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Regular GC-TOF observations at Taunus Observatory and Mace Head

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DFG InGOS

Overview

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- **Setup and developments of time-of flight mass-spectrometry at University Frankfurt**
  - General setup
  - Mass resolution
  - Limits of detections
  - Reproducibilities
  - Linearities
- **Collection sites: Taunus Observatory and Mace Head**
- **First results from the time series**
- **Summary and Outlook**

Available compact TOF instruments (known to me)

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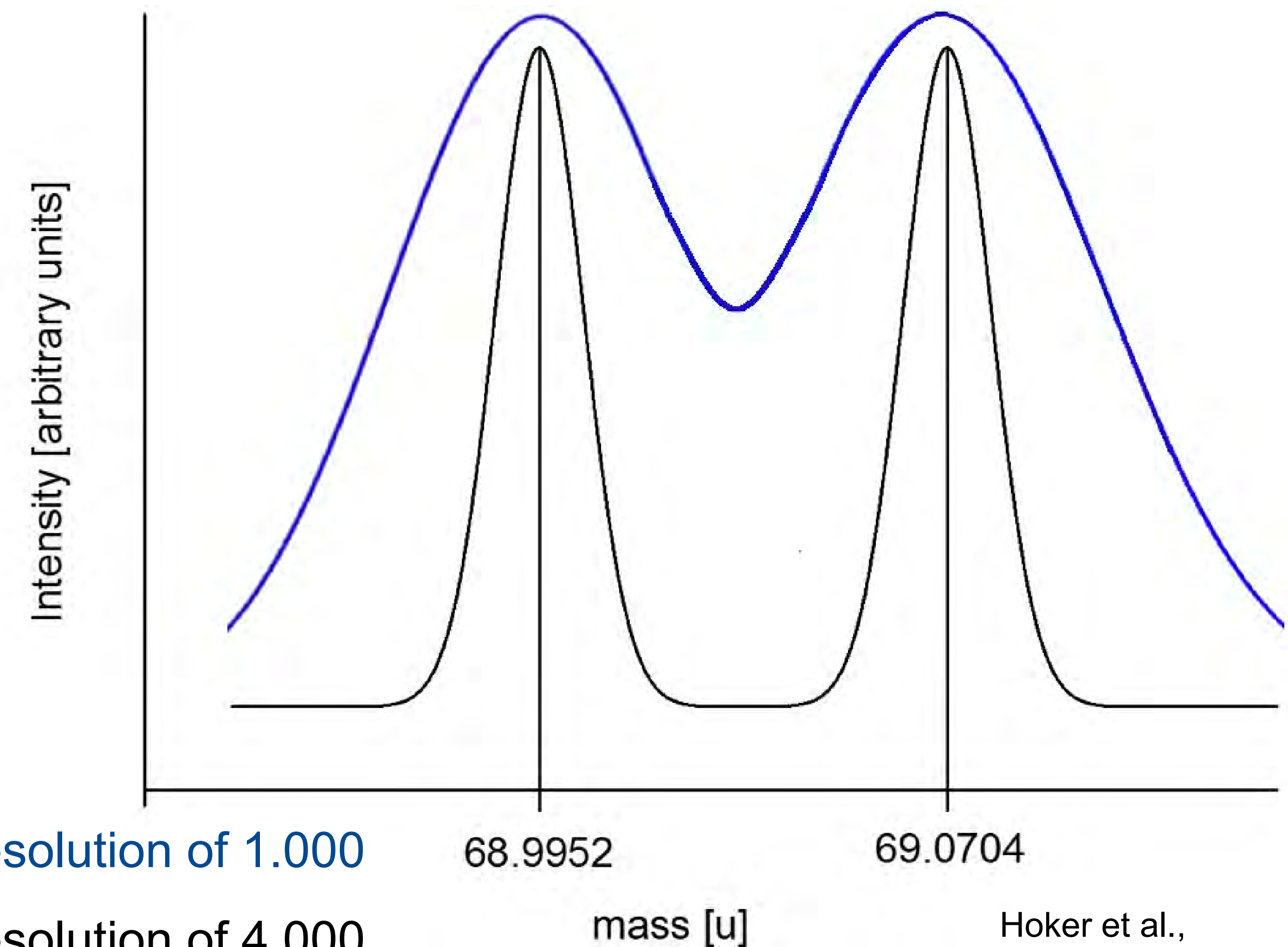
- **BenchTOF-dx (Almsco/Markes): direct ion extraction**
  - Mass resolution about 1.200
  - Quite compact
  - Build for coupling with Agilent GC

- **TOFWERK C-TOF and H-TOF: orthogonal ion extraction**
  - Used in Aerosol Mass Spectrometry
  - Used in Proton-Transfer Mass Spectrometrie (PTR-MS), as alternative to quadrupoles
  - Low resolution (800) for C-TOF, medium resolution (4.000) for H-TOF

- **Dani Master TOF**
  - Very compact, rather low resolution (1.500-2.000)
  - Claimed to be very sensitive
  - Difficult to evaluate (never seen it in operation…)

- **Agilent Q-TOF**
  - Very high resolution (12.000), very expensive, not really compact

Mass resolution: CF_3 vs. C_5H_9: 0.075 au mass difference



mass resolution of 1.000

mass resolution of 4.000

Hoker et al., AMT, 2015

Two TOF-MS systems operational at University Frankfurt: (ALMSCO BenchTOF-dx and TOFWERK

