Answers to the Reviewers, amt-2016-196

Dear Referees,

we thank you very much for the time and effort you put in reading and commenting our manuscript. We hope that we can address all your comments in a satisfying manner by additional explanations and changes to the manuscript. All your comments are listed in this document, followed by our response. Comments are in italics, our answers in standard font. Red font colour marks text added to or changed in the manuscript. Please find our…

- answers to referee #1 on p. 2 ff.,
- answers to referee #2 on p. 13 ff.,
- answers to referee #3 on p. 28 ff.,
- and further changes to the manuscript on p. 35 ff.

The mark-up version of the revised manuscript can be found on p. 36 ff. of this document.

on behalf of all authors,
Florian Obersteiner

Comments of referee #1

General comments:

The manuscript of Florian Obersteiner and co-authors with the title "A versatile, refrigerant free cryofocusing-thermodesorption unit for preconcentration of traces gases in air" presents a temperature swing adsorption unit for halogenated trace gases. A basic description of the setup of the developed preconcentration unit was already given in Obersteiner et al. AMT (2016) doi:10.5194/amt-9-179-2016 and other manuscripts of the authors. Nonetheless the presented manuscript adds details on the instrument design, optimisation, performance characteristics and application examples. The manuscripts give strengths and weaknesses of the novel design as uneven temperature distribution of the trap or problems in getting reliable temperature data.

Research on trace gases, e.g. halogenated components or GHG isotopologues is very active and the manuscript is therefore timely and of high interest for readers of AMT and potential future users of this technique. I have some concerns on the consistency of the structure of the manuscript, which could be improved as detailed below. In addition, the wording is sometimes colloquial and might be improved. I have a number of suggestions for technical corrections the authors might consider improving the consistency and readability of the manuscript.

In summary, I suggest publication in Atmospheric Measurement Techniques with minor revisions.

Specific comments:

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1 - *SI units should be used throughout the manuscript, e.g. "K" instead of "°C" for temperature.*

- The reviewer is correct in pointing out that temperature is not shown in SI unit but degrees Celsius. We decided to do so as °C is more common in gas chromatography and also sample preparation. For consistency, we use only this unit throughout the manuscript, although K could of course be used to express e.g. temperature differences. Because K would be cumbersome in many places, °C is, due to the easy conversion, equally appropriate for the understanding of the manuscript and we therefore suggest not to change the unit.

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2 - *Page 1 Line 25: The term "injection quality" is arbitrary and might be replaced.*

- We rephrased the sentence accordingly: "We present the instrumental design of the preconcentration unit and demonstrate capabilities and performance through the examination of analyte breakthrough during adsorption, repeatability of desorption and analyte residues in blank tests."

***3** - Page 4 – 8 Section 2 Instrumentation: The main focus of this section is on the technical description of the preconcentration device including hardware setup and preconcentration procedure. However, details on the hardware are partly missing; partly they are given in section 3 Characterisation. Please give all relevant technical information on components implemented in the preconcentration device including information on model; manufacturers etc. in section 2, where it is mentioned for the first time.*

- An earlier version of the manuscript was actually structured like the reviewer suggests – however, we then changed the structure to the current version as the idea was to give a principal description first and then give an example (including detailed technical information) which should stand exemplary for the preconcentration setup we describe.
- To make that point clearer, we
  - … changed the section title to Implementation of cryofocusing and thermodesorption
  - … restructured and extended the introduction of sect. 2: "[…] our analytical setups presented in Sala et al., (2014), Hoker et al., (2015) and Obersteiner et al., (2016). Technical details are listed in Table 1 for all three setups we operate. 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~~ was 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."~~
  - … added an overview table (Table 1) with relevant technical details on all three preconcentration setups we built; Sala et al. 2014, Hoker et al. 2015 and Obersteiner et al. 2016.

***4** - Page 4 Line 7-8: The sentence "A preconcentration system can only be as good as the analytical set-up behind it" is colloquial and might be deleted or rephrased. The overall performance of an analytical system might be either limited by the preconcentration unit or the analyser.*

- Deleted the sentence as the reviewer suggested.

***5** - Page 4 Line 13 ff: The title of the section is "loose" and might be change to something like "Setup of the preconcentration device and integration for GC applications". In this section the preconcentration device is described in detail for the first time and therefore reference to Figure 1 and 2 should be given. Technical information on all components in the preconcentration device with model number, manufacturer etc. should be added.*

- Rephrased the title as suggested: Preconcentration procedure and integration for GC application. A reference to Fig. 1 is already given in sect. 2.1; a reference to the technical drawing of the coldhead seems a bit misleading to us, as this part of sect. 2 is not dedicated to this specific part of the setup.
- Regarding technical details, please refer to our answer on comment #3.

***6** - Page 4 Line 14: Please give details on the applied adsorbents.*

- Please refer to our reply on comment #3.

***7** - Page 4 Line 19: The term "warm column" is imprecise and might be replaced or just deleted as details are given thereafter.*

- Deleted as suggested.

***8** - Page 4 Line 20 - 21: Please rephrase the sentence to something like: The system does not involve a separate refocussing procedure as used in other preconcentration systems (Miller et al. 2008) but the analytes are directly purged onto the GC column for further separation.*

- Rephrased the sentence accordingly: The system does not involve a refocussing procedure as implemented in other preconcentration systems (Miller et al., 2008). The analytes are purged directly onto the GC column for separation.

***9** - Page 4 Line 24 - 27: Please give details on the applied MFC. It is unclear how the MFC could be used for large sample volume, could it be: The MFC provides an alternative way to quantify the sample volume. Thereby, operation of the MFC without the downstream reference tank adds flexibility with respect to sample volumes larger than the reference tank.*

- The reviewer is exactly right with his assumption. The MFC integrates the sample flow and gives accurate results for volumes greater approximately 100 mL as we derived from a comparison experiment with the pressure sensor. The integration of smaller volumes seems to be inaccurate (underestimation), which is why we kept the reference volume tank installed.
- Rephrased the sentence: The MFC can also be used to determine the sample volume and thereby adds flexibility with respect to sample volumes larger than the reference tank.

***10** - Page 5 Line 6: The term "in this case" might be rephrased. I assume the two sample loops are not equivalent regarding temperature as one is closer to the Stirling cooler than the other one, which complicates the comparison of temperature data from both loops. How can these temperatures be compared – please comment on this?*

- ➢ Provided that the ambient temperature insulation of the coldhead is intact, we actually found no significant difference between both temperature sensor values (type Pt100; $\Delta T \sim 1$ K), likely due to the high thermal conductivity of the aluminium coldhead. We observed an increase of this temperature difference if less coldhead insulation is applied.
- ➢ Added a sentence to the manuscript to acknowledge this fact, p.5,l.8: "Provided that the coldhead insulation is sufficient and intact, no significant temperature differences occur between both traps due to the high heat conductivity of the aluminium".

***11** - Page 5 Line 19 – 22: Please give information on the Stirling cooler used in the presented work.*

- ➢ Please refer to our answer on comment #3.

***12** - Page 5 Line 25 – 29: This statement that an "idle time" is needed to reach TA after desorption is abstract as Figure 3 shows a constant cold plate temperature. From other statements later in the text I assume that at lower cold plate temperatures (e.g. -120°C) heating the trap during desorption affects the cold plate temperature – please comment on this?*

- ➢ The reviewer is right in pointing out that the y-scale of Fig. 3 makes it difficult to observe the rising temperature of the coldhead. There actually is a rise of ~4.5 K.
  - ○ We therefore added a second y-axis to display coldhead temperature and illustrate the point.
- ➢ As the thermal insulation between sample loop and coldhead is constant, heat flow increases if the temperature difference between coldhead and sample loop increases (thermodesorption at equal T_D but lower T_A). More heat flows into the coldhead and it therefore gets warmer.

***13** - Page 5 Line 27 – 28: The sub-sentence " … is transferred to the coldhead as the sample loop is kept directly inside with only …" might be rephrased.*

- Rephrased the sentence to make the point clearer: […] a certain amount of heat flows from the sample loop into the coldhead as the sample loop is kept directly inside with only a small amount of insulation.
- Please note: the term "sample loop" was changed to "trap" or "preconcentration trap" in response to comment #12 of referee #2.

***14** - Page 6 Line 10: Please give a number for the "slightly higher TA".*

- Added the info to the sentence, (~ −72 °C)

***15** - Page 6 Line 4 – 7 and Line 15 – 18: There seems to be a discrepancy between the statements on cooldown time given in Line 4 – 7 (18.6 vs. 8.5 minutes) and in Line 15 – 18 (90 vs. 30 s) for different TAof -120°C versus -80°C – Please comment?*

- The reviewer is correct in pointing out that these statements are given imprecisely. What is meant in the first statement is the total time of a measurement cycle. The second statement refers to the time needed until sample loop and coldhead reach equal temperatures after thermodesorption. This does not imply that T_A is also reached after that time.
- Rephrased the second statement/paragraph to clarify: "After desorption, sample loop temperature drops in an exponential decay shaped curve due to the decreasing temperature difference ΔT between coldhead and sample loop. After a desorption at TD ≈ 200 °C, sample loop and coldhead temperature reached similar temperatures after approximately 30 s cool-down time (TA = −80 °C). This time increases to about 90 s at −120 °C cold head temperature until ΔT reaches approximately zero. Considering the total run times shown in Table 1, sample loop cool-down to coldhead temperature is not a limiting factor to the overall cycle time."
- Please note: the term "sample loop" was changed to "trap" or "preconcentration trap" in response to comment #12 of referee #2.

***16** - Page 7 Line 16 ff: Measurement of the trap temperature and thus its control seems to be difficult with a sensor on the trap surface as it is affected by the cold plate. Would it be possible to use the sensor mounted within the second trap to control the temperature of the first although the traps are not identical?*

- While possible in principle, there are two reasons not to do so. First, construction and insulation would have to be equal for both traps, which is hard to ascertain. The other reason is that heating both traps would double the heat flow into the coldhead during desorption and thereby increase total cycle time.

***17** - Page 9 section 3: Would a title similar to "performance characteristics" be better?*

- Rephrased accordingly.

***18** - Page 9 section 3.1: As detailed above to improve readability detailed information on the preconcentration unit (e.g. Stirling cooler, MFC) should be given in section 2 and deleted here. Section 3.1 should mainly contain information on the specific set-up used to determine "performance characteristics" as breakthrough volume etc.*

- Please refer to our answer on comment #3.
    - Added a link to table 1 (technical details) at the end of the introductory part of sect. 3.
- In our opinion, the few technical details given in sect. 3 of the revised version of the manuscript do not hinder its readability and we therefore suggest to kept them.

***19** - Page 10 Line 19: The wording "stripe the air of nitrogen etc." should be rephrased.*

- Rephrased accordingly: With this preconcentration technique, the most abundant constituents of the air (nitrogen, oxygen and argon) are mostly removed from the sample.

***20** - Page 11 Line 8: In Table 2 the relative response is given in "%" please use consistent terms.*

- Changed as suggested from "1" to "100 %".

***21** - Page 13 – Page 14: Different wording are used to differentiate detrimental contamination effects: sample loop memory, system memory and system contamination. Please unify and simplify the wording and the ways how to test them, if possible beginning of the section 3.3.*

- We thank the reviewer for pointing out this inconsistency.
- Rephrased the introductory paragraph of sect. 3.3: "[…] retention time variance during a measurement series (~~qualitative aspect;~~ section 3.3.1). Additionally, the appearance and quantity of analyte signals in measurements of an analyte-free gas after sample measurements determine the number of analysable substances and ultimately measurement data quality. The discussion of analyte residues can be found in ~~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").~~"
- Rephrased the introductory paragraph of sect. 3.3.2: "Analyte residues can ~~originate from~~represent an inherent system contamination (1) or consti-tute a remainder from the previous sample (memory effect, (2)). Both types of residues can originate from different sources like the adsorptive material (sample loop), valve membranes etc. They are differentiated by either an always-present blank signal (1) or a blank signal that decreases to zero in repeated measurements of an analyte-free zero gas after sample measurements (2)."
- P. 14 l. 8 and l. 10: added "or contamination" as a differentiation between memory and contamination is not possible in this context.

