decomposition) are possible along the sample loop, which has to be taken into consideration when setting up and testing the preconcentration setup, i.e. to not exceed the temperature limit of the adsorptive material.

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3 Characterisation

This section discusses characterisation results (section 3.2 and 3.3) obtained with the GC-TOFMS instrument described in Obersteiner et al. (2016) as it covers the widest substances range (see supplementary information) and therefore allows the most differentiated analysis. A brief description of this analytical instrument is given in the following section 3.1; see Obersteiner et al. (2016) for details on GC and MS. We consider these results to be valid in principle also for our other GC-MS setup discussed by Hoker et al. (2015) and the GhOST-MS described by Sala et al. (2014) as all preconcentration setups rely on the same principal setup and similar components are used.

3.1 Analytical instrument

A Sunpower CryoTel CT free piston Stirling cooler (Ametek Inc., USA) is used for cooling of the coldhead. In the described setup, a water coolant system (Alphacool, Germany) originally intended for cooling of a personal computer's processing units removes heat from the Stirling cooler's heat rejection. Sunpower Stirling coolers are optionally also available with an air-fin heat rejection that requires a continuous air stream during operation. For sample loop heater control, a pulse-width modulation (PWM; 20 ms period, 1 µs minimum width) with a prescribed output is used (deterministic heater; see section 2.3). Heater operation during desorption is separated into a short initial "heat-up" stage with a high output of the PWM and a longer "hold" stage with lower heater output to maintain desorption temperature. The sample loop is packed with adsorptive material over a length of approximately 100 mm (~20 mg). Two different adsorptive materials were used in different sample loops installed in the course of this work; HayeSep D, 80/100 mesh (VICI International AG, Switzerland) and Unibeads 1S, 60/80 mesh (Grace, USA).

A Bronkhorst EL-FLOW F-201CM (Bronkhorst, the Netherlands) is used for sample flow control (downstream of the sample loop in order to avoid contamination) in combination with a Baratron 626 pressure sensor (0-1000 mbar, accuracy incl. non-linearity 0.25 % of reading, MKS Instruments, Germany) for analyte quantification by pressure difference measurement. An Agilent 7890 B gas chromatograph (GC) with a GS GasPro PLOT column (Agilent Technologies, Inc. USA; 0.32 mm inner diameter) using a ramped temperature program (45 °C to 200 °C with 25 °C min^{-1}) and backflush option is used for analyte separation. Purified helium 6.0 is used as carrier gas (Praxair Technologies Inc., German supplier; purification system:

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Vici Valco HP2). For analyte detection, a Tofwerk EI-TOF (model EI-003, Tofwerk AG, Switzerland) mass spectrometer (MS) is attached to the GC. All samples are dried using magnesium perchlorate kept at 80 °C prior to preconcentration. Artificial additions of analytes to the sample from the dryer were excluded by comparing measurements of dried and undried blank gas. All tubing upstream of the sample loop was heated to >100 °C to avoid substance loss to tubing walls.

Figure 4 shows a typical chromatogram from an ambient air sample for three selected mass-to-charge ratios (m/Q). Two different adsorptive materials were used in the course of this work (HayeSep D, Unibeads 1S) which showed partly differing adsorption and desorption properties; results are discussed separately if appropriate. To achieve high measurement precision and minimum uncertainties introduced by the preconcentration unit, both the analyte adsorption (preconcentration) and analyte desorption (injection) into the chromatographic system have to be quantitative and repeatable. The following section describes tests and results for the characterisation of both aspects.

3.2 Adsorption

The sample loop essentially is a micro packed chromatographic column with a limited surface area where sorption can take place. The low temperature during sample preconcentration shifts the steady state of analyte partitioning between mobile and solid phase mostly to the solid phase. This preconcentration technique “strips” the air of its most abundant constituents; nitrogen, oxygen and argon. Other, less volatile but still very abundant constituents like CO_2 are however trapped, depending on adsorption temperature. Elution of such species from the GC column after thermodesorption and injection can cause problems with regard to chromatography as well as detection, depending on GC configuration and detection technique. With the setup described here, the elution of CO_2 limits the analysable substance range as the detector shows saturation during the elution of CO_2. Regarding preconcentration of targeted analytes, the concept of an adsorption-desorption steady state suggests that at a certain point a breakthrough of analytes occurs, depending on a combination of loading of the solid phase with sample molecules and time to achieve steady state, in turn influenced by sample flow rate and pressure. Consequently, the maximum possible sample volume and/or minimum duration of preconcentration are dependent on the adsorptive material used, volatility (and concentration) of the targeted analytes as well as sample flow rate and pressure. For typical sample volumes of 0.5 L and 1.0 L (at standard temperature and pressure) and a constant sample

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back pressure of 2.5 bar abs., no significant impact of sample preconcentration flow was found within the tested range of 50 mL·min^{-1} to 150 mL·min^{-1} for any of the analysed substances. Higher or lower flow rates and pressure were not possible or suitable for practical reasons like flow restriction and valve operating pressure.

Substance breakthrough (i.e. substance-specific adsorption capacity) was analysed in volume variation experiments, comprising measurements of the same reference air with preconcentration volumes of up to 10 L and referencing the volume-corrected detector response against default preconcentration volumes of e.g. 1 L ("relative response"). Quantitative trapping is then indicated by a relative response of 1; a relative response <1 would indicate an underestimation (i.e. loss by breakthrough), a relative response of >1 would indicate an overestimation (i.e. increase by a memory effect from the preceding sample). To structure the following discussion, two classes of substances are formed and treated separately: "medium volatile substances" with boiling points > −30 °C (e.g. CFC-12, CCl_2F_2) and "highly volatile substances" with boiling points < −30 °C (e.g. HFC-23, CHF_3). The substances discussed are selected based on the criteria volatility and (preferably high) concentration. The adsorption of substances with lower volatility (BP > 30 °C) was assumed to be quantitative. Results discussed in the following are displayed in **Table 2**.