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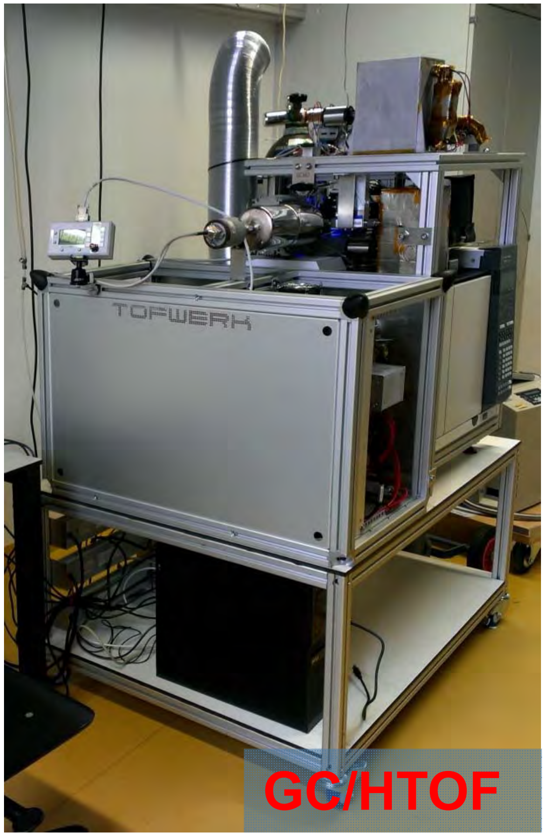
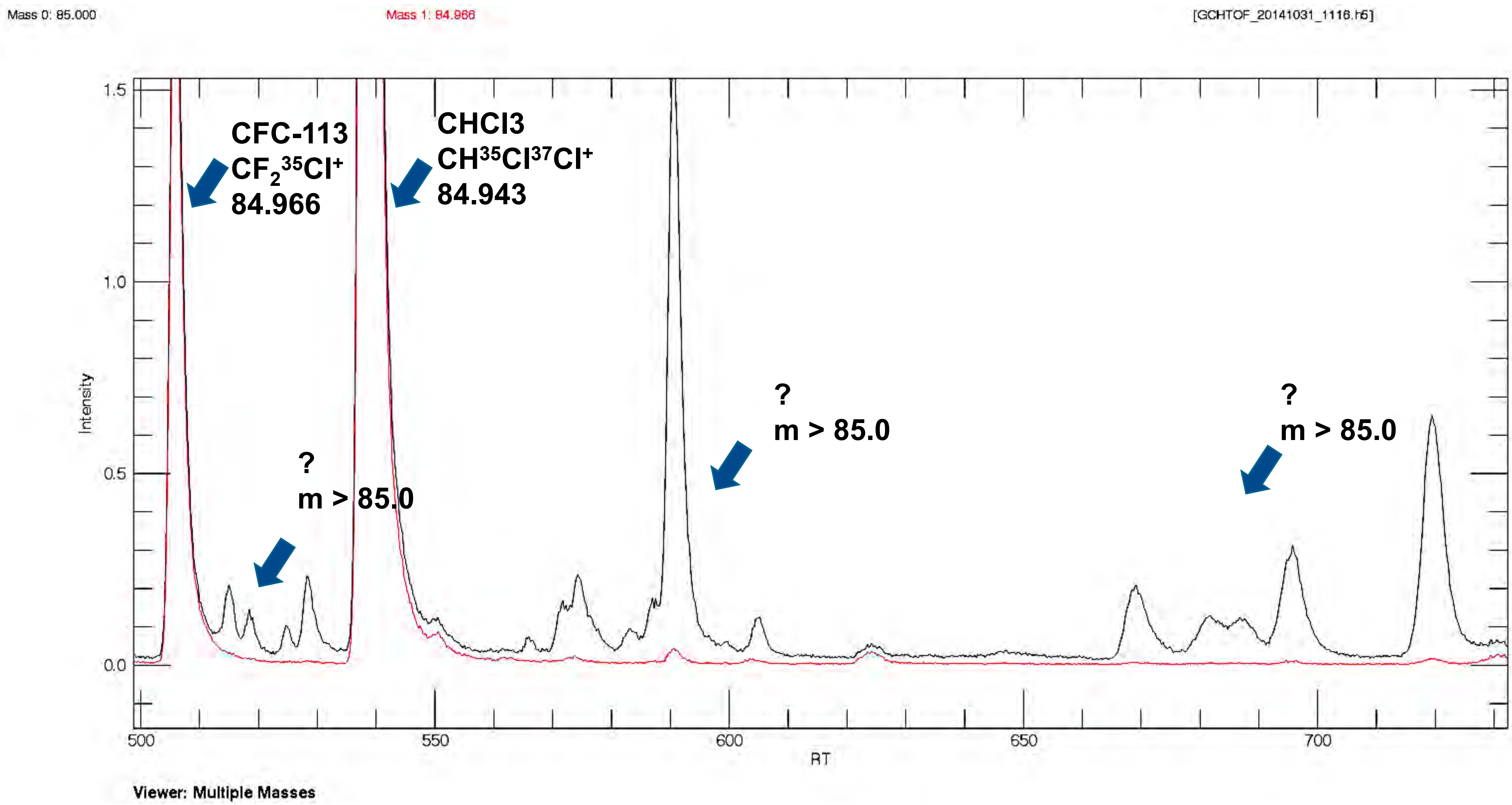
- BenchTOF-dx operated in parallel to Agilent 5975C QP with Agilent 7890 GC and self-built Stirling-cooler pre-concentration. 30 m GasPro column, 1l pre-concentration volume (split between two MS)
- H-TOF coupled with Agilent 7890B GC and fully automated Stirling-cooler based pre-concentration (own development)



GC/HTOF instrument: high mass resolution allows exact mass measurements!

- **Halocarbon fragments (red trace) have m/z < unit mass**
- **Hydrocarbons fragments have m/z > unit mass**



Limits of detection (S/N = 3) and Reproducibility

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- QP MS run in SIM mode, detecting several ions simultaneously (up to 6), running at 4 Hz.
- H-TOF for nominal mass /accurate mass

	MSD / LOD [ppq] (1 L preconcentration Volume)			
Substance	5975 QP	QP Scan	H-TOF	BenchTof-dx
CFC-11 (CCl_3F)	64	370	15/5	31
CFC-12 (CCl_2F_2)	48	241	25/17	25
H1211	43	276	78/50	27

	QP [%]	BenchTOF [%]	H-TOF [%]
CFC-12	0.22	0.23	0.22
CFC-11	0.14	0.16	0.28
Halon 1211	0.60	0.55	1.0

Linearity: BenchTOF-dx and Quadrupole

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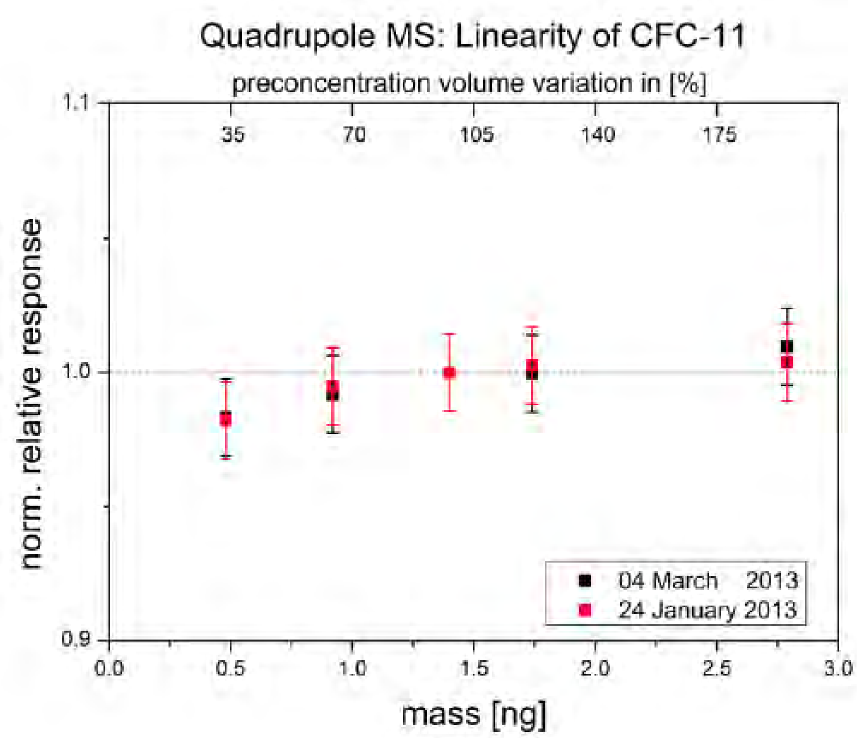