- P. 14 l.10: Added an explanation on why two methods were used for residue investigation (unloaded injection and zero-gas): "The differentiation between (a) and (b) allows a separate investigation, which memory effect or contamination could potentially be reduced by the choice of adsorptive material or parameters of the desorption process (e.g. T_D) (a) and which part has to be attributed to tubing, stream selection etc. (b)"
- Please note: the term "sample loop" was changed to "trap" or "preconcentration trap" in response to comment #12 of referee #2.

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22 *- Page 14 Line 18: "Concentration in the previous run"*

- Rephrased as the reviewer suggested: […], so extremely elevated concentrations of low-volatile substances in the previous run might lead to a memory effect […]

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23 *- Page 16 Line 3 ff: It would be good to state first what the inter-comparison is based on: The laboratory based instrumentation (GC-TOFMS) is compared to GC-QPMS and GC-MS. As GC-TOFMS and GC-QPMS are based on a similar preconcentration setup, and the preconcentration setup should be tested, it is unclear what we can learn from that.*

- We thank the reviewer for pointing out that the internal instrument comparison has to be differentiated from the comparison to the external instrument data.
- Rephrased the introductory sentence to clarify: "To ensure internal consistency of our laboratory instrumentation, five air samples were analysed with the GC-TOFMS instrument (Obersteiner et al., 2016) 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)" and further (p.16 l.16) "To test the overall performance, the comparison is extended to include in-situ measurement data from the online monitoring Medusa which uses a completely different preconcentration setup […]".

***24 -** Page 17 Line 14: Please give details on the argumentation related to the "potential temperature".*

- The motivation behind the tracer-tracer correlation is the study of atmospheric transport in the upper troposphere and lower stratosphere. Transport processes in the atmosphere are mostly adiabatic. Moving an air parcel along a surface of equal potential temperature (isentrope) does not require a change of its internal energy. In the stratosphere with its stable stratification, the quasi-horizontal transport along the isentropes is therefore fast while exchange between isentropes is slow. When considering the tracer-tracer correlation shown, a point in the correlation therefore represents air with a specific "transport history". As atmospheric transport is not the focus of this manuscript, we did not include any more information on why we use potential temperature to generate the colour code and not e.g. height where the measurement took place. Leaving out this information furthermore does not impede the conclusion that such a compact correlation can only be observed if measurement precision is sufficient.

Comments of B. R. Miller, referee #2

Some general comments: This manuscript describes the relatively simple design of a custom-designed preconcentration unit, which employs a Stirling cooler as the cold source for cryogenic preconcentration of trace atmospheric compounds. The basic design is common to several of their instruments, results of which have been published recently. The lack of need for an insulating vacuum chamber for these cold parts is an appealing characteristic as it greatly simplifies design, reduces cost and weight. The rapid analysis time that they have achieved also makes this a desirable field and laboratory instrument. The focus of the current manuscript is a detailed description and characterization common to these instruments, going beyond what was published in Hoker et al., 2015, Obersteiner et al., 2016 and Sala et al., 2014. The authors do present in-depth results of the chromatographic peak shape resulting from cryofocus and subsequent desorption of analytes. They also discuss results from analyte breakthrough tests and report some of their findings of system contamination.

I appreciated the depth of investigation of the 'analyte residues' issue. In such preconcentration methodologies, and at such low analyte mole fractions, these contamination issues can be a very difficult problem to investigate and rectify. So by sharing their observations, the authors are contributing to a knowledge base that may someday be useful in developing some remedies.

***1** - To add to the value of this residue investigation, I would like to see them include, for example in Table 4, which analyte contaminations they attribute to 'carry-over' from a previous sample, versus those derived from system hardware (e.g., outgassing of polymers, or desorption from surfaces), versus those derived from the carrier gas. In the text, they do allude to such finding with regard to a select set of analytes, but stop short of specification for each of the dozens of compounds listed in the table. Undoubtedly, there will be some analytes for which attribution is not readily discernible, but I would hope that they are able to elaborate with more useful details regarding more clear-cut cases.*

- We agree with the reviewer that some value can be added to the discussion with a more differentiated view on analyte residues. We therefore added "*m*" for residues we consider to be carry-overs ("memory" to keep the terminology used in the manuscript) and "*c*" for contaminations in table 4 (now table 5; in brackets, added to columns 5 & 6). Please note that we cannot give a clear source attribution of contaminations (or also memory) for each substance analysed in the frame of this work. Speculations with regard to contamination sources would not be of much use in our opinion as potential sources might be different for different instrumental setups, individual sources might disappear over time ("aging") etc.
- Supplement p.1, Table 5 Description. Added information to clarify the implications of the displayed results; (l.12): "Residues that a constant background (contamination), are marked with a "c", ones that represent a memory effect from a preceding sample are marked with an "m"".
- Please also consider our response on comment #16, which also refers to contamination source attribution.

***2** - Results from Table 4 present some difficulty in interpretation. For example, iodomethane shows a HayeSep D residue of 43.9%. This is, as defined in the caption, the ratio of the blank gas response to the preceding 1 L air sample, expressed as a percentage. The blank gas injection is defined as an injection of purified helium. From this information, we cannot deduce whether this high percentage is attributable to carry-over of analyte from the air injection into the subsequent blank injection, or if the carrier gas is contaminated with an iodomethane-like substance or if some hardware upstream from the adsorbent tube is outgassing or desorbing the contamination.*

- The reviewer is correct in criticising that no differentiation between carry-over and contaminations is made in table 5 (former table 4). This has now been changed; please see our response to comment #1.
- Regarding the iodomethane residues, please also see our response on comment #17. This substance is indeed difficult to analyse, although repeated measurements of the same reference gas show decent repeatability. We observe high residues in zero gas measurements with all three instruments here in Frankfurt and also with the GhOST-MS during the PGS campaign. We consider them to be both contamination and carry-over, as we found residues in the unloaded trap injections as well as a constant background signal in the helium we use as carrier gas and zero gas.

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3 *- Further difficulty in interpreting table 4 stems from the precision limitation that they impose. The authors exclude analytes from Table 4 that "...show poor precision 10%." With a 43.9% residue of unknown origin, how is a <10% precision justified for including iodomethane in this table? If this contamination comes from the carrier gas, and therefore might be assumed constant, one could correct responses accordingly, and obtain reasonable precisions and accuracies despite contamination. But carryover requires a very different data work-up (e.g., modelling the carry-over). Some explanation is in order here. There are other examples, e.g., HFO-1234yf, chloroethane, tetrachloroethene, etc.*

- Regarding the 10 % precision limit and some very high residues, please refer to our reply on comment #2 and #16. Note that the 10 % limitation means precision, not accuracy. Considering the large analyte residue of more than 40 % for CH_3I (both contamination and carry-over), we would not claim to be able to measure CH_3I without further data processing.
- System contaminations are also not that easy to characterise and correct in our opinion as they might depend on variable parameters like the age of the stainless steel tubing used (e.g. COS and CH_3Cl contamination), membrane aging, sample moisture etc. Carry-over is potentially more reproducible and can be modelled after investigation by dedicated experiments. With the manuscript, we did however not intend to provide a viable correction for any of the encountered contamination and carry-over issues.
- To address this in the manuscript, we rephrased the last paragraph of the summary section, p.19, l.32: "~~However, r~~Relatively large amounts of hydrocarbons remained in blank measurements. These ~~blanks~~ residues are not an inherent problem of the preconcentration setup but more likely due to the adsorptive materials, carrier gas or valve membrane materials used. We do not attempt to present a viable correction method for any of the encountered analyte residues here. More dedicated experiments are necessary to account for analyte-specific memory effect and/or contaminations e.g. by modelling the carry-over from one sample to another and subtracting contamination background. ~~Additional experiments are needed to reduce those uncertainties and extend~~By doing so, the applicability of the preconcentration unit can potentially be extended to quantitative hydrocarbon analysis".

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4 *- In reading the manuscript, it seemed odd to me that they omitted detailed analysis long-term reproducibility results, which for me is one of the principle 'bottom-line' results of characterization. The sharp, Gaussian-shaped peaks that they obtain are indeed a desirable trait of such an instrument. But in the intended applications of such an instrument, the value in the measurements comes from short-term repeatability and/or long-term reproducibility.*

- It is true that the manuscript leaves out instrument characterisation results regarding e.g. measurement precision or reproducibility. These characteristics are however not exclusively influenced by the preconcentration system but also by chromatography and detection. The influence of individual components is often hard or even impossible to disentangle. Details on such characteristics of our laboratory systems were given in the respective publications, Sala et al. (2014), Hoker et al. (2015) and Obersteiner et al. (2016). After the recent PGS campaign, we recently conducted characterisation experiments with the GhOST-MS, so up-to-date details for that instrument will follow in the future. We consider a discussion of "overall" instrument characteristics as beyond the scope of this work as it moves the focus away from the preconcentration system.
- To let the reader know of this exclusion, we added a sentence in the introduction, p. 3, l. 26: "Only characteristics of the preconcentration setup are discussed; instrument characteristics such as e.g. measurement precision or reproducibility can be found in the respective publications." and at the end of the introductory paragraph of sect. 3: "Please refer to the respective publications for the discussion of instrument characteristics like e.g. measurement precision or reproducibility which are not exclusively related to the preconcentration setup.".

***5 -** For a repeatability example, in their aircraft application, what uncertainties might one expect in a vertical profile so that an observed altitude gradient was statistically discernible, or not?*

- Added information on measurement precision and uncertainty to the caption of Fig. 8: "Preliminary measurement precision and calibration uncertainty: 0.4 % / 1.7 % (Halon 1301), 0.2 % / 0.9 % (Halon 1211)".
- The compactness of a correlation in the atmosphere can strongly vary depending on e.g. transport and mixing histories of the sampled air parcel; it is therefore hard to give an estimate for the true atmospheric correlation. The observed level of compactness can only be as high as measurement precision allows – which is why we choose this example to demonstrate measurement precision in the field. However, it is not the scope of this manuscript to analyse tracer correlations or atmospheric transport.

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6 - *In a long-term monitoring application with flasks (i.e., their laboratory instrument), they present a favourable comparison with the AGAGE Medusa instrument at Mace Head, Ireland, for one compound, CFC-12 over one summer. But for characterizing long-term reproducibility suitable for such monitoring programs, one needs to demonstrate this on time-scales of a year or more to argue the potential for comparability and compatibility of datasets. The one brief comparison example falls short of proving the "highly accurate measurement results" that they claim, and it would be beneficial to see reproducibility results for all compounds for which they believe their instrument is suitable to measure.*

- We agree with the reviewer that five data points of one substance are insufficient to attest comparable long-term monitoring results. This is also not the focus of this work. With the example shown, we want to demonstrate that good agreement of results from different instruments that both use the described preconcentration system and the Medusa-GC-MS can be achieved, at least for substances that are not subject to other issues like system contamination etc. For this reason, we would prefer not to extend this intercomparison in this paper.
- We took part in the InGOS Halocarbon Round Robin Intercomparison (IHRRI) with both our GC-MS instruments, so more results on the accuracy of our measurements will be found there, hopefully in the near future. Furthermore, we are working on the evaluation of the MHD time series that we analyse routinely with our GC-QPMS. Hopefully, we can prepare results including a comparison the Medusa-GC-MS at MHD station for a future publication.