Medium volatile substances. As a reference for halocarbon analysis, CFC-12 (CCl_2F_2) and CFC-11 (CCl_3F) were chosen due to their high mixing ratios of about 525 and 235 pmol·mol^{-1} (ppt, parts per trillion) in present-day, ambient air and moderate volatility with boiling points of −29.8 °C and +23.8 °C. For a volume of 10 L preconcentrated air on the Unibeads 1S sample loop, both substances showed a deviation from linear response of +0.6 % ± 0.42 % for CFC-12 and +0.6 % ± 0.22 % respectively for CFC-11. The positive deviation from linearity is still found within the 3-fold measurement precision determined for the experiment and could potentially be an artefact of the detector used which tends to slightly overestimate strong signals and underestimate weak signals; see section 3.4 in Obersteiner et al. (2016). Hence, no significant breakthrough or detector saturation was observed for both substances CFC-12 and CFC-11.

Highly volatile substances. More volatile compared to CFC-12 and CFC-11 but similar in mixing ratio is carbonyl sulfide (COS) with a boiling point of −50.2 °C and an ambient air mixing ratio of typically around 500 ppt. Against 1 L reference sample volume (sample mixing ratio: 525 ppt), COS showed a quantitative adsorption up to 5 L on the Unibeads 1S

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sample loop with a deviation from linear response of +0.9 % ± 0.80 %. At 10 L sample volume, a breakthrough occurred giving a deviation from linear response of −35.2 % ± 0.52 %. The substance analysed with highest volatility was HFC-23 with a boiling point of −82.1 °C and a current background air mixing ratio of ~40 ppt. Referenced against a sample volume of 0.5 L, significant breakthrough occurred at a sample volume of 2.5 L with a deviation from linear response of −39.2 % ± 2.75 %. The highest sample volume quantitatively adsorbed in the experiment was 1.0 L with a relative response of −0.3 % ± 2.75 % (HayeSep D sample loop). A similar behaviour was observed for ethyne (C_2H_2), with a sublimation point of −80.2 °C, a mixing ratio of approximately 610 ppt in the sample and a deviation from linear response of −20.2 % ± 1.22 % at 2.5 L sample volume (HayeSep D sample loop). However, ethyne was also analysed on the Unibeads 1S sample loop which gave a quite different result with a deviation from linear response of +10.1 % ± 0.51 %, thus breakthrough did not occur. The positive, non-linear response is caused potentially by a system blank (see also section 3.3). Unfortunately, HFC-23 could not be analysed in ambient air samples for comparison on the Unibeads 1S sample loop as its ion signals are masked by large amounts of CO_2 still eluting from the GC column at the retention time of HFC-23.

Concluding, the adsorption process was found to be substance specific as both HFC-23 and ethyne are comparably volatile but significantly less ethyne broke through despite its 15-fold elevated mixing ratio (Unibeads 1S sample loop). The comparison of ethyne breakthrough on the HayeSep D and Unibeads 1S sample loop suggests that the adsorption process is dependent on the chosen adsorptive material. A comparison of adsorptive materials is however not the focus of this work; such a comparative adsorption study was e.g. conducted for methane (CH_4) preconcentration by Eyer et al. (2014). From the comparison of the breakthrough observed for COS and the quantitative adsorption of CFC-12 and CFC-11, it can be concluded that volatility is the primary factor that determines breakthrough. Quantitative adsorption is not limited by principal adsorption capacity (i.e. the absolute number of molecules adsorbed) of the adsorptive material and material amount for a sample volume of up to 10 L and an adsorption temperature of −80 °C.

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3.3 Desorption

While adsorption is characterised by the quantitative trapping of highly volatile substances, desorption is characterised by sharpness and repeatability of the injection represented by chromatographic peak shape and retention time variance (qualitative aspect; section 3.3.1) as well as the amount of blank residues (quantitative aspect; section 3.3.2). Blank residues ("memory effect") have to be divided into residues that remain on the adsorptive material after desorption ("preconcentration residues" or "preconcentration memory effect") and residues that remain in the analytical setup (tubing etc.) upstream of the sample loop, thus had not reached the sample loop ("system residues" or "system memory effect").

3.3.1 Peak shape and retention time stability

To demonstrate injection sharpness, **Figure 5 A** shows the chromatographic signal of CFC-11 eluted from the GC column kept isothermal at 150 °C and **Figure 5 B** the chromatographic signal as observed with the ramped GC program. Both signals generally show a Gaussian peak shape with a slight tailing of the right flank. In comparison, the "unfocused" signal from the isothermal column reflecting the sharpness of the direct injection is wider by a factor of ~3 but still narrow enough to allow for good peak separation in most standard GC methods with runtimes between 10 to 30 minutes; the full peak width at half maximum (FWHM) was calculated to be 6.3 s (0.10 min) for the isothermal peak and 2.0 s (0.03 min) for the focused peak.