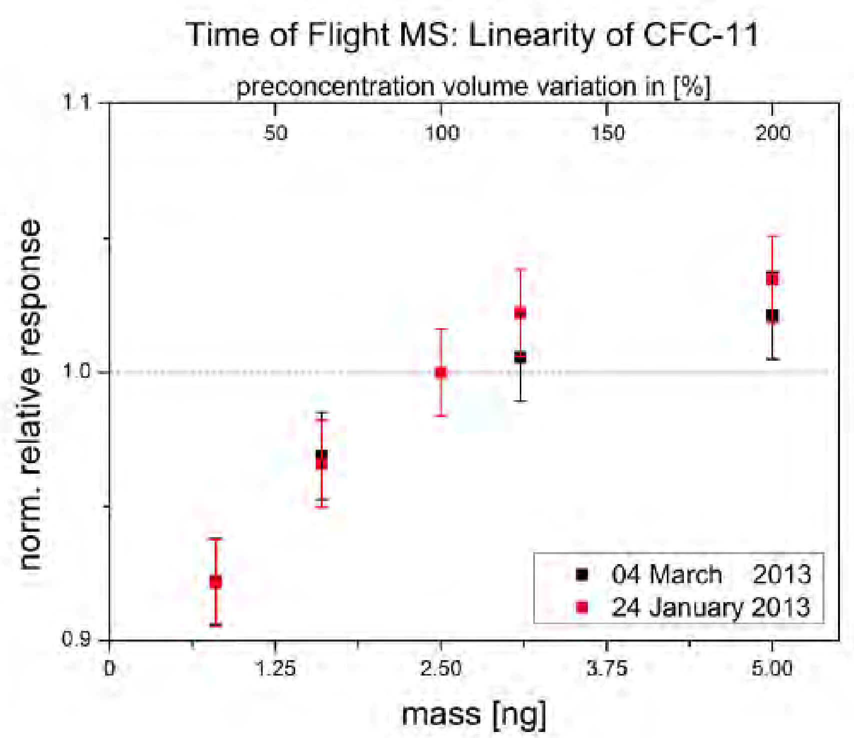

all error bars are 3 sigma standard deviations

Hoker et al., AMT, 2015

Linearity HTOF:
nominal mass vs. accurate mass

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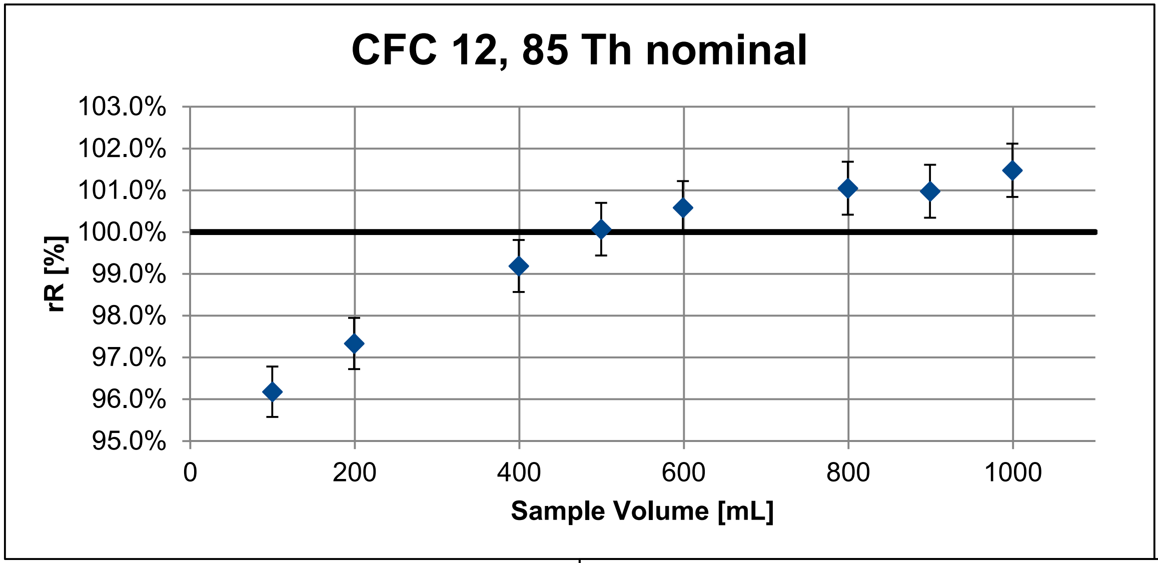
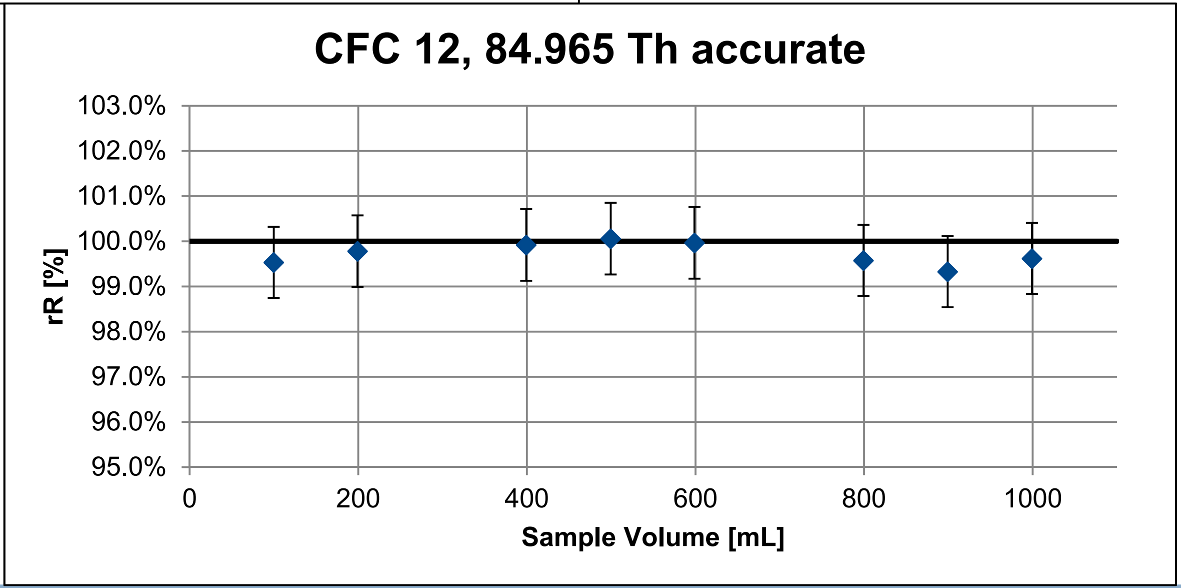


Non-linearities observed only for species with mixing ratio above 150 ppt.

Signal reflection for high signals leads to side peak for large signals at slightly higher masses

Reflection can be eliminated using accurace mass

Obersteiner et al., AMTD, 2015



Regular GC-TOF measurements as digital air archive

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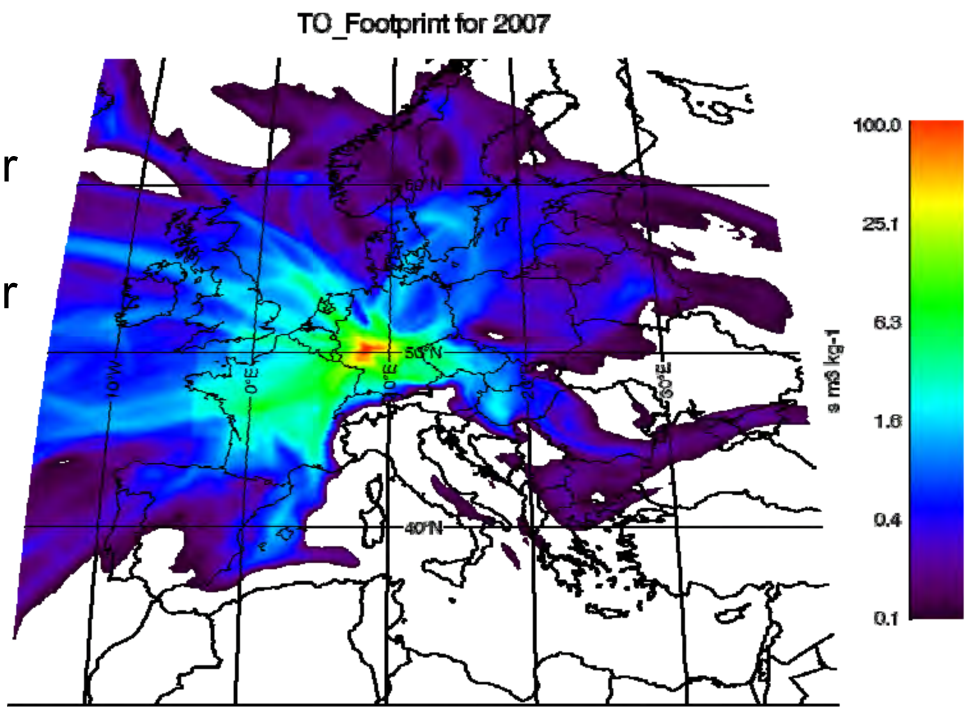
- The TOF will always measure the full mass spectrum with similar precision and detection limits as the Quadrupole MS in SIM mode and with high mass resolution.