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7 - Another component of characterization that the authors appeared to have overlooked is the potential for CO2-induced artefacts. The methodology appears to offer little in terms of mitigating the presence of this atmospheric constituent that is a million times more abundant than their target analytes. They do make the point that they do not attempt analysis of analytes which elute under the CO2. On their 20 mg of adsorbent, chilled to -80 C or -120 C, they need to show that the co-adsorption of CO2 does not adversely affect adsorption and/or desorption of their analytes. Consider that a 1-L sample of ambient air has order 0.4 ml STP of pure CO2, enough gas to fill a 50 cm length of their 1 mm I.D. tubing. While it is unlikely that they have quantitative adsorption of all the CO2, we aren't given any evidence that sufficient CO2 does not remain to disrupt the desorption of the other analytes and/or disrupt the sensitivity of the detector. In instruments in which no CO2 mitigation is performed, I have observed the co-desorption of CO2 to cause peak width and shape changes in certain co-adsorbed analytes. I have also observed short-term MS detector response reduction due to injection of CO2-containing samples, with subsequent 'rebound' in sensitivity with CO2-free samples. An experiment that the authors could perform to examine this detector issue is to sequence injections of CO2-containing and CO2-free air-like mixtures mixed in with injections of a reference standard gas. If the amount of injected CO2 is having an effect on the reference gas sensitivity, it will be apparent when the sample preceding the reference contained or did not contain CO2.

- The reviewer is correct in suggesting that there could be CO_2 induced artefacts.
- We added a sentence on p.19, l26 to acknowledge this fact; "Depending on GC- and detection system, this could induce artefacts in the detected signals […]".
- … and extended the discussion in sect. 3.2: "[…] like CO2 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 (e.g. peak tailing) as well as detection (e.g. detector saturation), depending on GC configuration and detection technique. With the setup described here, the elution of CO2 limits the analysable substance range as the detector shows saturation during the elution of CO2 (ionisation switched off until tolerable CO2 levels are reached). A CO2 removal technique could therefore significantly improve chromatographic performance and extend the substance range of the current preconcentration system. At lower adsorption temperatures, even with CO2 removal, a similar problem could however be caused by other gases, like e.g. xenon (boiling

point: −108 °C), which is still more abundant by three orders of magnitude in the atmosphere than the targeted analytes discussed here”.

- We agree that CO_2 is probably not trapped quantitatively and it actually doesn’t elute in the form of a clearly defined peak that one would expect from a proper desorption. The m/Q 44 (CO_2^+) signal baseline drops until about 10 minutes (right flank of the CO_2 “peak”) which implies that the GC column is heavily overloaded with CO_2. For example, the m/Q 44 baseline intensity at the retention time of CFC-12 exceeds the peak apex intensity of the CFC-12 quantifier ion signal on m/Q 85. This could potentially be another possible explanation for the observed peak tailing of other analytes. Besides CO_2, also H_2O could potentially cause artefacts, as the $Mg(ClO_4)_2$ sample dryer only allows drying to a few ppm, which is still sufficient to overload the detector and cause difficulties in GC.
- Regarding detector sensitivity, the discussion is specific for the analytical setup and not really adds to a characterization of the preconcentration itself which is why we excluded it in the manuscript. Currently, we account for the issue by switching the MS filament on not until the amount of CO_2 eluting from the GC has reached a tolerable level (detector specific). Especially the TOFs suffer from that issue as they do not allow filtering ions of specific m/Q signals but only broad m/Q intervals (high pass filter) before they are extracted towards the detector. The large amounts of CO_2 (fragment) ions can, if not filtered or at least attenuated, harm the detector multichannel plate and overload the analogue to digital converter if the filament is switched on too early or its emission current is too high (or if filter settings are not properly set; which is also true for the QPMS). If on the other hand a high pass filter is used, any m/Q < 44 is also suppressed and respective signals are excluded from evaluation. Potential detector sensitivity drift during a measurement series induced by the repeated injections of large amounts of CO_2 can be compensated by repeated measurements of the calibration gas within the measurement series (see also Obersteiner et al. 2016). A rebound effect (increasing detector sensitivity) is unlikely in our opinion as ambient air samples always contain CO_2 and normally no CO_2-free zero gas is measured within a measurement series.

***8** - Table 2 and corresponding text present unbelievably precise chromatographic retention times, given that this represents 112 injections of various samples. Are these the correct units? Taking CFC-11 for example, 0.006%/100*7.25s*60s/min yields 0.19s standard deviation for the CFC-11 retention time. Also, if the fourth column truly is a variance, then the units would be the square of the measurement units, i.e., sec(sup)2. Same applies to line 25 of page 13, where the units would be sec(sup)2.*

- We thank the reviewer for pointing out that there is missing information here. The values shown were mean values over three measurement series. We extended the data basis by another measurement series and rephrased the table caption to clarify: "Values derived as arithmetic means over 4 measurement series from different dates (April 2015 to June 2016), comprising 149 individual measurements (~37 per series) of 19 different ambient air samples using the ramped GC program".
- We checked the calculation and found it to be correct. The unit of the variance shown in table 4 is changed to s^2. We also added the information on p.13, l.25: "Four measurement series were investigated, comprising 149 individual measurement and 19 different ambient air samples".
- To show that there is actually more variability between measurement series than within individual measurement series, we added the min-to-max range of the mean retention time variance.

***9** - Retention times vary over time scales on the order of a week in such instruments due to several factors. First, their retention times should vary inversely with ambient pressure. Their electronic pressure control (EPC) of their gas chromatograph references atmospheric pressure such that as ambient pressure increases, the chromatographic pressure gradient between EPC and the absolute vacuum of the detector increases, causing retention time to decrease.*

- We thank the reviewer for providing this information to the discussion, although we think that this aspect is beyond the scope of this manuscript as it refers only to the GC system. We therefore did not investigate the dependence of retention times on ambient pressure. The basic question here would be against what the EPCs are referenced (ambient air pressure, vacuum etc.).

***10** - Another run-to-run variable is the flow resistance of the gas in the heated adsorbent tube. Figure 3 illustrates quite large temperature oscillations during desorption. Are these oscillations really so reproducible that the gas viscosity is identical in each run?*

- The oscillation is a result of the heater's pulse width modulation – which had a quite long period of 100 ms and 1 ms minimum increment when the results shown in Fig.3 were recorded (see also Fig.3 caption). We recently improved that to 10 ms period and 20 µs minimum increment (see description in sect. 3.1) but found no evident improvements in injection repeatability (.1 kHz is still a relatively low PWM frequency). This suggests that the temperature oscillation plays a minor role for the actual trap (resp. desorption process; at least in terms of overall repeatability / measurement precision), although it is observable in the dummy trap. The more important factor is presumably the repeatability of the short-time mean temperature of the trap during desorption.
- We added two sentences on the issue to the manuscript, p.8 l.10: "An effect of this temperature oscillation during desorption on gas flow through the adsorbent (and thereby on injection) cannot be excluded. However, our experience with different heater setups (feedback controlled and deterministic, with different pulse width modulation periods) suggests that it plays a minor role at most for the actual trap; at least in terms of overall measurement repeatability".

***11** - The authors are commended for making the substance breakthrough experiments. However, their conclusions regarding "quantitative trapping" (e.g., page 11, line 8) are only valid if one assumes that the instrument is linear in response, an assumption for which no evidence is provided. For example, the greater than 100% response ratio of ethyne may be attributable to "memory effect" as they claim, but the 0.3% to 1.4% 'residue' for ethyne listed in table 4 does not support the observed 109% 'breakthrough result' reported in table 2. There are more definitive tests for characterizing breakthrough, several of which are described in the 1999 thesis work of Dr. Brian Greally from the University of Bristol, UK. Use of the technique of varying the volume of sample gas is one method to examine system non-linearities, but this must be accompanied by a confirming technique such as analysis of a suite of air-like gases of differing analyte mole fraction.*

- We thank the reviewer for pointing out that the results of the volume variation experiment require a more differentiated interpretation.
- Please consider that it is beyond the scope of this work to investigate detector non-linearities; for that matter, refer to e.g. Hoker et al. 2015 or Obersteiner et al. 2016. Results from volume variation experiment also suffer from the fact that not the concentration of individual analytes is varied but that of all. This might cause a different detector response than one would achieve with a single elevated concentration and might also vary depending on the used reference gas as air matrices could be different. Consequently, also in the investigation of non-linearities, the volume variation experiment has to be interpreted against this background. The other experiment, a series of analyte dilutions in e.g. synthetic air, on the other hand heavily relies on the quality of the dilution, i.e. how accurately dilution factors can be determined. These might furthermore be substance-specific (depending on e.g. volatility). Unfortunately, we do not own such a dilution series that contains high mole fractions needed for a breakthrough experiment in Frankfurt.
- Regarding the 109 % relative response of ethyne for the high preconcentration volume, a detector non-linearity cannot be totally excluded. However, the message here is that a breakthrough is unlikely due to the relative response greater than 100 %. We changed the wording of the respective sentence (p. l.) to clarify: "ethyne was also analysed on the Unibeads 1S trap which gave a quite different result with a deviation from linear response of +10.1 % ± 0.51 %, thus breakthrough ~~did not occur~~is unlikely. The positive, non-linear response is caused potentially by a system blank (see also

section 3.3) or non-linear detector response". Moreover, we think that it is difficult to compare a zero-gas blank value with 1 L preconcentration volume with an overestimated concentration in a volume variation experiment with a preconcentration volume of 10 L.

Specific comments:

***12** - The authors refer to their micro-packed adsorbent tube as a 'sample loop', which I find an unusual use of the term. The use of the term 'sample loop' in the general literature usually refers to an open tubular device which is used to measure the sample volume, typically by pressure measurement under fixed temperature and volume assumptions. I would suggest using a more common terminology for their adsorbent tube.*

- The term is indeed unappropriated; changed to "preconcentration trap" or "trap" (several places in the manuscript, including Fig. 1 and Fig. 2).

***13** - Pg. 3, line 9: LN2 and Ar used for cooling in these kinds of instruments are not typical examples of 'refrigerants', but of cryogens. Refrigerants undergo expansion (cooling) and subsequent recompression cycles.*

- We thank the reviewer for commenting on this imprecise wording.
- Changed title of the manuscript to "A versatile, refrigerant and cryogen-free cryofocusing thermodesorption unit for preconcentration of traces gases in air"
- Rephrased wording in the abstract: "Reliable operation is ensured by the Stirling cooler, which does ~~not require refilling of a liquid refrigerant~~neither contain a liquid refrigerant nor requires refilling of a cryogen. At the same time it ~~while allowing~~allows significantly lower adsorption temperatures compared to commonly used Peltier elements".
- Introduction, p.3: replaced "refrigerant-based" with "cryogen-based" as suggested.
- Summary, p.19, l.2: added "cryogen-based": "A single-stage, refrigerant- and cryogen-free sample preconcentration unit".
- P. 19, l.18, changed: "~~refrigerant~~cryogen-based" as LN_2 / LAr based cooling options are meant here.

***14** - Pg. 4, line 28: "self-written control software" should be changed to "custom-written" or similar.*

- Rephrased as suggested, "custom-written"

***15** - Pg. 10, line 19: ": : :strips the air of its most abundant constituents: : :" makes it sound like you are preconcentrating N2, O2, etc., and not the trace target compounds.*

- Rephrased, please see our response on comment #19 of referee #1.

***16** - Pg. 14, line 16: "In general, most of the detected analyte residues are most probably caused by system contaminations (HFCs from fittings, solenoid valve membrane etc.) : : :" By 'solenoid valve membranes, are you referring to those in the EPCs?*

- Yes, the EPCs of the GC might be a source; the helium that we use as blank/zero gas also goes through an EPC so that we get a suitable pressure for preconcentration. We think that basically anything that is not full metal could be a source, from back pressure regulator membranes to the coating of the rotary valve head. It is therefore hard to say which source is dominant or which source emits what compound. To emphasise this aspect, we added information and rephrased beginning on p.14, l.17: "A distinct attribution of specific sources was not attempted. Please also note that potential contamination sources might be different for different instrumental setups, individual sources might disappear over time ("aging") etc. ~~In principal~~Regarding system memory (including the trap), the amount […]".