Injection quality can further be judged by the stability of retention times of the first chromatographic signals obtained with the ramped GC program, as these are only very little influenced by the chromatographic system (in particular there is nearly no refocusing on the chromatographic column). **Table 3** shows retention times and their variability expressed as relative standard deviation and variance as well as the chromatographic signal width (FWHM) of the respective substance. Variances are less than 0.02 s on average. Together with signal width, they decrease reversely proportional to retention time, which shows the increasing influence of chromatographic separation (from HFC-23 to CFC-11 in **Table 3**). Even at incomplete refocusation by gas chromatography, the desorption procedure of the preconcentration unit gives close to Gaussian peak shapes except a slight tailing of the right flank. The tailing effect could potentially be reduced by refocusing the high-volatile analyte fraction on a second sample loop. The high repeatability of the injection is shown by the low variability in retention time of the first signals in the chromatogram (**Table 3**).

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3.3.2 Analyte residues

Analyte residues can originate from inherent system *contamination* or constitute a remainder from the previous sample (*memory effect*). Analyte residues were investigated with (a) an unloaded injection after multiple 1 L ambient air sample injections, i.e. subsequent thermodesorption of the sample loop without switching to load-position between runs (see **Figure 1**) and (b) the preconcentration of 1 L helium from the carrier gas supply using the same path as the sample, including dryer etc. after multiple 1 L ambient air sample measurements. Analyte residues on the sample loop (*sample loop memory*) as well as carrier gas contaminations are investigated by (a) while (b) includes analyte residues within the tubing upstream of the sample loop, i.e. stream selection, sample dryer etc. (*system memory*). To get the most complete picture possible, 65 substances were analysed, most of them halo- and hydrocarbons (see supplementary information for a detailed list) on both a HayeSep D as well as a Unibeads 1S sample loop. Substances with low measurement precision (> 10 %) were excluded from the investigation.

In general, most of the detected analyte residues are most probably caused by system contaminations (HFCs from fittings, solenoid valve membranes etc.) or carrier gas contaminations (hydrocarbons) as they show a constant background. In principal, the amount of a residue is dependent on volatility and concentration, so extremely elevated concentrations of low-volatile substances might lead to a memory effect that was not detected in the current investigation with 1 L preconcentration volume of unpolluted ambient air. Detailed results for the two different adsorptive materials tested are discussed in the following.

Unibeads 1S adsorptive material. 13 of 65 substances (20 %) did show detectable residues on the sample loop which did not represent a system memory but a system contamination, e.g. from the carrier gas, sealing materials etc. as they were always present and did not disappear in subsequent unloaded injections. Respective residues were generally larger with increasing boiling point (e.g. n-propane < benzene). Most of them were hydrocarbons and the halocarbons chloro- and iodomethane (CH_3Cl, CH_3I) and chloroethane (C_2H_5Cl) as well as HFC-134 (CHF_2CHF_2). No further CFCs, HCFCs, PFCs or HFCs were detected in the unloaded sample loop injection (see Obersteiner et al. (2016) for a discussion of detection limits). Of the remaining 52 substances, 36 also did not show any detectable residues in the helium blank. Of the 17 substances that did show residues (contamination and memory effect combined), 7 had residues below 0.5 % of the signal area determined in the preceding ambient air measurement. Again, residues were found mostly for hydrocarbons but not CFCs or HCFCs. Concluding,

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the Unibeads 1S sample loop seems to be a good choice for halocarbon monitoring measurements (one measurement per sample) as there were nearly no halocarbon residues in subsequent helium blank measurements.

HayeSep D adsorptive material. The HayeSep D sample loop showed a considerably higher amount of sample loop residues with 22 detectable substances from the selected 65 (34 %). Again, most of these substances were hydrocarbons but also some halogenated compounds like Tetrachloromethane (CCl_4) and Bromoform ($CHBr_3$). Of the remaining 43 substances, 28 were undetectable in the helium blank (system free of contamination and memory effect). 13 of the detectable substances showed responses of < 0.5 % relative to the preceding ambient air sample, also including CFC-11 with 0.05 % and CFC-113 with 0.2 %. While the named halogenated compounds CCl_4 and $CHBr_3$ as well as CFC-113 and CFC-11 were undetectable in subsequent blank gas measurements, residues of many hydrocarbons were persistent, suggesting a system contamination. In summary, the HayeSep D sample loop showed an overall higher number of residues which is likely caused by a higher desorption temperature of the Unibeads 1S sample loop which can be heated faster and to a higher temperature without degrading the material. Nevertheless, the residues on both adsorptive materials were on a tolerable level (below average measurement precision) for flask measurements with multiple measurements per sample.

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4 Application

4.1 Laboratory operation: flask sample measurements

For quality assurance of the laboratory instrumentation, five air samples were analysed and compared to our reference GC-QPMS (gas chromatograph coupled to a quadrupole mass spectrometer) which uses a similar preconcentration setup (Hoker et al., 2015). Consistent results with the NOAA network (National Oceanic and Atmospheric Administration) were demonstrated for the GC-QPMS in the past during the IHALACE intercomparison (Hall et al., 2014), however with a different sample preconcentration using liquid nitrogen (Brinckmann et al., 2012; Laube and Engel, 2008; Laube et al., 2010). The current laboratory setup using the Stirling cooler-based preconcentration has been described by Hoker et al. (2015) and has shown very consistent results with previous measurements. The samples for the application and intercomparison discussed here were collected between July 7th and September 11th 2015 at Mace Head Atmospheric Research Station in Ireland (53°20′ °N, 9°54′ °W, 30 m above sea level). Samples were filled "moist" (no sample drying) into 2 L electro-polished stainless steel flasks (two flasks in parallel per sampling date). The comparison is extended to include in-situ measurement data from the online monitoring Medusa GC-MS (Miller et al., 2008) operated by the AGAGE (Advanced Global Atmospheric Gases Experiment) network at Mace Head Station. Medusa GC-MS data points were chosen within ±1 hour of the flask samples' sampling time. **Figure 6** shows a comparison of absolute quantification results for CFC-12 (CCl_2F_2). Very good agreement within the 1-fold measurement error is achieved in comparison to the Medusa GC-MS and within the 2-fold measurement error in comparison to the reference GC-QPMS. While the Medusa GC-MS is calibrated with secondary calibration gases (AGAGE flasks H-265 and H-266; CFC-12 scale: SIO-05), both our instruments were calibrated with different ternary calibration gasses, referenced to the same secondary calibration gas (AGAGE flask H-218; CFC-12 scale: SIO-05). Taking into account that all three instruments were calibrated with different calibration gases which rely on the same calibration scale but are based on a chain of intercalibrations, this result stands proof for highly accurate measurement results, excluding the absolute scale error.