- Start of regular sampling (weekly flask pair) at Taunus observatory near Frankfurt in late 2013 using BenchTOF and Quadrupole MS.

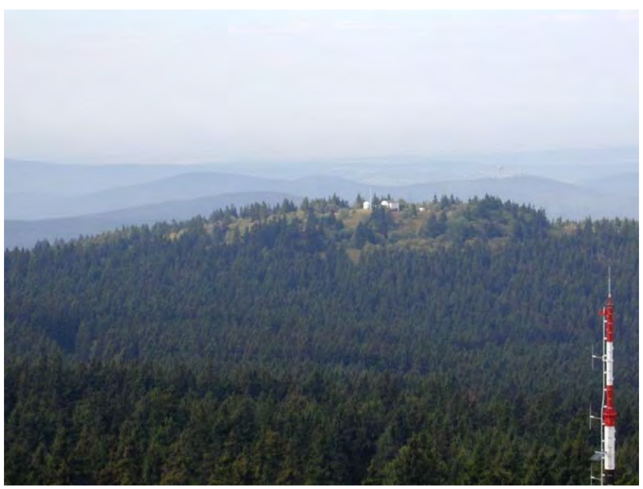
- Sampling at Mace Head started in March 2014; about two flask pairs per month under clean air condition (just after filling the NOAA halocarbon flasks)

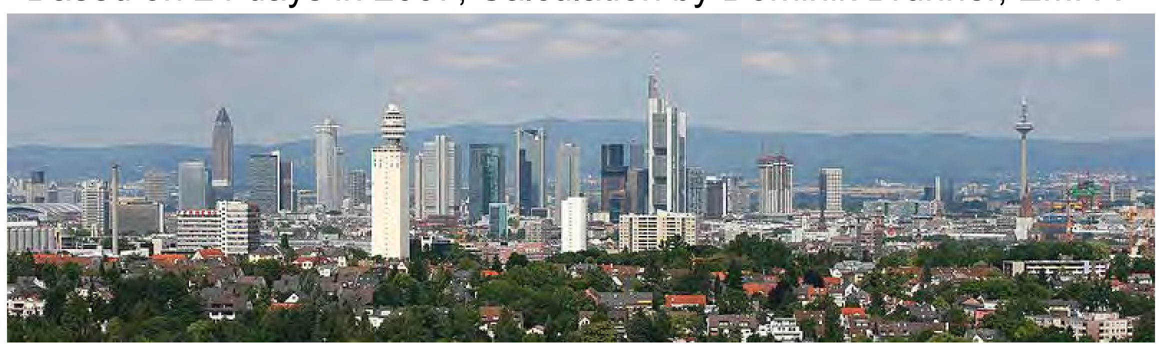
The Station – Kleiner Feldberg: Taunusobservatorium (TO)

- Between Frankfurt and the rural area „Hintertaunus“
- 825 m over seal level, mostly over the planetary boundary layer
- The geographic location allows air from Frankfurt city (very occasional), from the rural area and sometimes from the North Sea. Large Caption area; moderately polluted.



Based on 24 days in 2007; Calculation by Dominik Brunner, EMPA





Examples of GC/TOF (BenchTOF) measurements: HCFC-22 at Mace Head; comparision with AGAGE

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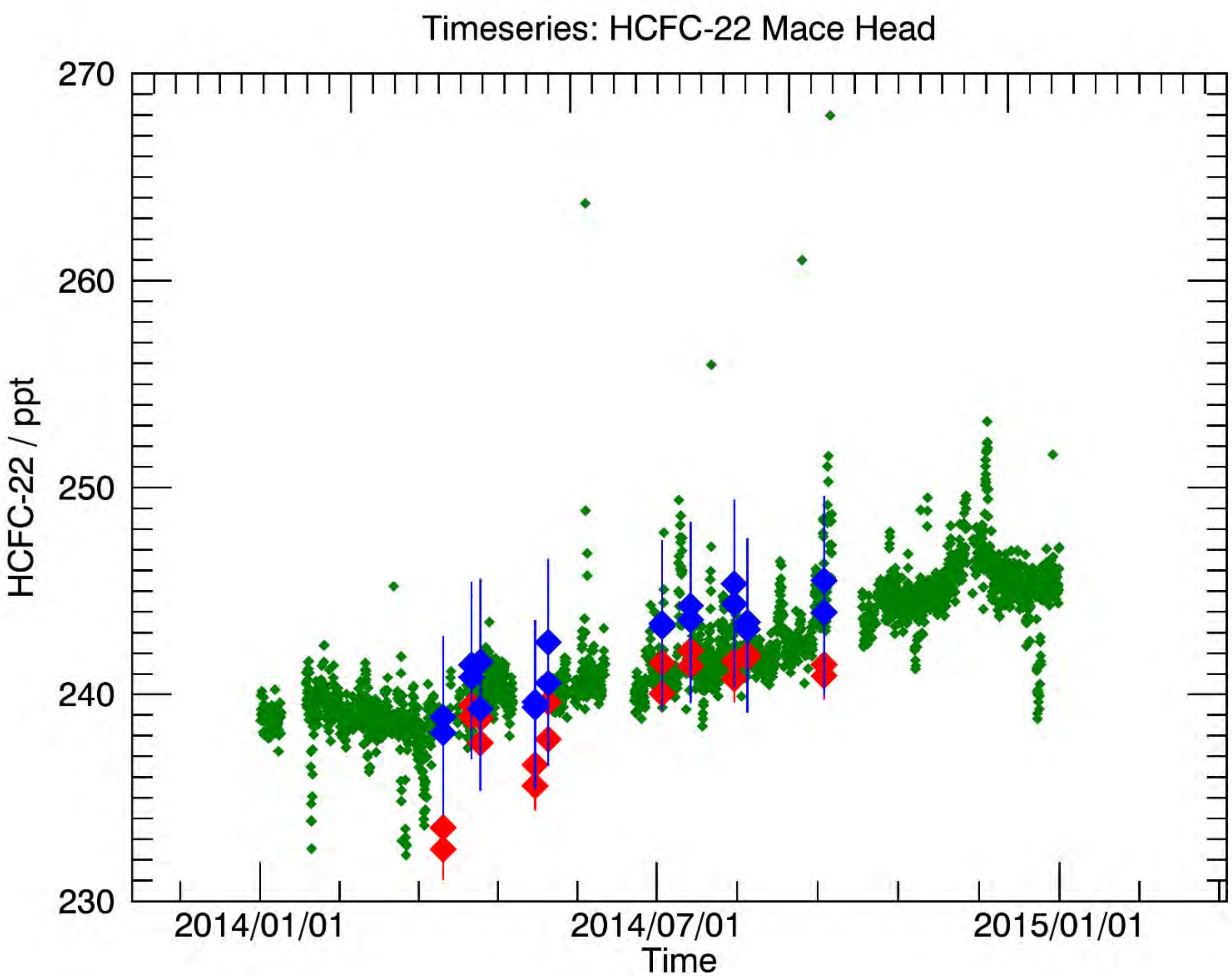