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17 - *Table 4 caption: Why is it that some analytes that show large residues, e.g., iodomethane at 43.9% for HayeSep D, are included in this table when the caption states that those that ": : :show poor precision 10% were excluded?*

- The values reported in table 5 (manuscript's supplement) represent relative analyte signals as is explained in the description text. In the analysis of repeated measurements of the same sample, iodomethane showed a quite stable detector response, thus the measurement precision we deduced is relatively good: approximately 3 % for both in-situ as well as laboratory instruments (current, unpublished value; the value named in Hoker et al. 2015 is a bit better (~1 %)). Considering the high residues, we have to conclude that at the moment we can measure CH_3I with decent precision but likely inaccurate.
- Values for measurement precision are not named in this manuscript; please also see our response on comment #4.

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18 - *Figure 4 caption and elsewhere: "n-propane" should be simply "propane"*

- Rephrased accordingly.

Comments of referee #3

In this article Obersteiner and co-workers present a novel device to sample highly volatile compounds without the need of a cooling agent. Although it has been designed for two specific gc-ms systems, its use in many applications, where cooling agents are not available, is conceivable. The device has been very thoroughly characterized and its strengths and weaknesses are described in the paper. I only have some remarks to improve the structure and the readability of the publication.

I would suggest publishing the article with minor revisions in Atmospheric Measurement Techniques.

***1** - Page 2, Line 13: The term 'direct measurement' is not unambiguous., I would rephrase this sentence.*

- Rephrased the sentence as suggested: "[…]too low for immediate detection and quantification by means of instrumental analytics without further sample processing steps"

***2** - Page 3, Line 3 Is there literature on the PerkinElmer system?*

- The PerkinElmer "Turbomatrix" thermodesorber can be found in publications (e.g. Palmer et al. (2005), doi:10.1071/EN05078, iodocarbon analysis or Jones et al. (2009), doi:10.5194/acp-9-8757-2009, also iodocarbon analysis); however not very frequently in publications that evolve around the analysis of halogenated trace gases to our knowledge.

***3** - Page 4, Line 19 Write flushed in direction opposite to sampling flow (instead of backwards)*

- Rephrased as suggested.

***4** - Page 5, Line 30 The term chromatographic runtime is not clear to me. Does it mean that the chromatographic separation is the time limiting step?*

- The reviewer is correct in pointing out that this expression lacks definition; rephrased to clarify: "the total duration of the chromatogram (chromatographic runtime)"

***5** - Page 6, Line 10 Use time resolution (instead of number of measurements per time)*

- Rephrased as suggested.

***6** - Page 6, Line 16 reach (instead of reached)*

- Rephrased as suggested. Please also see our changes in this paragraph in response to reviewer #1, comment #15.

***7** - Page 6, Line 11 Why should an increased preconcentration flow increase the time resolution? Is it due to the decreased size of the cold head?*

- We thank the referee for pointing out that there is something unclear. We rephrased and complemented on p.6, l.3: "[…]various factors determine the minimum cycle time (i.e. sample measurement frequency) including:
  - Sample preconcentration: volume of the sample to preconcentrate and preconcentration flow
  - Sample desorption: duration and T_D as well as insulation of the trap
  - Cool-down of trap and coldhead after desorption: targeted adsorption temperature T_A, cooling capacity (i.e. heat lift around T_A) and coldhead insulation as well as ambient temperature

  Shortening of any of these steps can theoretically shorten the overall cycle time and thereby increase time resolution; however, there might be no benefit in doing so if there are other limitations like the time it takes to record the chromatogram of a sample injection.

- Added information on p.6, l.7: "However, the overall time resolution of the laboratory instrument is limited by the GC with a total time of 19.6 minutes per chromatogram".

***8** - Page 6, Line 18 The difference of total run time, overall cycle times and minimum cycle time is not clear to me. Is the time resolution of e.g. the GhOST-MS equivalent the minimum cycle time plus the time for cool-down, or is the cool-down phase already during the GC runtime? You write that the sample-loop cool down time is not a limiting factor. But on page 17 line 8 you write that the cycle time of the GhOST-MS is indeed limited by the cooldown of the adsorptive material. Isn't it the cooldown time? Maybe a schematic diagram of the runtime with the cool down-time, the desorption time and the chromatographic runtime could help to avoid any confusion on the different cycle times.*

- We thank the reviewer for pointing out that there is missing information here, i.e. the total time it takes to measure one sample, including preconcentration and gas chromatography (again including GC temperature program and cool-down of the column to starting temperature; see also our reply on comment #7).
- Added a column (5) to table 2, "Experimental total time needed for one measurement". Rephrased header of column 4 to "minimum preconcentration cycle time" to clarify the difference. Please note: an additional table was introduced in response to reviewer #1; the "cycle-time table" is now table 2.
- The GhOST-MS uses a low thermal mass (LTM) module that contains the main chromatographic column and allows very short chromatograms. The chromatographic runtime of the GhOST-MS is 2.9 minutes plus approx. 1.2 minutes needed to cool the column down to starting temperature after a chromatogram has finished (ambient air driven by a 150 W fan). The total measurement time in this case is actually limited by both the GC column cool-down time and the cool-down time of the coldhead (comp. to our other instruments, only T_A~ −72 °C can be achieved).

***9** - Page 7, Line 27 A short description of the 'stages' should be already included here.*

- The wording of the named section is indeed slightly inconsistent; rephrased the sentence beginning in l. 26, p. 7: "Very good results were achieved with a two-stage, deterministic heater setup with a fast heat-up (stage 1), a small overshoot ~~between stage 1 and 2 of the heating phase~~ of T_D and preservation of T_D (stage 2) with only a small drift and fluctuation."

***10** - Page 10, Lines 7-14 The importance of desorption for the chromatographic peak shapes is very nicely discussed in chapter 3.3. Hence, Figure 4 should be discussed in chapter 3.3 and not already here.*

- ➢ The reviewer is right that Fig. 4 better fits in the discussion of desorption than in the introductory paragraph where is just shown and not discussed.
- ➢ Moved the reference to Fig. 4 to sect. 3.3, p. 13, at the end of the introductory paragraph (slightly rephrased): “Figure 4 shows a typical chromatogram ~~from an~~recorded after desorption and injection of a preconcentrated ambient air sample for three selected mass to charge ratios (m/Q).”.
- ➢ Added another reference to Fig. 4 on p.13 l.22 : “[…] as these are only very little influenced by the chromatographic system (see also Figure 4)”.

***11** - Page 10 Line 20 When atmospheric ozone is trapped in the cryofocus it can degrade the alkenes mentioned in the supplement. Has the influence of ozone on the recovery of VOCs been investigated?*

- ➢ This is an interesting aspect but has not been investigated. Considering that ozone destruction is catalysed on hot stainless steel surfaces, we would assume that the amount of ozone that reaches the adsorptive material is probably small. This is however speculation and was not tested experimentally. Our focus is on the analysis of halogenated tracers; results for some VOCs were included in this work to show that there is potential to extend the substance range by at least some species of this class. A detailed investigation would however go beyond the scope of this work.
- ➢ To acknowledge this fact, we added a sentence to the discussion of adsorption, sect. 3.2, first paragraph: “Interactions of other, reactive species like ozone with analytes (e.g. alkenes) during trapping and desorption were not investigated in this work”.

***12** - Page 11, Line 1 How is the back pressure of 2.5bar generated? From figure 1 the sample loop should have ambient or reduced pressure during sampling.*

- The reviewer is right in pointing out that it is not made clear in which part of the system the pressure applies. The value refers to the value indicated by the low pressure manometer of the back pressure regulator of the sample flask which was used for the test (high pressure sample, ~145 bar abs.).
- Added explanation in the text to clarify: "[…] sample back pressure of 2.5 bar abs. (back pressure indicated by the regulator of the sample flask)".

***13** - Page 13, Line 14 Peak tailing is by definition on the right flank, so I would propose to simply write peak tailing or tailing.*

- Rephrased accordingly, also on p. 15.

***14** - Page 13, Line 30 You write that the tailing effect could potentially be reduced by refocusing the high-volatile analyte fraction on a second sample loop. How can this be achieved? Do you need a third valve for it, or would you place it in front of the main column?*

- By the refocusation, the spatial spread of the analyte molecules on the adsorptive material / GC column is reduced. There are different ways how to achieve refocusation; one of them would be to cool the first part of the column (pre-column in our setup) or even the whole GC oven e.g. with LN_2. There are commercial solutions for this method available from GC manufacturers or suppliers of analytical hardware like e.g. Gerstel, Germany. The other method would be to add a second sample loop after the first one, which is cooled and heated separately. A possible setup is realised in the Medusa preconcentration system, see Fig. 1 in Ben Miller's paper on the Medusa (Miller et al. 2008).
- Rephrased on p.13 l.29: "~~The~~ Parts of this tailing effect which originate from desorption could potentially be reduced by refocusing the high-volatile analyte fraction on a second trap (e.g. Miller et al., 2008)".
- Peak tailing could also (partly) be caused by tubing and valve used to connect pre- and main column in our GC configuration, so the adsorption/desorption process is

potentially not the only origin of this effect. Another factor could be CO_2 loading of the GC column, please see our reply on comment #7 of reviewer #2. This was however not tested experimentally so we did not include this speculation in the manuscript.

Further changes to the manuscript

- Multiple occasions: replaced “manuscript” by “paper”
- Abstract, l.18: “~~single-stage~~” (superfluous)
- p.2 l.26: rephrased for better definition: “[…] and preferentially cryogen- and refrigerant-free, pure electrical operation. Liquid cooling agents (cryogens) like […]”.
- p.19 l.4: rephrased for more precise wording: “trap and desorb a wide range of halo- halogenated trace gases and potentially also hydrocarbons”.
- p.19 l.9: replaced: “~~sample loop blanks~~analyte residues”.
- Acknowledgements: added “Finally, we thank B. R. Miller and two anonymous referees for reviewing the manuscript”.
- Supplement p.1, Table 5 Description. Rephrased, l.12: “Substances that are not detected regularly in ambient air samples or show poor measurement precision ≥ 10 % were excluded from the analysis” to clarify.

Mark-up version of revised the manuscript

- see next page -

A versatile, refrigerant- and cryogen-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~~neither contain a liquid refrigerant nor requires refilling of a cryogen. At the same time it,~~ while allowing~~allows 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 analyte breakthrough during adsorption, repeatability of desorption and analyte residues in blank tests. ~~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.

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~~ immediate detection and quantification by means of instrumental analytics without further sample processing steps. 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~~ paper 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- and refrigerant-free, pure electrical operation. Liquid cooling agents (cryogens) 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 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~~cryogen-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~~cryogen-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~~paper, 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). Only characteristics of the preconcentration setup are discussed in this paper; instrument characteristics such as e.g. measurement precision or reproducibility can be found in the respective publications. 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.

2 ~~Instrumentation~~Implementation of cryofocusing and thermodesorption

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). Technical details are listed in **Table 1** for all three setups we operate. 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~~was 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~~ Preconcentration procedure and ~~gas flow in~~integration for 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 in direction opposite to sampling flow~~backwards~~ onto the~~ warm~~ chromatographic column with a carrier gas. The system does not involve a refocussing procedure as implemented in other preconcentration systems (Miller et al., 2008); instead, the analytes are purged directly onto the GC column for separation~~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~~trap during preconcentration ("stripped air"; mainly nitrogen and oxygen) is collected in a previously evacuated reference volume tank 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~~trap and reference volume for sample flow control. The MFC can also be used to determine the sample volume and thereby adds flexibility with respect to sample volumes larger than the reference tank. ~~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~~custom-written control software. It operates the preconcentration unit automatically, i.e. controls system parameters like ~~sample loop~~preconcentration trap temperature by cooling and heating concomitant with system states like preconcentration, desorption etc.