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4.2 Aircraft in-situ operation: GhOST-MS

Reliability of operation is best demonstrated with the in-situ GC-MS GhOST-MS[1]. **Figure 7** shows a chromatogram obtained from the injection of a preconcentrated sample volume of 100 mL of ambient air. With a chromatographic runtime of 2.9 minutes and a total cycle time of 4.1 minutes (see also **Table 1**), a data frequency is achieved that is very high for a GC-MS system with a total of 27 identified and simultaneously measured species on m/Q of bromine, chlorine and iodine in negative chemical ionisation mode using argon as reagent gas. The cycle time is limited by cooldown of the adsorptive material (HayeSep D) to −70 °C needed to quantitatively trap the earliest eluting analyte, Halon 1301 ($CBrF_3$). The very good overall performance of the GhOST-MS including the preconcentration unit used in this in-situ application can be inferred from actual measurement data obtained during a research flight of the recent PGS campaign (POLSTRACC/GW-LCycle/SALSA) of the HALO aircraft on flight 160226a (PGS-14). **Figure 8** shows a tracer-tracer correlation between Halon 1301 and Halon 1211 ($CBrClF_2$). The measurements are colour-coded to show potential temperature θ. As expected, the lowest mixing ratios are observed at the highest potential temperature. Both tracers have relatively long steady-state lifetimes of 72 years for Halon 1301 (58-97, derived from model data and observations) and 16 years for Halon 1211 (10-39, model data) (SPARC, 2013) so that a compact correlation of mixing ratios of these two traces gases is expected in the stratosphere (Plumb and Ko, 1992). Due to its relatively low boiling point (−57.8 °C), Halon 1301 is the first species eluting from the chromatographic column. The shape of the chromatographic peak is thus strongly influenced by the injection, as refocusing on the chromatographic column is expected to play a negligible role. As a correlation derived from measurement data can only be as compact as the measurement precision allows, the compactness of the correlation shown in **Figure 8** gives an indication of the high measurement precision achieved with the GhOST-MS. The fact that this compact correlation includes a substance whose precision is strongly influenced by its thermodesorption shows that the sample preconcentration system on GhOST-MS is able to reproducibly trap and desorb even low boiling compounds like Halon 1301.

GhOST-MS has been deployed during a total of more than 200 flight hours on the HALO aircraft without a single failure of the preconcentration unit. In addition, measurements with GhOST-MS were performed as part of the SHIVA campaign in Borneo, providing a complete bromine budget for the upper tropical troposphere up to about 13 km (Sala et al., 2014). The

[1] Manuscript on the current GhOST setup and characterisation in preparation by Keber et al.

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preconcentration unit presented here therefore is not only able to provide high precision but is also able to operate reliably under difficult conditions like aircraft operation with varying humidity and temperatures, including operation during humid and hot conditions in the tropics.

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5 Summary and conclusion

A single-stage, refrigerant-free sample preconcentration unit for ambient air analysis is presented and characterised. The setup has proven to be applicable for both in-situ and laboratory operation and can quantitatively trap and desorb a wide range of halo- and hydrocarbons (see supplementary information). The use of different adsorptive materials is possible with the setup; two of which were used during this work, HayeSep D and Unibeads 1S. Both materials are well suited for analysis of halogenated trace gases in general. While HayeSep D is an established material for this task, Unibeads 1S potentially is a good alternative that has better heat tolerance and showed fewer sample loop blanks in the presented characterisation.

The preconcentration unit is positioned between more sophisticated but also more expensive and complicated solutions like e.g. the Medusa preconcentration unit described by Miller et al. (2008) and setups that use less powerful, Peltier-based cooling options that sacrifice adsorption temperature and therefore reduce the trappable substance range. The described setup is unique in terms of the used cooling technique, a Stirling cooler. The latter allows very low temperatures of −120 °C tested in this work and −173 °C reported by Eyer et al. (2016) for the preconcentration of methane with a comparable Stirling cooler without having to rely on a cooling agent like liquid nitrogen or liquid argon. The Stirling cooler as a cooling option is ideally suited for in-situ, remote-site operation, where refrigerant-based cooling options are very difficult to operate and space is limited – like the aircraft-based in-situ GC-MS instrument GhOST-MS. Moreover, the absence of mechanical/moving parts as well as the lack of necessity of vacuum insulation of cooled parts facilitates installation and maintenance. No exchange of adsorption tubes is necessary. Overall, the setup is relatively cheap with the Stirling cooler being the most expensive part by far.