AGAGE

GUF QP

GUF TOF

AGAGE data are partially preliminary and courtesy of Simon O'Doherty

Examples of GC/TOF (BenchTOF) and QP measurements: CFC-11 at Taunus Observatory (TO)

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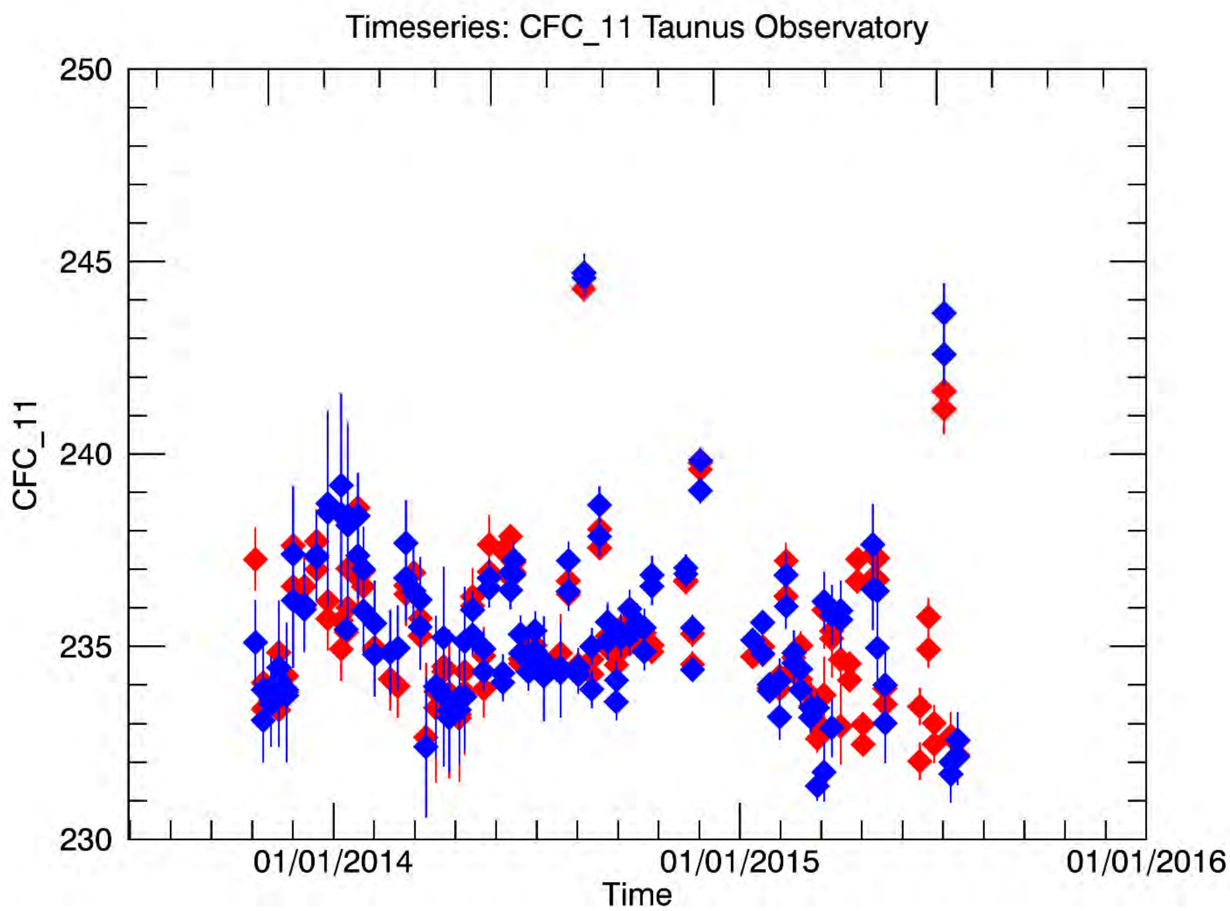

GUF QP

GUF TOF

Example for later Reanalysis of TOF data HFC-227ea, identified in late 2014

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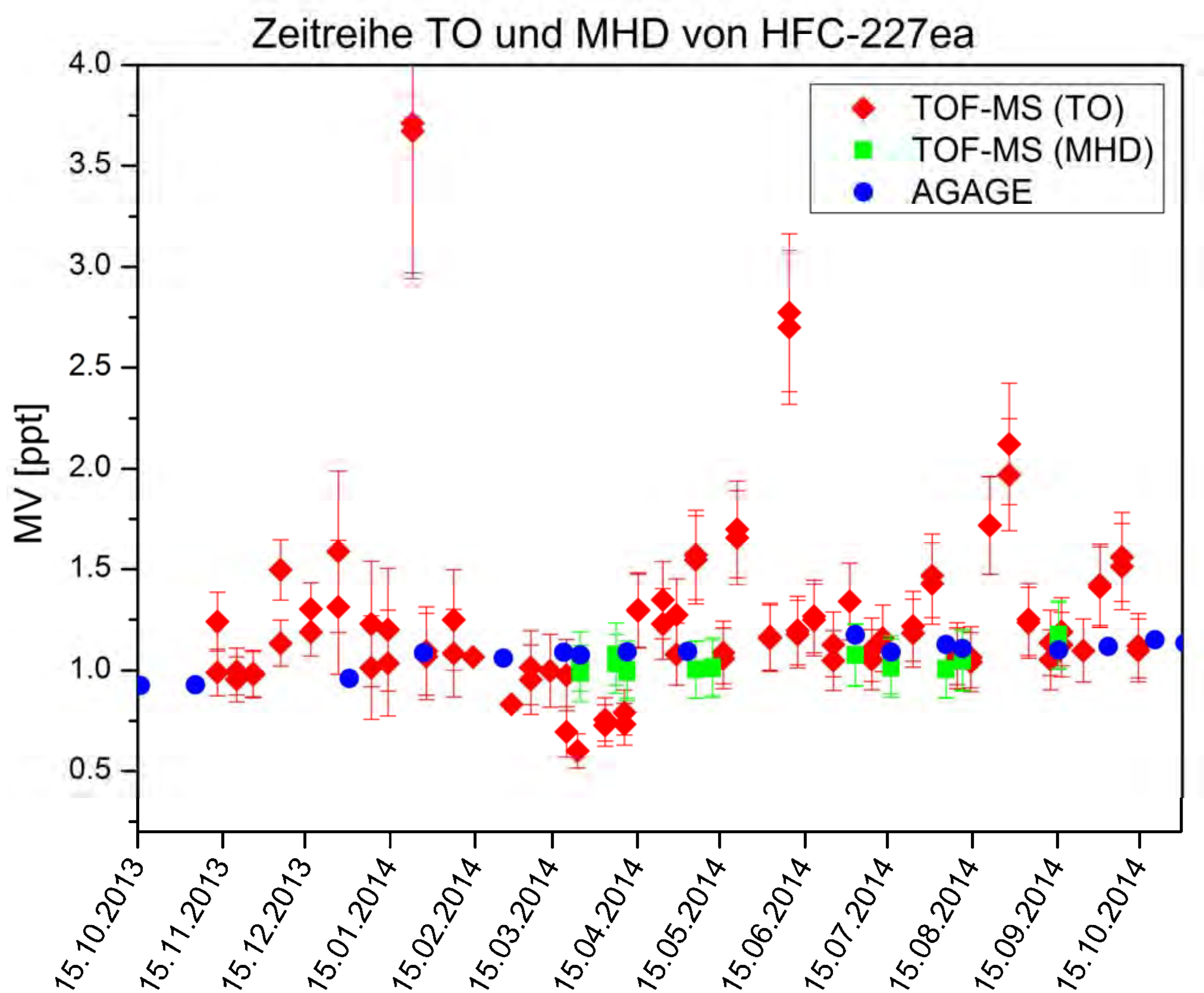

Summary and Outlook

- TOF MS always delivers full-scan mass information and has a very high potential to replace quadrupole MS with some significant advantages:
  - Much faster, Full scan, Higher mass resolution
- Reproducibilities of TOF measurements are on the same order as quadrupole measurements
- Limits of detection of TOF mass spectrometers is as good or better than quadrupole MS in SIM.
- Non-linearity needs careful evaluation. Accurate mass may help to improve linearity.
- GC-TOF still needs to be field proven and demonstrate to be as robust as the QP-MS.