2.2 Cryofocusing: preconcentration trap ~~sample loop~~ and cooling technique

A stainless steel tube with 1/16" outer diameter (OD) and 1 mm inner diameter (ID) is used as preconcentration trap~~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~~trap and coldhead. The coldhead can contain two ~~sample loops~~traps; 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~~trap heater. For that purpose, a thin temperature sensor is inserted into the empty tube. Provided that the coldhead insulation is sufficient and intact, no significant temperature differences occur between both traps due to the high heat conductivity of the aluminium. To save space and avoid mechanical, moving parts, the preconcentration trap ~~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~~trap and coldhead. Consequently, it determines coldhead warm-up rate during desorption and ~~sample loop~~trap 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 (77 K) 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~~trap over the series of measurements. However, during thermodesorption, a certain amount of heat flows from the heated trap into the coldhead~~is transferred to the coldhead~~ as the preconcentration trap~~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~~ total duration of the chromatogram (chromatographic runtime) allows coldhead and ~~sample loop~~trap to cool down after thermodesorption and return to T_A before preconcentrating the next sample.

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

- Sample preconcentration: volume of the sample to preconcentrate and preconcentration flow
- Sample desorption: duration and T_D as well as insulation of the trap
- Cool-down of trap and coldhead after desorption: 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~~

Shortening of any of these steps can theoretically shorten the overall cycle time and thereby increase time resolution; however, there might be no benefit in doing so if there are other limitations like the time it takes to record the chromatogram of a sample injection. To give a practical example,

Table 2 shows cycle times derived from routine operation data. ~~With the laboratory setup, a~~A total time per ~~measurement~~ preconcentration cycle 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). However, the overall time resolution of the laboratory instrument is limited by the GC with a total time of 19.6 minutes per chromatogram. Data from the in-situ setup shown in

Table 2 demonstrates that ~~even shorter~~very short 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 (~ −72 °C)~~T_A~~ and a faster GC. General measures to increase ~~the number of measurements per time~~time resolution would be to increase the preconcentration flow, reduce the sample size (see in-situ setup), improve the coldhead and ~~sample loop~~trap insulation and increase the cooling capacity.

After desorption, ~~sample loop~~ temperature of the trap drops in an exponential decay shaped curve due to the decreasing temperature difference ΔT between coldhead and ~~sample loop~~trap. After a desorption at $T_D \approx 200$ °C, preconcentration trap~~sample loop~~ and coldhead temperature reach~~ed~~ similar temperatures after approximately 30 s cool-down time ($T_A = -80$ °C). ~~The cool-down~~This time increases to about 90 s at −120 °C cold head temperature until ΔT reaches approximately zero. Considering the total run times shown in

Table 2, ~~sample loop~~trap cool-down to coldhead temperature ~~time~~ is not a limiting factor to the overall cycle time. Consequently, thermal insulation of the ~~sample loop~~trap could still be increased, thereby decreasing coldhead warm-up during desorption.

2.3 Thermodesorption: preconcentration trap~~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~~trap 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~~trap 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~~trap during desorption. Differences of around 100 °C were found in comparison to temperature measured within the ~~sample loop~~trap (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~~trap 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~~trap as well as the coldhead. Very good results were achieved with a two-stage, deterministic heater setup with a fast heat-up (stage 1), a small overshoot ~~between stage 1 and 2 of the heating phase~~of T_D and preservation of T_D (stage 2) 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~~trap is getting warmer, heating rate drops resulting in a mean heating rate of about 80 °C s^{-1} during stage 1.

If a deterministic heater is used instead of a feedback controlled heater, ~~sample loop~~ the temperature of the trap becomes directly dependent on coldhead temperature (more precisely: heat flow from the ~~sample loop~~trap 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~~trap temperature increases as well. This effect can be observed in **Figure 3** as a slight upward drift of the ~~sample loop~~trap temperature (red curve, temperature measured within the ~~sample loop~~trap) during stage 2. The absolute temperature differences caused by this drift as well as the oscillation amplitude are small (in **Figure 3**: approximately 20 °C min. to max. and 4 °C standard deviation without trend correction) compared to the temperature difference between coldhead and ~~sample loop~~trap during heating (about 300 °C). An effect of this temperature oscillation during desorption on gas flow through the adsorbent (and thereby on injection) cannot be excluded. However, our experience with different heater setups (feedback controlled and deterministic, with different pulse width modulation periods) suggests that it plays a minor role at most for the actual trap; at least in terms of overall measurement repeatability.

Besides the problem of differing inner and outer temperature of the ~~sample loop~~trap during heating, temperature was not found to be distributed homogeneously alongside the empty ~~sample loop~~trap 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~~trap, potentially due to (a) difficulties in accurately measuring the inner temperature (wall contact of sensor) and (b) inhomogeneity in ~~sample loop~~trap 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~~actual preconcentration trap. 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~~trap, 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.

3 ~~Characterisation~~Performance characteristics

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 (see **Table 1**). Please refer to the respective publications for the discussion of instrument characteristics like e.g. measurement precision or reproducibility which are not exclusively related to the preconcentration setup.

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~~To control the heater of the trap, 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~~trap is packed with adsorptive material over a length of approximately 100 mm (~20 mg). Two different adsorptive materials were used in different ~~sample loop~~traps 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~~trap 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: 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~~trap 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 preconcentration trap~~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~~ With this preconcentration technique, ~~"strips" the air of its~~the most abundant constituents of the air~~;~~ (nitrogen, oxygen and argon) are mostly removed from the sample. 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 (e.g. peak tailing) as well as detection (e.g. detector saturation), 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 (ionisation switched off until tolerable CO_2 levels are reached). A CO_2 removal technique could therefore significantly improve chromatographic performance and extend the substance range of the current preconcentration system. At lower adsorption temperatures, even with CO_2 removal, a similar problem could however be caused by other gases, like e.g. xenon (boiling point:

−108 °C), which is still more abundant by three orders of magnitude in the atmosphere than the targeted analytes discussed here. Interactions of other, reactive species like ozone with analytes (e.g. alkenes) during trapping and desorption were not investigated in this work.

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 back pressure of 2.5 bar abs. (back pressure indicated by the regulator of the sample flask), 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 100 %; a relative response <100 % would indicate an underestimation (i.e. loss by breakthrough), a relative response of >100 % 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 3**.

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~~trap, 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 ~~sample loop~~trap 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~~trap). 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~~trap). However, ethyne was also analysed on the Unibeads 1S ~~sample loop~~trap which gave a quite different result with a deviation from linear response of +10.1 % ± 0.51 %, thus breakthrough ~~did not occur~~is unlikely. The positive, non-linear response is caused potentially by a system blank (see also section 3.3) or non-linear detector response. Unfortunately, HFC-23 could not be analysed in ambient air samples for comparison on the Unibeads 1S ~~sample loop~~trap 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~~trap). The comparison of ethyne breakthrough on the HayeSep D and Unibeads 1S ~~sample loop~~trap 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.

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 during a measurement series (~~qualitative aspect; ~~section 3.3.1). Additionally, the appearance and quantity of analyte signals in measurements of an analyte-free gas after sample measurements determine the number of analysable substances and ultimately measurement data quality. The discussion of analyte residues can be found in ~~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”)~~. **Figure 4** shows a typical chromatogram ~~from an~~recorded after desorption and injection of a preconcentrated ambient air sample for three selected mass-to-charge ratios (m/Q).

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 peak 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 (see also **Figure 4**). ~~(i~~In particular, there is nearly no refocusing on the chromatographic column~~)~~. **Table 4** 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. Four measurement series were investigated, comprising 149 individual measurement and 19 different ambient air samples. Variances are less than 0.02 s^2 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 4**). Even at incomplete re-focusation 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 ~~Parts of this tailing effect which originate from desorption could potentially be reduced by refocusing the high-volatile analyte fraction on a second ~~sample loop~~trap (e.g. Miller et al., 2008). The high repeatability of the injection is shown by the low variability in retention time of the first signals in the chromatogram (**Table 4**).

3.3.2 Analyte residues

Analyte residues can ~~originate from~~represent an inherent system *contamination* (1) or constitute a remainder from the previous sample (*memory effect*, (2)). Both types of residues can originate from different sources like the adsorptive material (preconcentration trap), valve membranes etc. They are differentiated by either an always-present blank signal (1) or a blank signal that decreases to zero in repeated measurements of an analyte-free zero gas after sample measurements (2).

Analyte residues were investigated with (a) ~~an ~~unloaded injections after multiple 1 L ambient air sample injections, i.e. subsequent thermodesorption of the ~~sample loop~~trap 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~~trap (*preconcentration trap~~sample loop~~ memory or contamination*) as well as carrier gas contaminations are investigated by (a) while (b) includes analyte residues within the tubing upstream of the ~~sample loop~~trap, i.e. stream selection, sample dryer etc. (*system memory or contamination*). The differentiation between (a) and (b) allows a separate investigation, which memory effect or contamination could potentially be reduced by the choice of adsorptive material or parameters of the desorption process (e.g. T_D) (a) and which part has to be attributed to tubing, stream selection etc. (b).

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~~trap. 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.

A distinct attribution of specific sources was not attempted. Please also note that potential contamination sources might be different for different instrumental setups, individual sources might disappear over time (“aging”) etc. ~~In principal~~Regarding system memory (including the trap), the amount of a residue is dependent on volatility and concentration, so extremely elevated concentrations of low-volatile substances in the previous run 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~~trap 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~~trap 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, the Unibeads 1S ~~sample loop~~trap 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~~trap showed a considerably higher amount of preconcentration trap~~sample loop~~ residues (unloaded injection) 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~~ or 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~~trap showed an overall higher number of residues which is likely caused by a higher desorption temperature of the Unibeads 1S ~~sample loop~~trap 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.

4 Application

4.1 Laboratory operation: flask sample measurements

~~For quality assurance of the~~To ensure internal consistency of our laboratory instrumentation, five air samples were analysed with the GC-TOFMS instrument (Obersteiner et al., 2016) 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). To test the overall performance, ~~The~~ 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.

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 2**), 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 cool-down 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

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

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.

5 Summary and conclusion

A single-stage, refrigerant- and cryogen-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-~~ halogenated trace gases and potentially also 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-~~ 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~~analyte residues 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~~cryogen-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. Depending on GC- and detection system, this could induce artefacts in the detected signals and ~~Due~~ also 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, r~~Relatively large amounts of hydrocarbons remained in blank measurements. These ~~blanks~~ residues are not an inherent problem of the preconcentration setup but more likely due to the adsorptive materials, carrier gas or valve membrane materials used. We do not attempt to present a viable correction method for any of the encountered analyte residues here. More dedicated experiments are necessary to account for analyte-specific memory effect and/or contaminations e.g. by modelling the carry-over from one sample to another and subtracting contamination background. ~~Additional experiments are needed to reduce those uncertainties and extend~~By doing so, the applicability of the preconcentration unit can potentially be extended to quantitative hydrocarbon analysis.

Acknowledgements

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Tables

Table 1. **(NEW)** Technical configuration of the three preconcentration setups we operate. For futher details on the full instruments (e.g. gas chromatography or detection), please refer to the respective references. T_D is given as a temperature range as it can be determined only indirectly (see sect. 2.3).