The simplicity of the single-stage design also has a downside; a major problem is the trapping of large amounts of CO_2 and injection into the detection system (see also section 3.2), especially when using trapping temperatures below -80 °C. Due to this limitation, the current configuration is not applicable to highly volatile compounds like CF_4, C_2F_6 or C_2H_6. Cooling capacity should however be sufficient to ensure quantitative trapping of such compounds on a suitable adsorptive material. Therefore, a starting point for future improvement is removal of CO_2 to extend the already large substance range by compounds of higher volatility. Regarding desorption, no blank residues were found for halocarbons that would cause concern or render the setup unsuited for halocarbon analysis (see “Appendix B: Blank Residues”). However,

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relatively large amounts of hydrocarbons remained in blank measurements. These blanks are not an inherent problem of the preconcentration setup but more likely due to the adsorptive materials used. Additional experiments are needed to reduce those uncertainties and extend the applicability of the preconcentration unit to quantitative hydrocarbon analysis.

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Tables

Table 1. Cycle times at T_A of -80 °C / -120 °C (laboratory setup) and -70 °C (in-situ setup), based on operational data. Laboratory setup configuration: Sunpower CryoTel CT Stirling cooler, preconcentration volume: 500 mL at 100 mL·min^{-1}, $T_D \approx 200$ °C for 3 min. In-situ setup configuration: Twinbird SC-TD08 Stirling cooler, preconcentration volume: 100 mL at 100 mL·min^{-1}, $T_D \approx 200$ °C for 1 min. Adsorptive material, both setups: HayeSep D. Due to a smaller coldhead, cooling rate and warm-up during desorption are considerably larger with the in-situ setup, despite the shorter desorption time.

T_A [°C]	cooling rate at T_A [°C·min^{-1}]	warm-up during desorption [°C]	minimum cycle time including preconcentration after T_A is reached [min]
Laboratory instrument (GC-TOFMS)			
−80	−2.2	7.7	8.5
−120	−1.2	16.3	18.6
In-situ instrument (GhOST-MS)			
−70	−4.1	13.5	4.1

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Table 2. Results from a volume variation experiment, comprising measurements of the same reference air with preconcentration volumes (PrcVol) of up to 2, 5 and 10 L. Laboratory setup, adsorptive material Unibeads 1S. Volume-corrected detector response is referenced against calibration preconcentration volumes of 1 L (rR). rR <100% indicates underestimation (e.g. loss by breakthrough); rR >100% indicates overestimation (e.g. increase by a memory effect from the preceding sample or contamination). Breakthrough is observed for COS at a preconcentration volume of 10 L while ethyne shows signs of a system contamination (rR >100% despite a higher volatility compared to COS). CFC-12 and CFC-11 show no indication of breakthrough, with all deviations from 100% rR below 3 σ.

Substance	PrcVol [L]	rR	rR: 1 σ	PrcVol [L]	rR	rR: 1 σ	PrcVol [L]	rR	rR: 1 σ
Ethyne (C_2H_2)	2	102.0%	0.66%	5	108.9%	0.70%	10	109.2%	0.70%
Carbonyl sulfide (COS)		102.2%	0.82%		100.9%	0.81%		64.8%	0.52%
CFC-12 (CCl_2F_2)		99.9%	0.41%		100.7%	0.42%		100.6%	0.42%
CFC-11 (CCl_3F)		100.2%	0.21%		100.5%	0.22%		100.6%	0.22%

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Table 3. Retention times t_R with relative standard deviations rSD and variances in [s] for selected substances (same as **Table 2**) as well as their respective average signal width expressed as FWHM in [s]. Values derived from 112 individual measurements of different ambient air samples using the ramped GC program. Sample loop adsorptive material: HayeSep D. HFC-23 is the first detectable substance, least separated by chromatography. CFC-11 can be considered a reference for optimal chromatographic performance of the given setup.

Substance	t_R [min]	t_R rSD	Variance [s]	Avg. Peak Width [s]
HFC-23 (CHF_3)	3.01	0.105%	0.0386	4.09
Ethyne (C_2H_2)	3.74	0.047%	0.0118	2.77
Carbonyl sulfide (COS)	3.86	0.040%	0.0092	2.29
CFC-12 (CCl_2F_2)	5.01	0.014%	0.0018	2.26
CFC-11 (CCl_3F)	7.25	0.006%	0.0008	2.24

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Figures

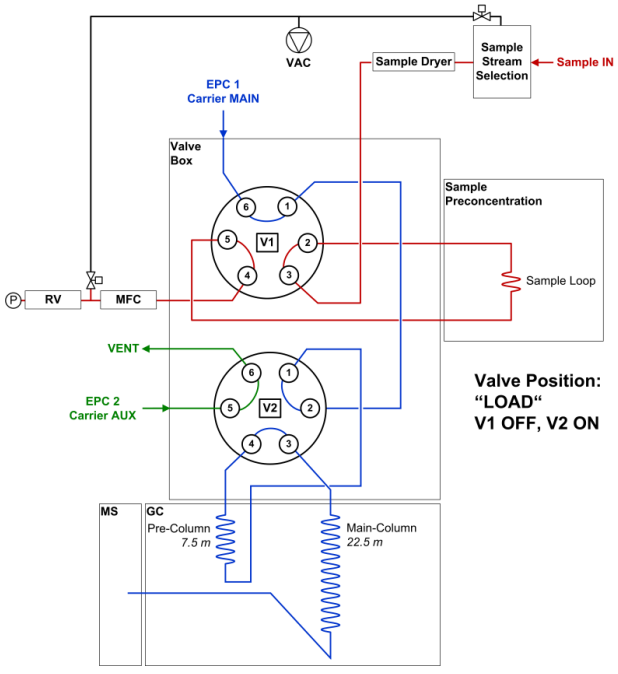

Figure 1. Flow scheme showing the gas flow during preconcentration. Two electronic pressure controllers, EPC 1 and EPC 2, control the carrier gas flow. The two 6-port 2-position rotary valves V1 and V2 are set to OFF/ON position. A sample is preconcentrated (red flow path); sample components not trapped in the sample loop flow through the mass flow controller (MFC) into the reference volume (RV). By switching V1 to ON position (for desorption), the sample loop is injected onto the GC column. Sample loop as well as reference volume and stream selection valves are evacuated prior to the preconcentration of the next sample. By switching V2 to OFF, it separates pre- and main-column; the pre-column is flushed backwards. This prevents high-boiling, non-targeted species from reaching the main-column.