Summary and Outlook

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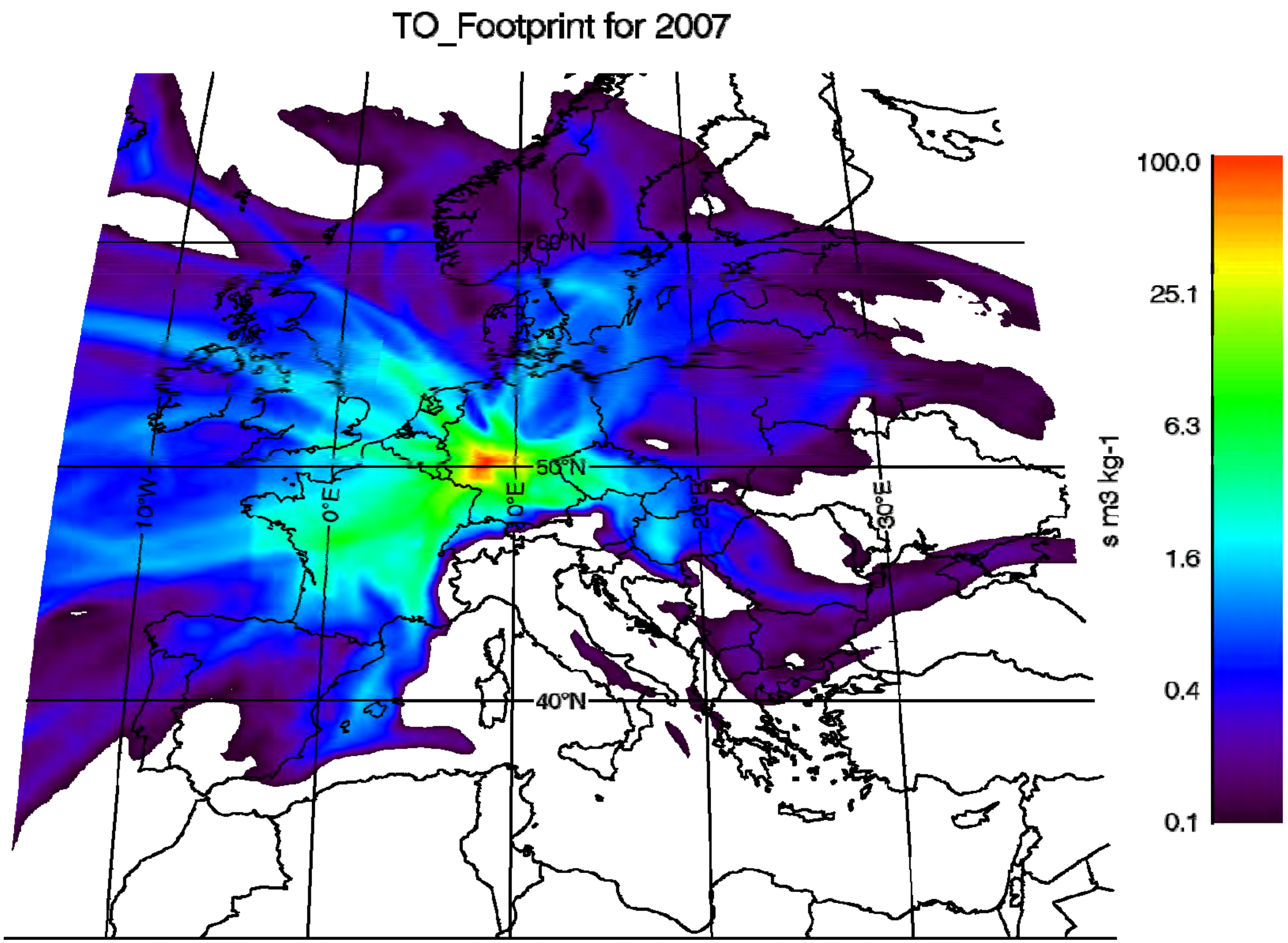
- Digital air archiving using GC-TOF measurements may supplement real air archiving

- Currently one remote station (MHD) with about 2 samples per month under clean air conditions and one slightly polluted station (TO) with weekly samples. Further automatization and improvement in data quality is planned.

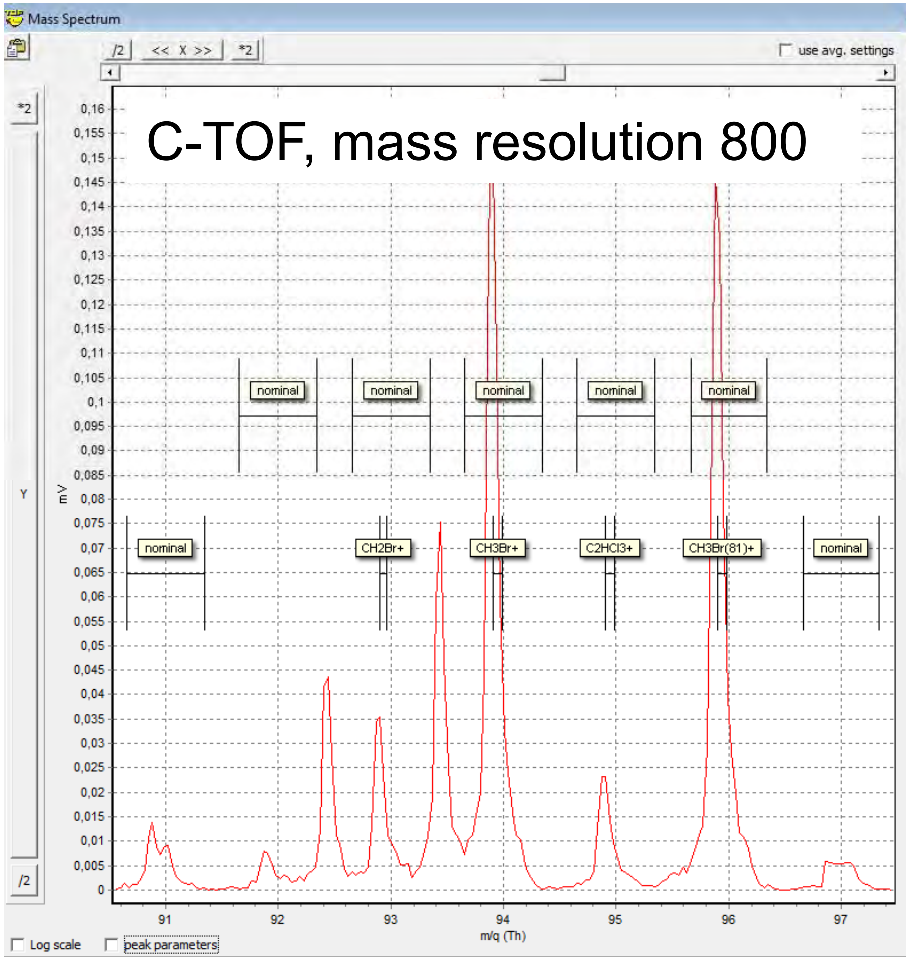
- We plan to continue the measurements and make the chromatograms available to other groups in the future.

