GC/TOF-MS as a new method for halocarbon observation in the atmosphere

<u>F. Obersteiner</u>, H. Bönisch and A. Engel

Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt am Main

Motivation

- Halocarbons in the atmosphere: Huge variety of ozone depleting and radiatively active species [1, 2], as illustrated in figure 1.
- New compounds found to be introduced to the atmosphere, see HFOs like HFC-1234yf.
- GC/TOF-MS ideally suited for identification and quantification due to full mass range acquisition, mass resolution and sensitivity.

Figure 1:

Mole fractions (parts per trillion, ppt) of selected halogenated trace gases (only most abundant species) and their temporal evolution over the last three decades. Adapted from [2].



Instrument Development

Development of a new GC/TOF-MS from scratch: completed and running fully automated since November 2014 as shown in figure 2.



Figure 2

GC/HTOF setup. The instrument is placed on a movable frame to facilitate construction as well as modifications and allow relocation. Front: TOF-MS, back: GC with preconcentration unit on top. Underneath: DAQ PC and power supplies.

> Specifications

- Cryogenic preconcentration down to -120°C, cooled by Stirling cooler
- pressure sensor and/or MFC
- GC: 30 m GasPro PLOT with backflush system, 19 min total runtime per measurement
- MSD: Tofwerk HTOF model, EI ion source, 14 bit ADC with 1.6 GS/s DAQ
- Mean mass resolution up to 4000 $m/\Delta m$ with mean absolute mass accuracy found at \leq 5 ppm
- Identified substance portfolio: currently 68 compounds

Sample volume determination by

First Results I

Benefits from Mass Resolution: Sensitivity Improved limits of detection (LOD) by using exact mass intervals and thereby reducing noise, see table 1.

 Table 1: LOD (S/N=3) in pg/L air sample for BenchTOF-dx (Markes, Inc.) and HTOF (Tofwerk AG) nominal

and exact masses. Values for the BenchTOF as published in [3]. HTOF measurements were conducted with the same reference gas. Limits of quantification were found around S/N \approx 15.

LOD [pg/L]			_	HTOF exact vs. BenchTOF:
Substance	1) BenchTOF	2) HTOF nominal	3) HTOF exact	LOD lower by factor of
CFC-11	0.17	0.14	0.05	3.4
Halon 1211	0.18	0.25	0.16	1.1
Iodomethane	0.07	0.02	0.006	11.7

Benefits from Mass Resolution: Measurement Accuracy Gain of measurement accuracy by using exact mass information and thereby reducing background signals, see figure 3.



Measurement Precision

GC/HTOF measurement precision (nominal masses) up to best performance of our in-house twin-MS system. Overview and comparison of nominal and exact masses are shown in figures 4 and 5.



Figure 4:

Double-logarithmic plot of the signal-to-noise ratio (x-axis) vs. according measurement precision (y-axis) of 46 substances (blue squares), evaluated on nominal masses. Data taken from repeated measurements of the same reference gas.

Figure 5: Comparison of nominal and exact mass results for 46 substances (red squares) in respect to relative changes in signal-to-noise (Δ S/N, x-axis) and changes in measurement precision (Δ MP, y-axis). Data taken from repeated measurements of the same reference gas.

Figure 3:

Excerpt from a chromatogram showing Methylchloroform (CH₃CCl₃) on ion masses 97 and 99 Th (black and red curve). Coeluation of a substance with matching nominal but deferring exact masses can be compensated by integrating only the exact masses of Methylchloroform (green and blue curve) for quantification. Integration of the actual CH₃CCl₃ signal lead to a ca. 50% lower concentration determination in the sample.

First Results II



Figure 6: Barplots showing the deviation of relative detector responses from a target of 100% during a volume variation experiment comparing 8 volumes of the same reference gas (0.1 to 1 L against a calibration volume of 0.5 L). A, left: evaluation of nominal masses. B, right: evaluation of exact masses. Error bars: 1-fold measurement precision expressed as the mean error of mean of all volume samples. Substance selection according to measurement precision $\leq 1\%$ (nominal masses).

> First Application GC/HTOF delivered consistent results with the quadrupole-MS from our twin-MS system in the INGOS round robin test, see figure 7.



Conclusion and Outlook

- CARIBIC samples (J. Williams, MPI Mainz).

Literature & Acknowledgements

ating Lead Authors), Engel, A., Krüger, K., O'Doherty, S., Sturges, W.T., Blake, D., Dorf, M., Fraser, P., Froidevaux, L., Jucks, K., Kreher, K., Kurylo, M.J., Mellouki, A., MILLER, J., NIELSEN, O.-J., ORKIN, V.L. PRINN, R.G., RHEW, R., SANTEE, M.L., STOHL, A. AND VERDONIK, D. (2011): Ozone-Depleting Substances (ODSs) and Related Chemicals, Chapter 1 in Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project–Report No. 52, World Meteorological Organization, Geneva, Switzerland HARTMANN, D.L., A.M.G. KLEIN TANK, M. RUSTICUCCI, L.V. ALEXANDER, S. BRÖNNIMANN, Y. CHARABI, F.J. DENTENER, E.J. DLUGOKENCKY, D.R. EASTERLING, A. KAPLAN, B.J. SODEN, P.W. THORNE, M. WILD AND P.M. ZHAI, 2013: Observations: Atmosphere and Surface. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change[Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press. Cambridge, United Kingdom and New York, NY, USA 3] HOKER, J., OBERSTEINER, F., BÖNISCH, H. AND A. ENGEL: Application of GC/Time-of-Flight-MS for halocarbon trace gas analysis and comparison with GC/Quadrupole-MS. Atmos. Meas. Tech

Discuss., 7, 12323-12355, 2014 The authors would like to thank the Deutsche Forschungsgemeinschaft (DFG) for funding the project under research grant EN367/12-1 and the Laboratory for Air Pollution/Environmental Technology of the Swiss EMPA for providing substance identification samples.

GOETHE

UNIVERSITÄT FRANKFURT AM MAIN

obersteiner@iau.uni-frankfurt.de

Benefits from Mass Resolution: reduced Non-Linearity System non-linearities reduced by using exact masses, see figure 6.

Barplot showing the relative deviation in calculated mixing ratio (MR) between quadrupole-MS and HTOF as the mean deviation per substance of all four INGOS round robin test flasks. Error bars were calculated by adding the error of mean (all samples) from quadrupole and HTOF. Substances were selected according to measurement precisions $\leq 1\%$ on the GC/HTOF system.

• High mass resolution gives significant improvements in respect to sensitivity, measurement accuracy and reduction of nonlinearities, while measurement precision is only slightly affected. • GC/HTOF system operational and intended for sample analysis like the Taunus Observatory & Mace Head flask series, CH₃³⁷Cl/CH₃³⁵Cl isotope ratios in samples from F. Keppler (University of Heidelberg) as well as the analysis of selected