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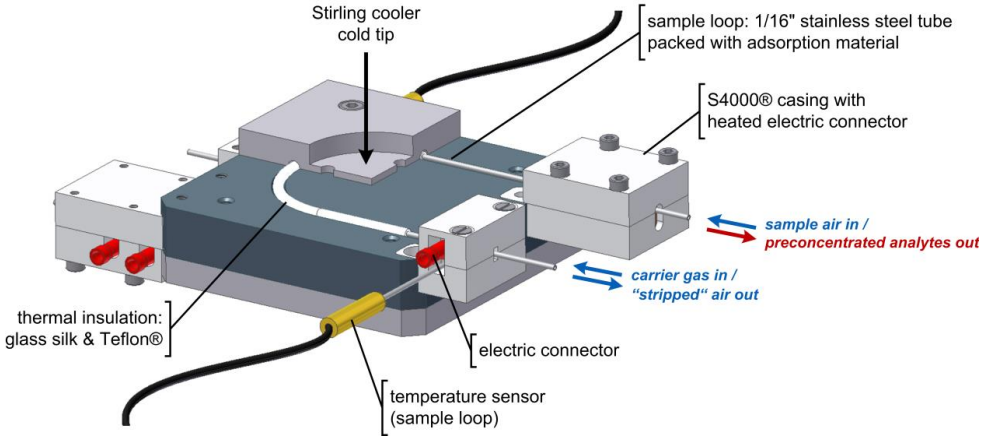

Figure 2. Technical drawing of the coldhead and sample loop placed inside. Three plates of anodized aluminium can hold two sample loops. The Stirling cooler's cold tip screwed to the coldhead removes heat for cooling. Heat for sample desorption is generated by a current directly applied to the sample loop. The electric connector in the direction of sample flow (upper right side of the drawing) is heated constantly to 150 °C to avoid a cold point due to the mass of the electric connector and its proximity to the coldhead (S4000® insulation material: Brandenburger, Germany).

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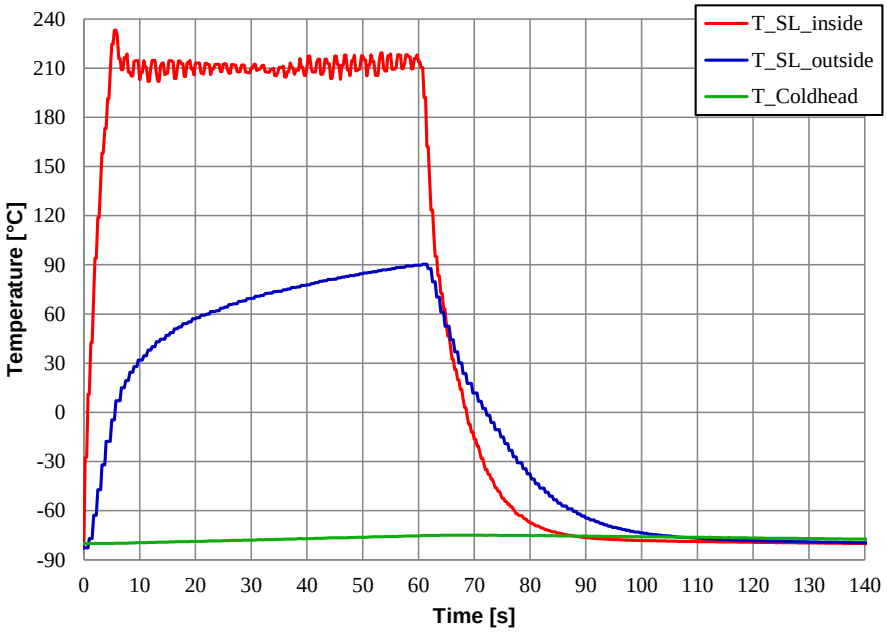

Figure 3. Desorption temperature curve inside the sample loop with a preceding adsorption temperature of −80 °C and a subsequent cool-down from desorption to adsorption temperature. Red curve, "T_SL_inside": signal from temperature sensor shifted inside the sample loop. Blue curve, "T_SL_outside": temperature sensor signal from the sensor welded to the outer sample loop tubing wall. Green curve, "T_Coldhead": temperature of the coldhead. Deterministic heater, output in this example: 50 % in stage 1, held 5 s, and 30 % in stage 2, held 55 s. The periodic oscillation of T_D observed is a result of a very slow pulse width modulation used in the testing setup: 100 ms period with 10 ms minimum increment.