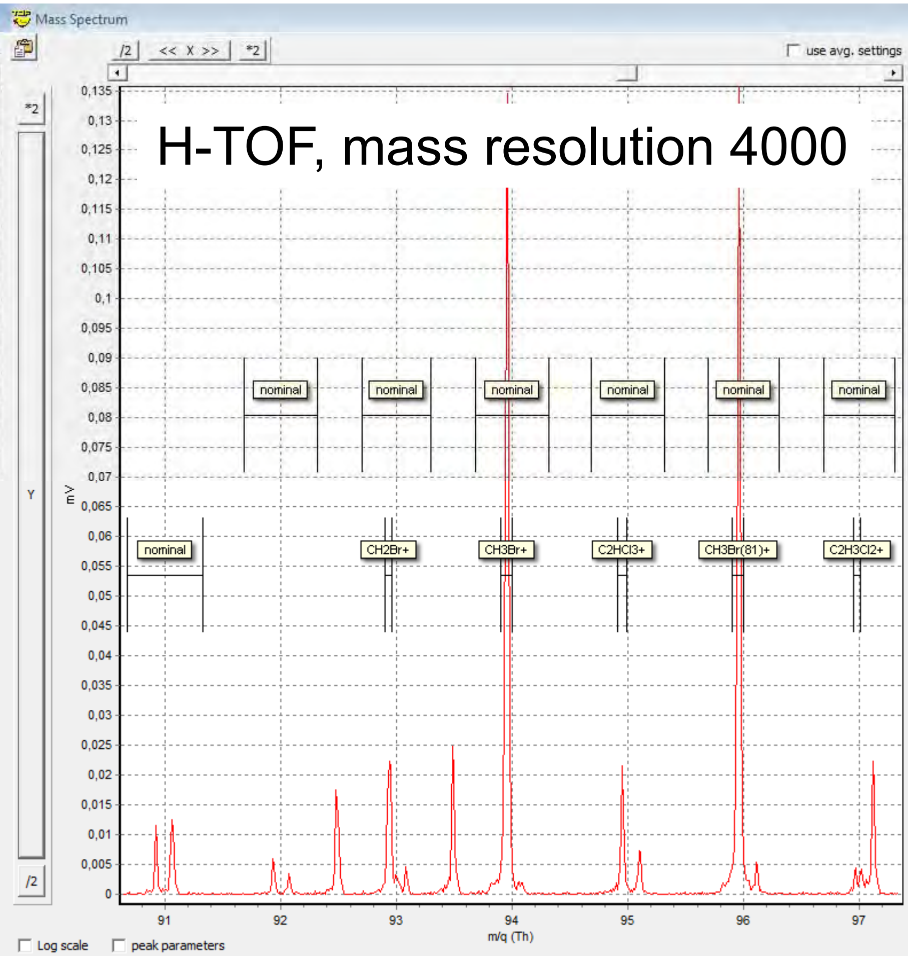
The Station – Kleiner Feldberg: Taunusobservatorium (TO)



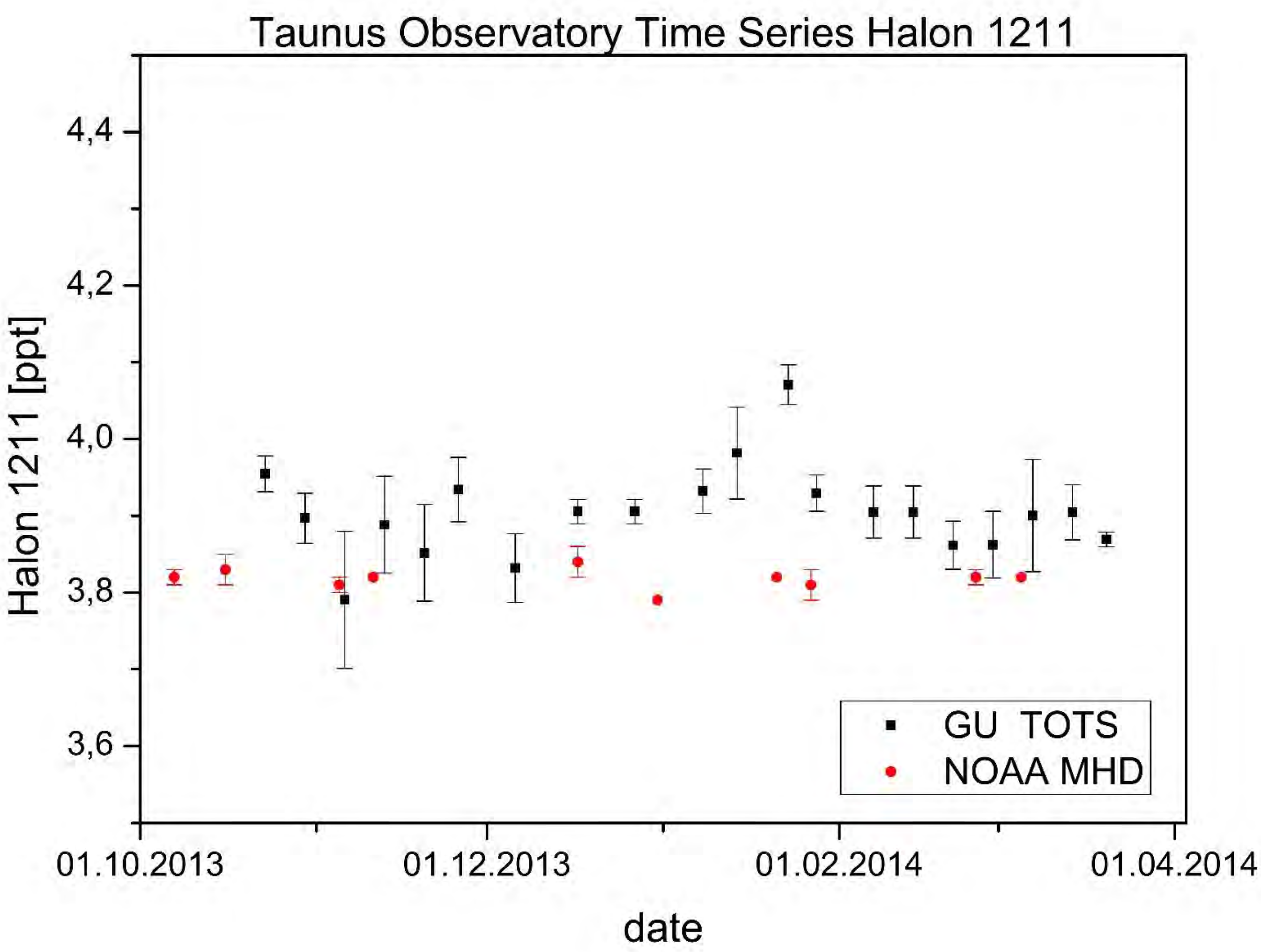
Based on 24 days in 2007; Calculation provided by Dominik Brunner, EMPA