Instrument	**GhOST-MS (in-situ)**	**GC-QPMS (laboratory)**	**GC-TOFMS (laboratory)**
Reference	Sala et al. 2014	Hoker et al. 2015	Obersteiner et al. 2016
Adsorptive Material, type	HayeSep D, VICI, Switzerland	HayeSep D	HayeSep D (default) / Unibeads 1S, Grace, USA (testing purposes)
Adsorptive Material, approx. packed volume [mm^3]	12	20	20
Stirling Cooler	SC-TD08, Twinbird, Japan	M150, Global Cooling, USA (not available anymore)	CryoTel CT, Sunpower (Ametek), USA
T_A [°C], routine operation	<−70, depending on ambient temperature as cooler operates at limit	−80 (cooling capacity would allow −120)	−80 (cooling capacity would allow <−120)
T_D [°C]	180-220	180-220	180-220
reference volume [L]	2 (1 tank)	2-16 (4 tanks)	2 (1 tank)
pressure sensor	Setra 204E, Setra Systems, USA	Setra 204, Setra Systems	Baratron 626, MKS Instruments, Germany
MFC	IQ-Flow IQF-200C, Bronkhorst, the Netherlands	EL-FLOW F-201CM, Bronkhorst	EL-FLOW F-201CM
Evacuation Pump	MD-1 vario SP, Vacuubrand, Germany	Trivac NT 5, Leybold (Oerlikon), Germany	MD-1 vario SP
Control/Operation	LabVIEW & cRIO, National Instruments, USA	LabVIEW & cRIO	LabVIEW & cRIO

Table 2. 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 preconcentration cycle time ~~including pre-concentration after T_A is reached~~ [min]**	**(NEW) Experimental total time needed for one measurement [min]**
Laboratory instrument (GC-TOFMS)				
−80	−2.2	7.7	8.5	19.6
−120	−1.2	16.3	18.6	19.6
In-situ instrument (GhOST-MS)				
−70	−4.1	13.5	4.1	4.1

Table 3. 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%

Table 4. (Updated Values) Retention times t_R with relative standard deviations rSD and variances ~~in [s]~~ for selected substances (same as **Table 3**) as well as their respective average signal width expressed as FWHM ~~in [s]~~. Values derived ~~from~~ as arithmetic means over 4 measurement series from different dates (April 2015 to June 2016), comprising 149 individual measurements (~37 per series) of 19 different ambient air samples using the ramped GC program. For retention time variance, maximum to minimum differences over the 4 measurement series are given in brackets. ~~Sample loop~~Trap 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^2]**	**Peak Width [s]**
HFC-23 (CHF_3)	3.01	0.107%	0.042 (0.0440)	4.235
Ethyne (C_2H_2)	3.74	0.045%	0.011 (0.0111)	2.773
Carbonyl sulfide (COS)	3.86	0.039%	0.009 (0.0145)	2.674
CFC-12 (CCl_2F_2)	5.01	0.039%	0.009 (0.0093)	2.457
CFC-11 (CCl_3F)	7.25	0.016%	0.003 (0.0050)	2.462

Figures

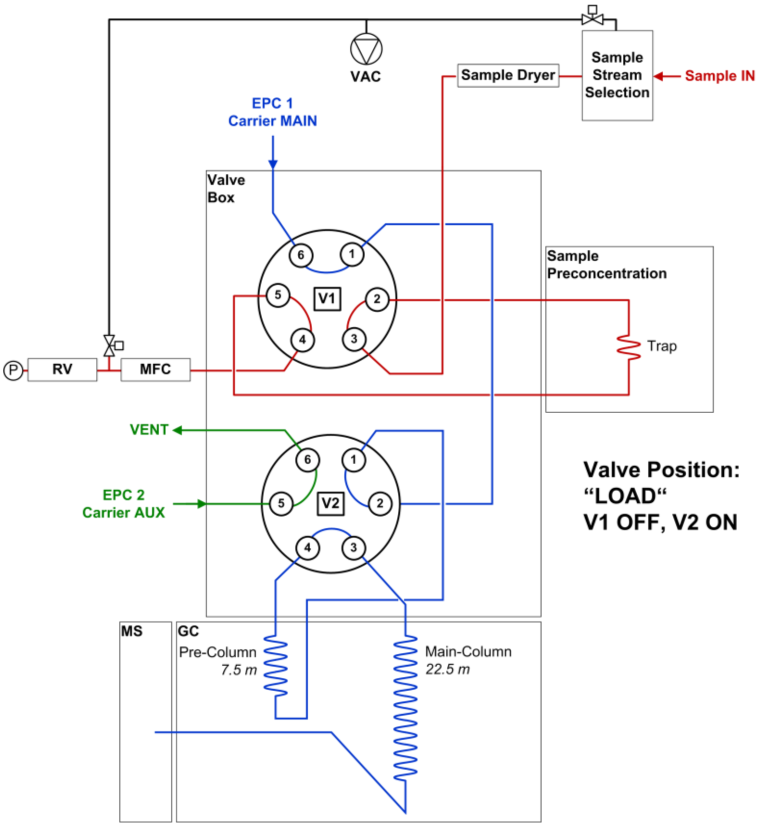

Figure 1. Flow scheme showing the gas flow during preconcentration. Two electronic pressure controllers, EPC 1 and EPC 2, control the carrier gas flow. The two 6-port 2-position rotary valves V1 and V2 are set to OFF/ON position. A sample is preconcentrated (red flow path); sample components not trapped~~ 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~~preconcentration trap is injected onto the GC column. ~~Sample loop~~Trap 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.

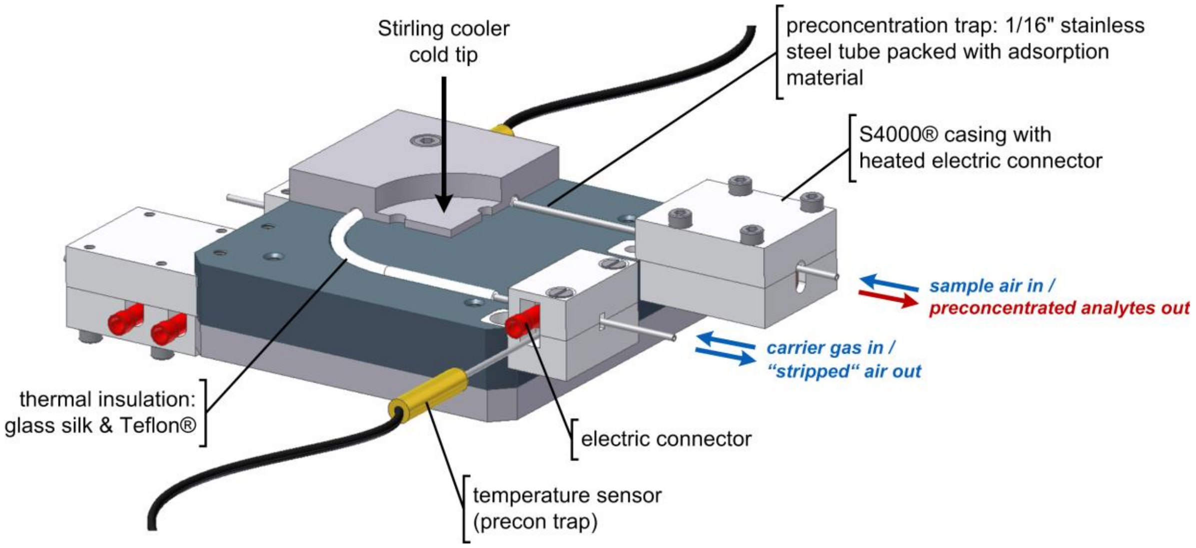

Figure 2. Technical drawing of the coldhead and ~~sample loop~~preconcentration trap placed inside. Three plates of anodized aluminium can hold two ~~sample loops~~traps. The Stirling cooler’s cold tip screwed to the coldhead removes heat for cooling. Heat for sample desorption is generated by a current directly applied to the ~~sample loop~~tubing of the trap. 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).

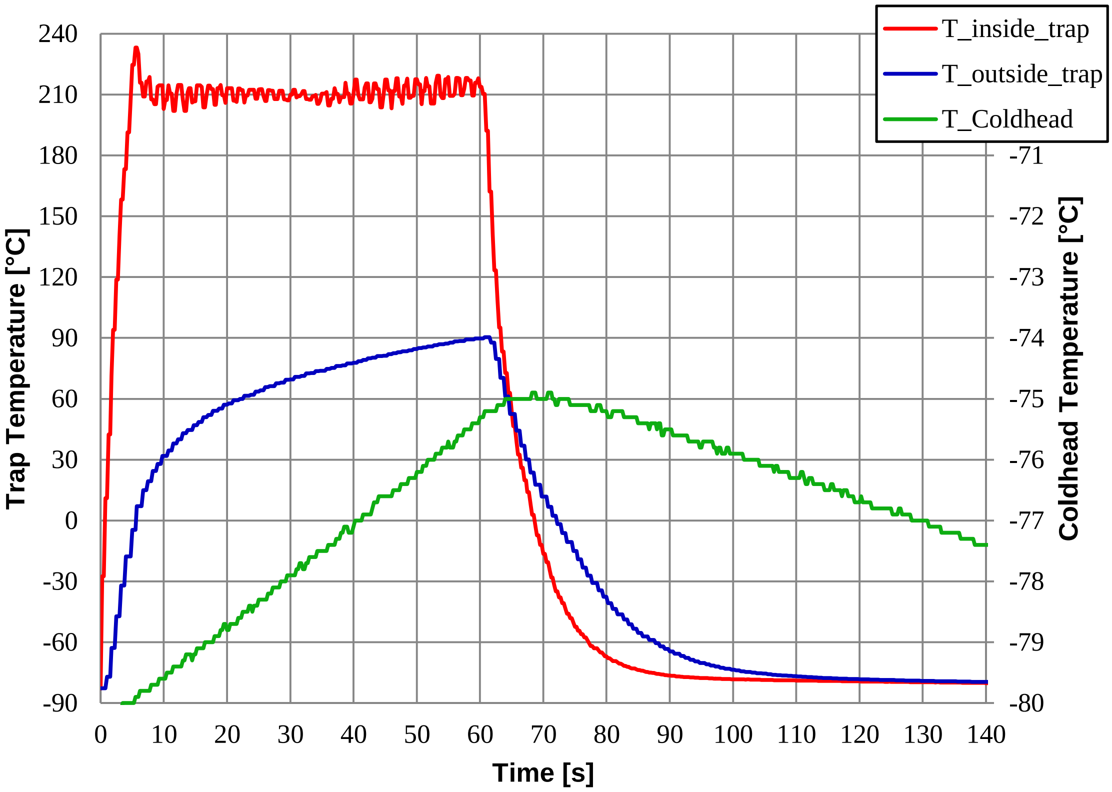

Figure 3. Desorption temperature curve inside the ~~sample loop~~dummy trap (empty tube) with a preceding adsorption temperature of −80 °C and a subsequent cool-down from desorption to adsorption temperature. Left y-axis, ~~Red~~ red curve, “T_~~SL_~~inside_trap”: signal from temperature sensor shifted inside the ~~sample loop~~trap;~~.~~ ~~Blue~~ blue curve, “T_~~SL_~~outside_trap”: temperature sensor signal from the sensor welded to the outer ~~sample loop~~trap tubing wall. Right y-axis, ~~Green~~ 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.