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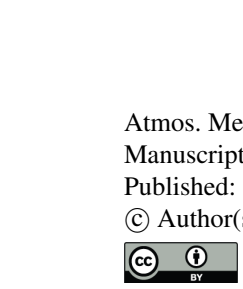

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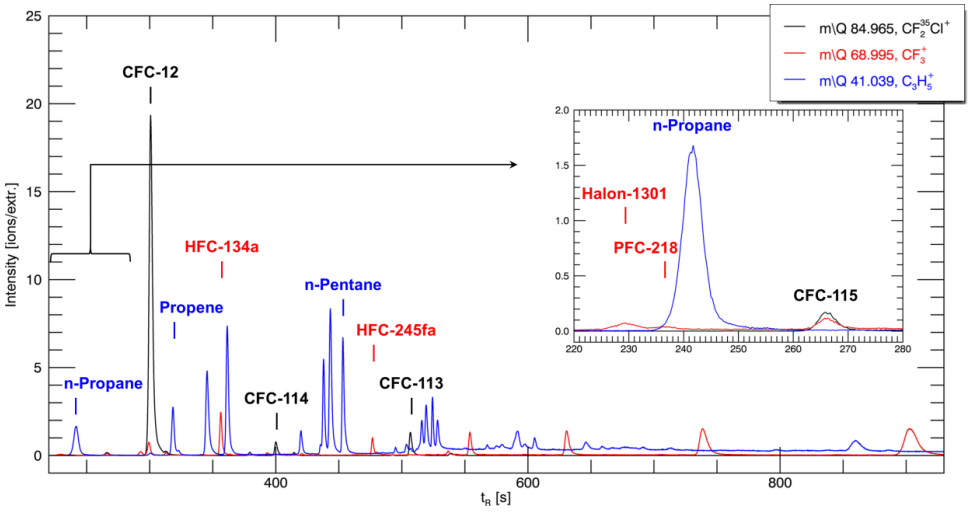

Figure 4. Chromatogram from a 1 L ambient air sample obtained with the GC-MS setup described in Obersteiner et al., 2016. X-axis: retention time t_R in seconds. Y-axis: signal intensity expressed as ions per extraction which are derived from a 22.7 kHz TOFMS extraction rate, averaged to yield a mass spectra rate of 4 Hz. X- and Y-axis description also valid for the magnified section. Black graph: mass-to-charge ratio (m/Q) = 84.965 signal from a typical CFC fragment ion $CF_2{}^{35}Cl^+$. Red graph: m/Q = 68.995 signal from a typical PFC or HFC fragment ion $CF_3{}^+$. Blue graph: m/Q = 41.039 signal from a typical hydrocarbon fragment ion $C_3H_5{}^+$. The magnified section shows the chromatographic peak of n-propane and three other compounds to demonstrate injection quality of substances least re-focused by chromatography.

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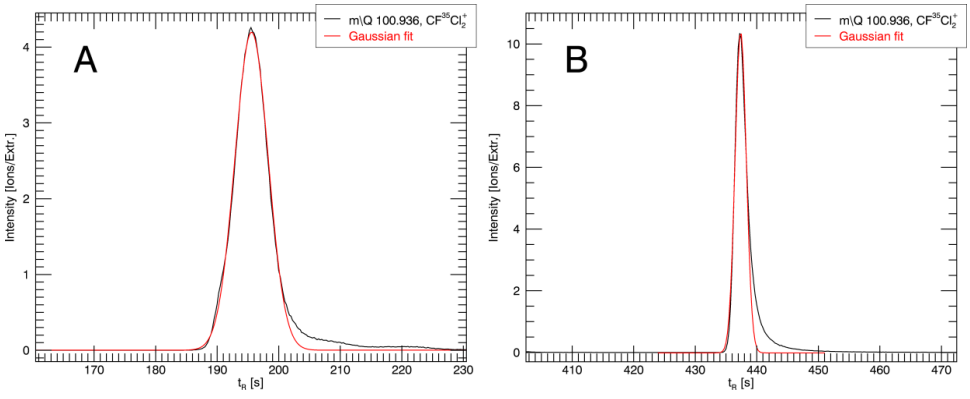

Figure 5. Comparison of chromatographic peak shapes of the $CF^{35}Cl_2^+$ fragment ion signal of CFC-11 ($CFCl_3$), from an injection of 1 L preconcentrated ambient air onto the GC column kept isothermal at 150 °C (A) and onto the GC column kept at 45 °C and ramped to 200 °C subsequently (B) (see section 3.1). X-axis: retention time t_R in seconds; t_R interval shown is 70 s in both plots. Y-axis: signal intensity expressed as ions per extraction (see **Figure 4**). The red curve shows a Gaussian fit for comparison of actual peak shape and a peak shape that is considered ideal. FWHM of fit: (A) 6.3 s (0.10 min) and (B) 2.0 s (0.03 min). Adsorptive material: Unibeads 1S.

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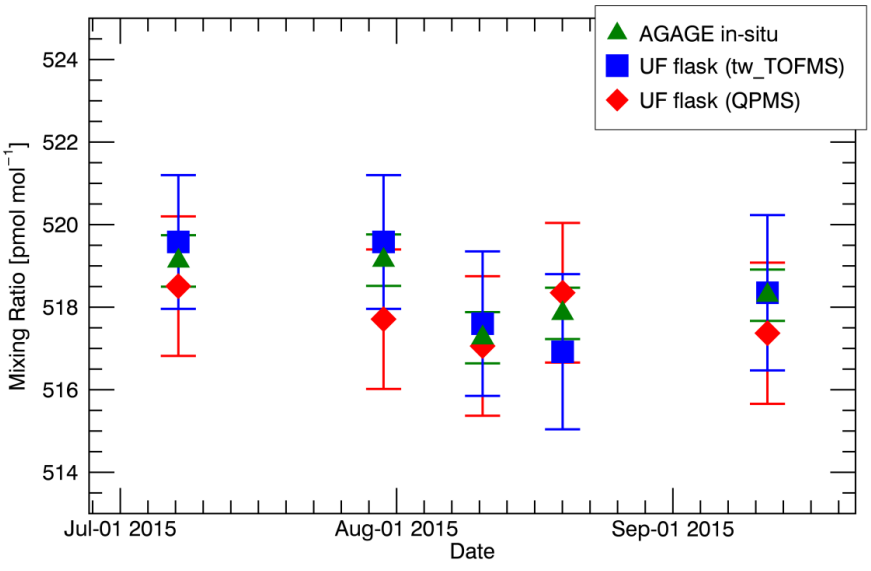