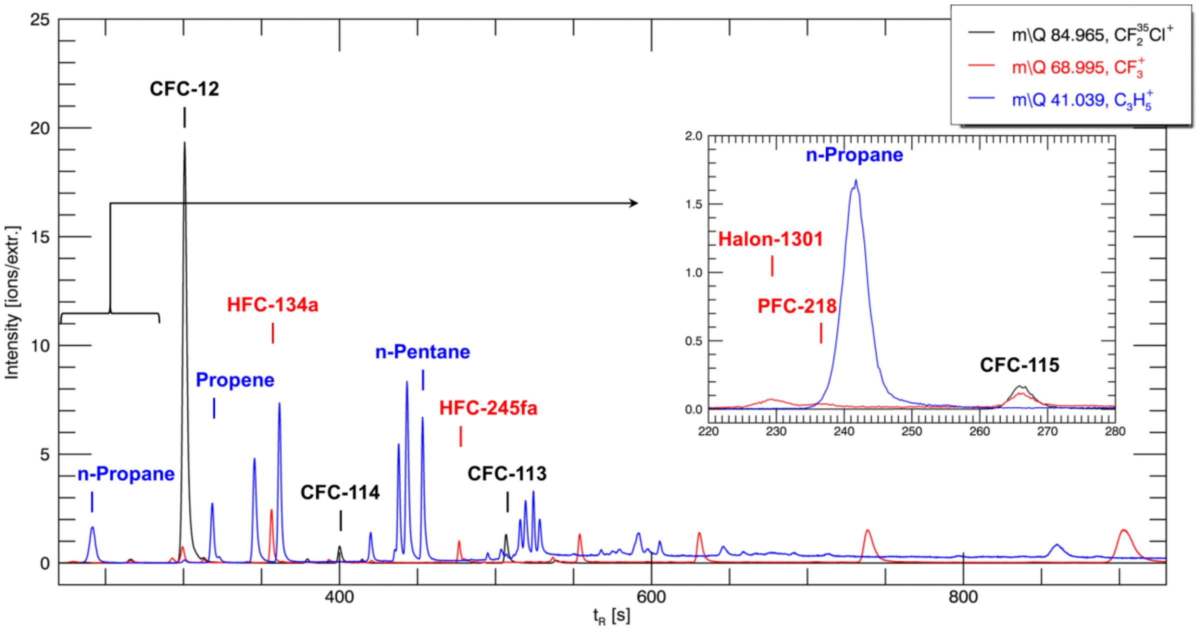

Figure 4. Chromatogram from a 1 L ambient air sample obtained with the GC-MS setup described in Obersteiner et al., 2016. X-axis: retention time t_R in seconds. Y-axis: signal intensity expressed as ions per extraction which are derived from a 22.7 kHz TOFMS extraction rate, averaged to yield a mass 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.

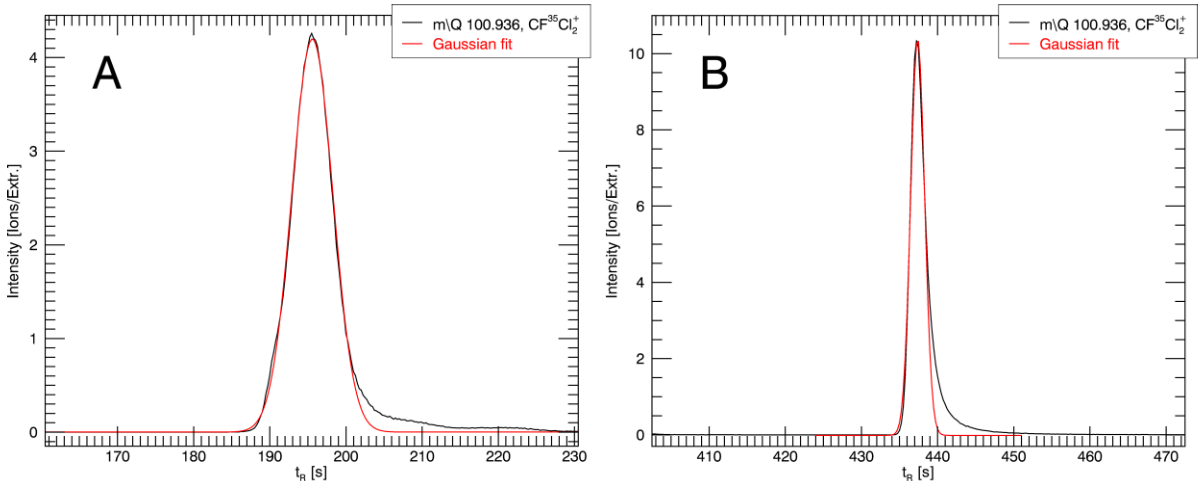

Figure 5. Comparison of chromatographic peak shapes of the CF^{35}Cl$_2^+$ fragment ion signal of CFC-11 (CFCl$_3$), from an injection of 1 L preconcentrated ambient air onto the GC column kept isothermal at 150 °C (A) and onto the GC column kept at 45 °C and ramped to 200 °C subsequently (B) (see section 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.

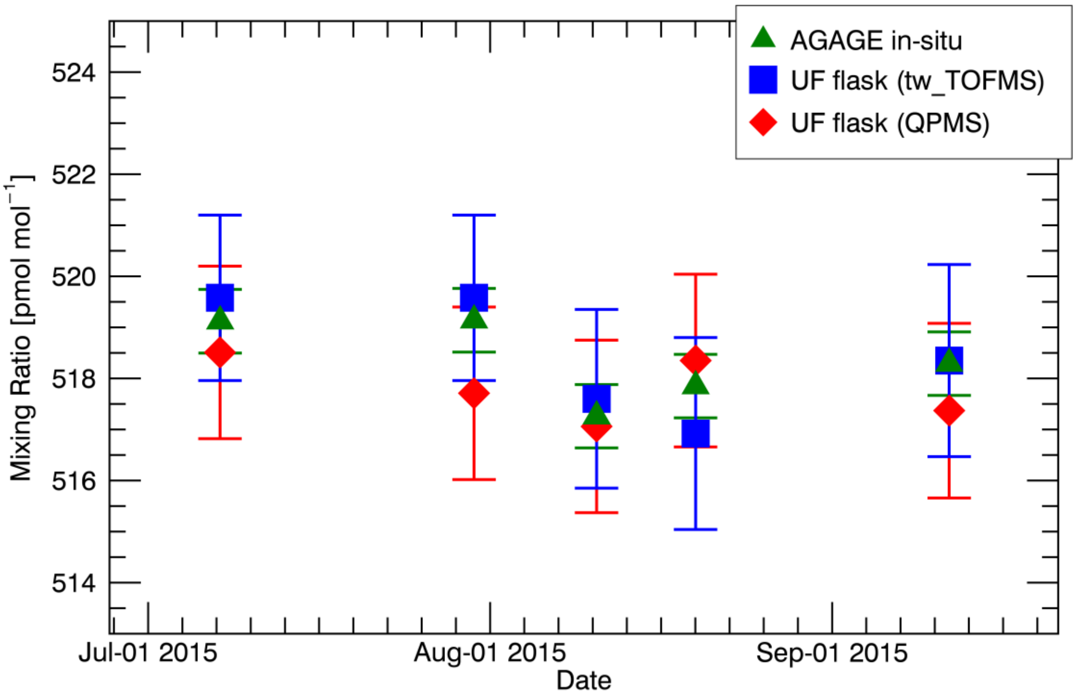

Figure 6. CFC-12 (CCl_2F_2) mixing ratios at Mace Head Atmospheric Research Station, Ireland (53°20′ °N, 9°54′ °W, 30 m above sea level) derived from 2 L stainless steel flask samples measured with the instrument in description (GC-TOFMS, blue squares), our reference instrument (GC-QPMS, red diamonds) 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.

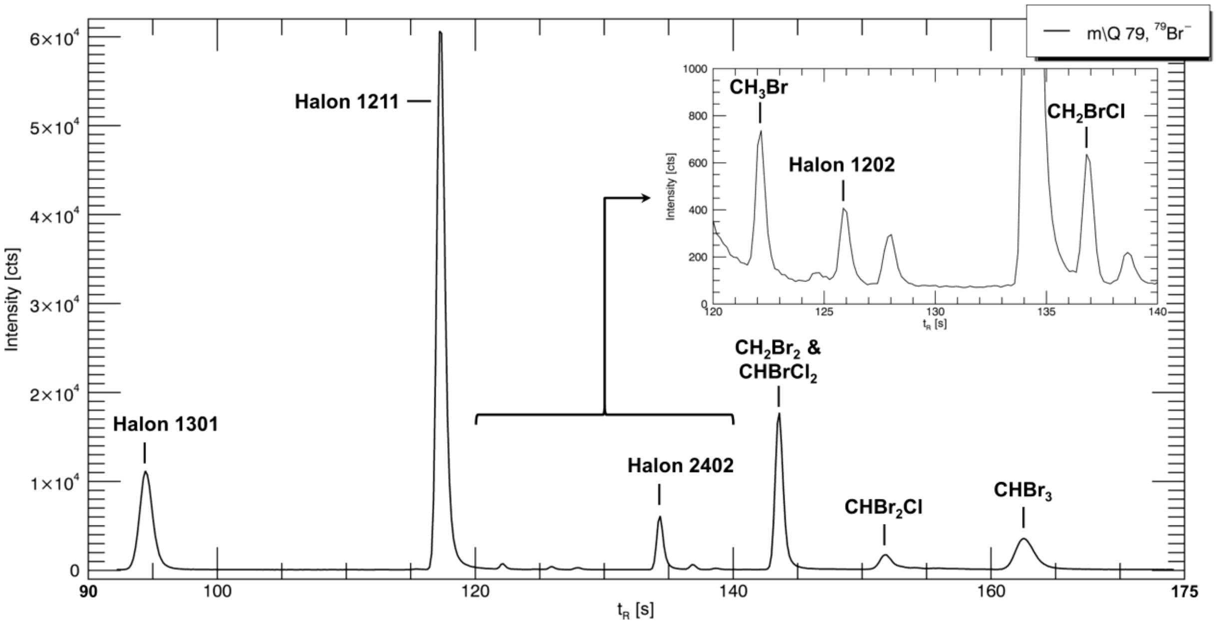

Figure 7. Chromatogram from a preconcentration of 0.1 L ambient air obtained with the in-situ GC-MS setup GhOST-MS. X-axis: retention time t_R in seconds. Y-axis: signal intensity in counts, arbitrary unit. MS: Agilent 5975C in negative chemical ionization mode (reagent: argon). Black graph: mass-to-charge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

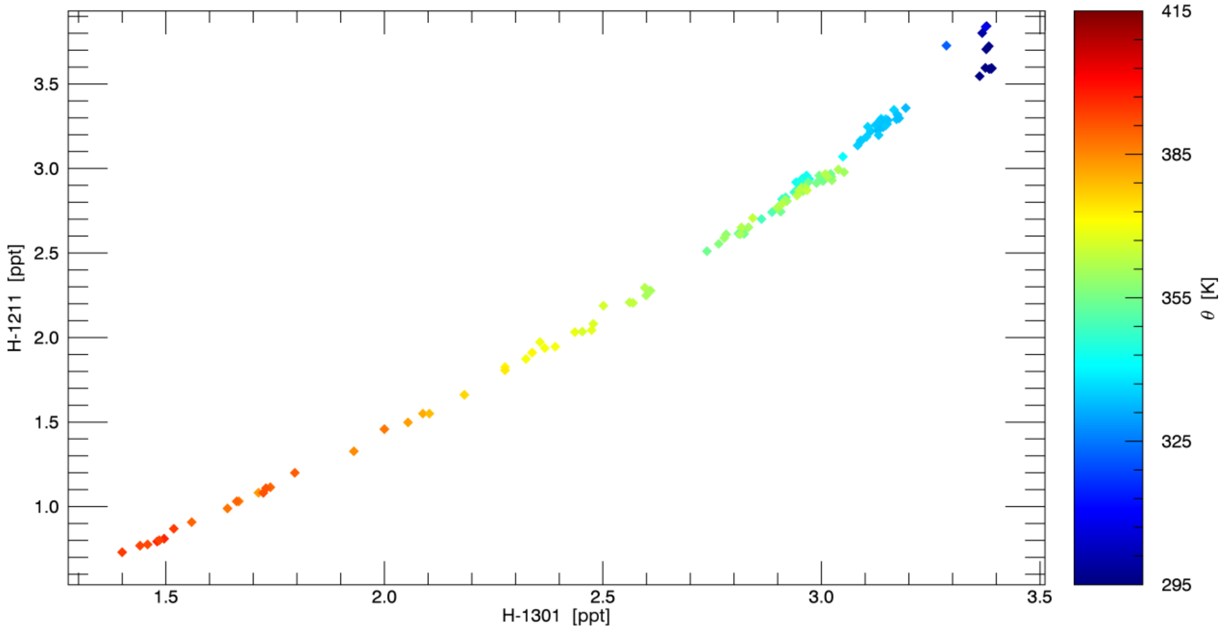

Figure 8. Tracer-tracer correlation of Halon 1301 ($CBrF_3$, x-axis) vs. Halon 1211 ($CBrClF_2$, y-axis). Color code indicates potential temperature θ in [K]. Data was obtained during the POLSTRACC mission with the HALO aircraft, flight 160226a (PGS-14). Preliminary data; calibration scale of Halon 1301 and 1211: SIO-05. Preliminary measurement precision and calibration uncertainty: 0.4 % / 1.7 % (Halon 1301), 0.2 % / 0.9 % (Halon 1211).