Figure 6. CFC-12 (CCl_2F_2) mixing ratios at Mace Head Atmospheric Research Station, Ireland (53°20′ °N, 9°54′ °W, 30 m above sea level) derived from 2 L stainless steel flask samples measured with the instrument in description (GC-TOFMS, blue squares), our reference instrument (GC-QPMS, red diamonds) and values taken from the online measurement data of the in-situ Medusa GC-MS (green triangles). Error bars: 1-fold measurement precision of each instrument (Medusa system: typical precision taken from Miller et al. (2008)). Calibration scale, all instruments: SIO-05.

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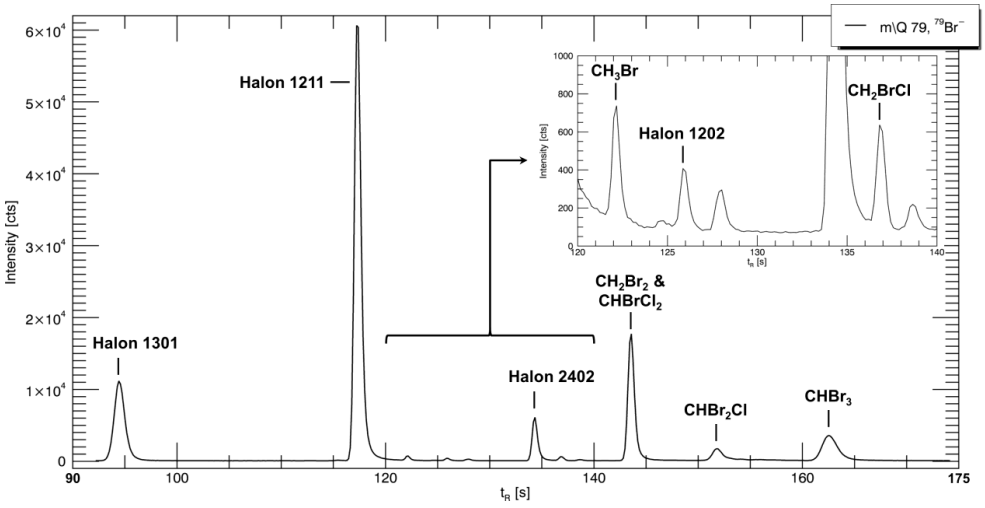

Figure 7. Chromatogram from a preconcentration of 0.1 L ambient air obtained with the in-situ GC-MS setup GhOST-MS. X-axis: retention time t_R in seconds. Y-axis: signal intensity in counts, arbitrary unit. MS: Agilent 5975C in negative chemical ionization mode (reagent: argon). Black graph: mass-to-charge ratio m/Q = 79 signal of $^{79}Br^-$ ions from brominated trace gases.

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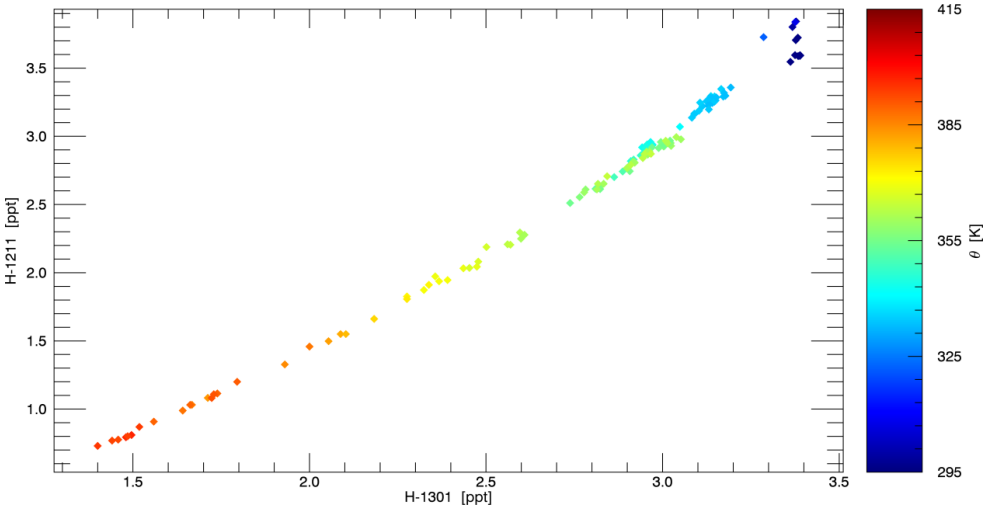

Figure 8. Tracer-tracer correlation of Halon 1301 ($CBrF_3$, x-axis) vs. Halon 1211 ($CBrClF_2$, y-axis). Color code indicates potential temperature θ in [K]. Data was obtained during the POLSTRACC mission with the HALO aircraft, flight 160226a (PGS-14). Preliminary data; calibration scale of Halon 1301 and 1211: SIO-05.