Supplementary Information

Table 5 shows a list of substances detected up to the time of completion of ~~the~~ this ~~manuscript~~paper. Identifications based on ambient air samples as well as synthetic mixtures. Substances are separated into six classes (e.g. CFCs and HCFCs, PFCs and HFCs etc.), which are listed in arbitrary order. Within each class, substances are sorted according to their boiling point (bp) in [°C]. Chemical sum formula as well as retention time t_R in [min] on the GS GasPro PLOT column listed in columns two and three. Columns 5 & 6 show analyte residues in [%], expressed as chromatographic signal area determined in a blank gas measurement relative to a signal area determined in a preceding 1 L ambient air sample. Blank gas: purified helium 6.0 (Praxair, Germany). "Residue HayeSep D" denotes residues found with HayeSep D as adsorptive material, "Residue Unibeads 1S" shows the same for Unibeads 1S as adsorptive material. Residues that a constant background (contamination), are marked with a "*c*", ones that represent a memory effect from a preceding sample are marked with an "*m*". Substances that are not detected regularly in ambient air samples or show poor measurement precision ≥ 10 % were excluded from the analysis ("not analysed"; n.a.). If no residue was detected or the detected residue was ≤ 0.01 %, a "not detected" (n.d.) is assigned to the respective substance.

Table 5. List of detectable substances and blank residues. Descriptions are given in the text.

Class/Name	**Formula**	**t_R [min]**	**bp [°C]**	**Residue HayeSep D**	**Residue Unibeads 1S**
CFCs & HCFCs					
HCFC-22	$CHClF_2$	5.20	-41	n.d.	n.d.
CFC-115	$CClF_2CF_3$	4.48	-39	n.d.	n.d.
CFC-12	CF_2Cl_2	5.02	-30	n.d.	n.d.
HCFC-124	CHF_2CF_2Cl	6.85	-12	n.d.	n.d.
HCFC-142b	CH_3CClF_2	6.87	-10	n.d.	n.d.
HCFC-31	CH_2ClF	6.40	-9	n.a.	n.a.
CFC-114	$CClF_2CClF_2$	6.67	4	n.d.	n.d.
HCFC-133a	$C_2H_2ClF_3$	7.55	6	n.d.	n.d.
HCFC-21	$CHFCl_2$	7.32	9	n.d.	n.d.
CFC-11	$CFCl_3$	7.28	24	n.d.	n.d.
HCFC-141b	CH_3CCl_2F	8.42	32	n.d.	n.d.
HCFC-1121	$CHClCFCl$	8.05	35	n.a.	n.a.

Class/Name	**Formula**	**t_R [min]**	**bp [°C]**	**Residue HayeSep D**	**Residue Unibeads 1S**
HCFC-132b	$CH_2ClCClF_2$	9.08	46	n.d.	n.d.
CFC-113	CCl_2FCClF_2	8.45	48	0.2% (m)	n.d.
HCFC-225ca	$CF_3CF_2CHCl_2$	9.37	51	n.a.	n.a.
HCFC-225cb	$CClF_2CF_2CHClF$	9.57	56	n.a.	n.a.
CFC-112	$CFCl_2CFCl_2$	10.33	92	n.d.	n.d.
HCFC-131	CCl_3CH_2F	12.38	103	n.a.	n.a.
PFCs & HFCs					
HFC-23	CHF_3	3.01	-82	2.6% (c)	n.a.
HFC-41	CH_3F	4.38	-78	n.a.	n.a.
HFC-32	CH_2F_2	4.20	-52	n.d.	n.d.
HFC-125	CHF_2CF_3	4.87	-49	0.4% (c)	1.3% (c)
HFC-143a	CH_3CF_3	5.00	-48	n.d.	n.d.
HFC-161	C_2H_5F	6.85	-38	n.a.	n.a.
PFC-218	C_3F_8	4.02	-37	n.d.	n.d.
PFC-216	C_3F_6	4.58	-30	n.a.	n.a.
HFO-1234yf	$CHFCHCF_3$	5.72	-28	6.9% (c)	14.9% (c)
HFC-134a	CH_2FCF_3	5.92	-26	n.d.	n.d.
HFC-152a	CH_3CHF_2	6.53	-25	n.d.	n.d.
HFC-134	CHF_2CHF_2	6.32	-23	1.1% (c)	3.0% (c)
HFC-227ea	CF_3CHFCF_3	6.52	-16	n.d.	n.d.
HFO-1234ze	$CHFCHCF_3$	6.27	-16	n.d.	n.d.
PFC-318	$c\text{-}C_4F_8$	5.68	-6	n.d.	n.d.
HFC-236fa	$CF_3CH_2CF_3$	7.22	-1	n.d.	n.d.
HFC-329ccb	C_4HF_9	7.67	15	n.a.	n.a.
HFC-245fa	$CF_3CH_2CHF_2$	7.92	15	n.d.	n.d.
HFO-1233zd	$CHClCHCF_3$	7.82	19	n.a.	n.a.
HFC-356mff	$C_4H_4F_6$	8.35	25	n.a.	n.a.
HFC-365mfc	$CF_3CH_2CF_2CH_3$	9.27	40	n.a.	n.a.
Halons					
Halon-1301	$CBrF_3$	3.87	-58	n.d.	n.d.
Halon-1211	$CBrClF_2$	6.32	-4	n.d.	n.d.
Halon-1202	CF_2Br_2	7.45	23	n.a.	n.a.
Halon-2402	$CBrF_2CBrF_2$	8.53	47	n.d.	n.d.
Halon-2311	$CF_3CHBrCl$	9.30	50	n.a.	n.a.

Class/Name	Formula	t_R [min]	bp [°C]	Residue HayeSep D	Residue Unibeads 1S
Chloro-, Bromo- & Iodocarbons					
Chloromethane	CH_3Cl	6.02	-24	0.5% (c)	0.6% (c)
Bromomethane	CH_3Br	7.00	4	3.4% (c)	1.8% (c)
Chloroethane	C_2H_5Cl	7.92	12	25.5% (c)	8.6% (c)
Dichloromethane	CH_2Cl_2	8.17	40	0.4% (c, m)	0.2% (c)
Iodomethane	CH_3I	8.00	42	43.9% (c, m)	46.2% (c, m)
Trichloromethane	$CHCl_3$	8.92	61	1.4% (c, m)	0.7% (c, m)
Bromochloromethane	CH_2BrCl	9.03	68	n.d.	n.d.
Methyl chloroform	CH_3CCl_3	9.93	74	n.d.	n.d.
Tetrachloromethane	CCl_4	9.08	77	1.1% (m)	n.d.
Trichloroethene	C_2HCl_3	9.55	87	n.d.	n.d.
Bromodichloromethane	$CHBrCl_2$	10.10	90	n.d.	n.d.
Dibromomethane	CH_2Br_2	10.03	96	n.d.	n.d.
Dibromochloromethane	$CHBr_2Cl$	11.53	119	n.d.	n.d.
Tetrachloroethene	C_2Cl_4	10.62	121	23.9% (c, m)	5.2% (c, m)
Tribromomethane	$CHBr_3$	13.50	147	11.2% (m)	n.d.
Diiodomethane	CH_2I_2	15.00	181	n.a.	n.a.
Sulfur-containing and other halogenated compounds					
Sulfuryldifluoride	SO_2F_2	4.20	-55	n.d.	n.d.
Carbonyl sulfide	COS	3.77	-50	0.4% (c)	0.1% (c)
Chlorotrifluoroethylene	C_2F_3Cl	4.92	-28	n.a.	n.a.
Perfluorotetrahydrofuran	C_4F_8O	5.87	2	n.a.	n.a.
3-chloropentafluoropropene	CF_2CFCF_2Cl	8.07	8	n.d.	7.6% (c)
Desflurane	$CF_3CHFOCHF_2$	8.42	24	n.a.	n.a.
Carbon disulfide	CS_2	6.54	46	4.0% (c)	0.8% (c)
Isoflurane	$CHF_2OCHClCF_3$	9.83	49	n.a.	n.a.
Sevoflurane	$CF_3CF_3CHOCH_2F$	10.35	59	n.a.	n.a.

Class/Name	**Formula**	**t_R [min]**	**bp [°C]**	**Residue HayeSep D**	**Residue Unibeads 1S**
Hydrocarbons and Aldehydes					
Ethyne	C_2H_2	3.75	-81	0.3% (c)	1.4% (c)
Propene	C_3H_6	5.38	-48	35.2% (c)	28.5% (c)
~~n-p~~Propane	C_3H_8	4.09	-42	0.4% (c)	0.1% (c)
Propyne	C_3H_4	7.17	-23	n.d.	n.d.
Formaldehyde	CH_2O	7.62	-19	n.a.	n.a.
Isobutane	C_4H_{10}	5.79	-13	0.7% (c)	1.0% (c)
Isobutene	C_4H_8	7.32	-7	n.d.	75.3% (c)
1-butene	C_4H_8	7.38	-6	n.a.	n.a.
1,3-butadiene	C_4H_6	7.32	-4	n.a.	n.a.
n-butane	C_4H_{10}	6.05	-1	0.3% (c)	0.1% (c)
trans-2-butene	C_4H_8	7.02	1	25.3% (c)	19.8% (c)
cis-2-butene	C_4H_8	7.24	4	n.a.	n.a.
Acetaldehyde	C_2H_4O	11.26	20	99.2% (c, m)	82.0% (c, m)
2-methylbutane	C_5H_{10}	7.40	28	0.4% (m)	0.2% (m)
Isoprene	C_5H_8	8.67	34	n.a.	n.a.
n-pentane	C_5H_{12}	7.57	36	0.7% (m)	0.3% (m)
trans-2-pentene	C_5H_{10}	8.47	36	n.d.	22.2% (c, m)
cis-2-pentene	C_5H_{10}	8.56	37	n.a.	n.a.
2-methylpentane	C_6H_{14}	8.61	60	0.8% (m)	1.0% (m)
3-methylpentane	C_6H_{14}	8.71	63	1.8% (m)	n.d.
n-hexane	C_6H_{14}	8.71	68	1.5% (c)	n.d.
Benzene	C_6H_6	11.00	80	2.5% (c)	5.2% (c)
Cyclohexane	$c\text{-}C_6H_{12}$	8.82	81	n.d.	n.d.
n-heptane	C_7H_{16}	10.06	98	23.1% (c, m)	4.0% (m)
Toluene	C_7H_8	14.52	111	17.4% (c, m)	9.8% (c, m)