Mass spectra of Methylbromide: C-TOF vs H-TOF

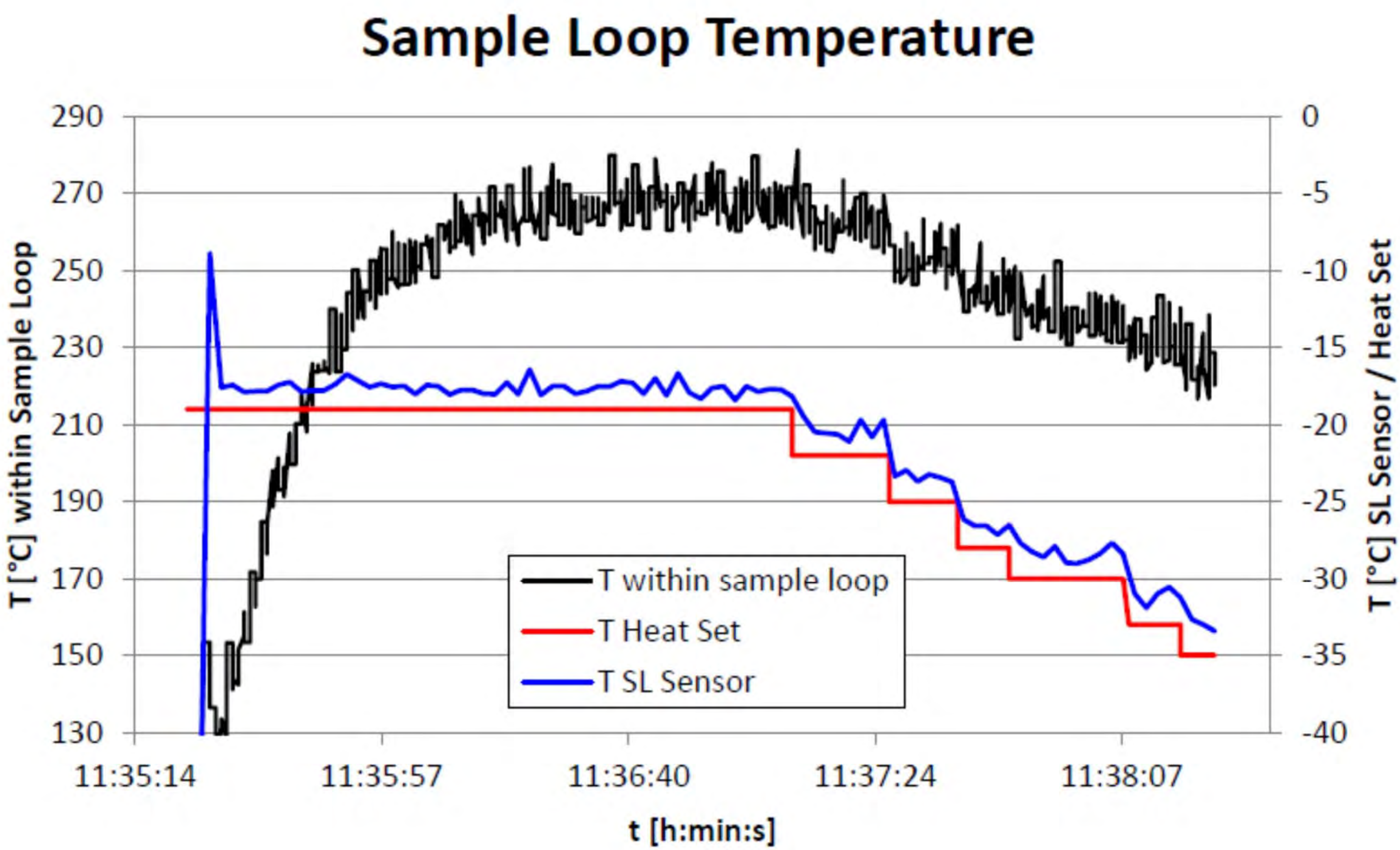




Examples of TO measurements: halon 1211



Temperature inside loop



Examples of TO measurements: CH_3CCl_3

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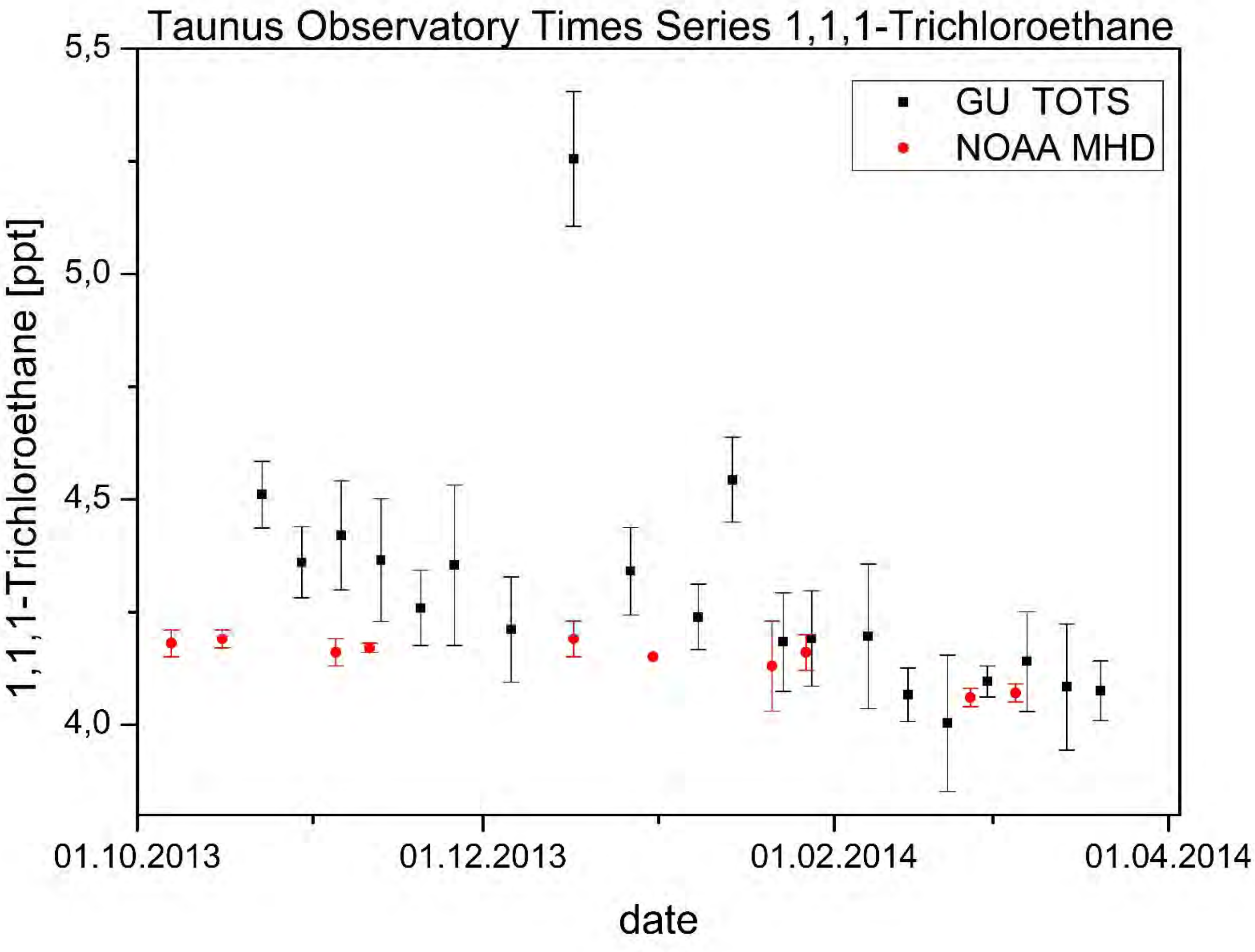
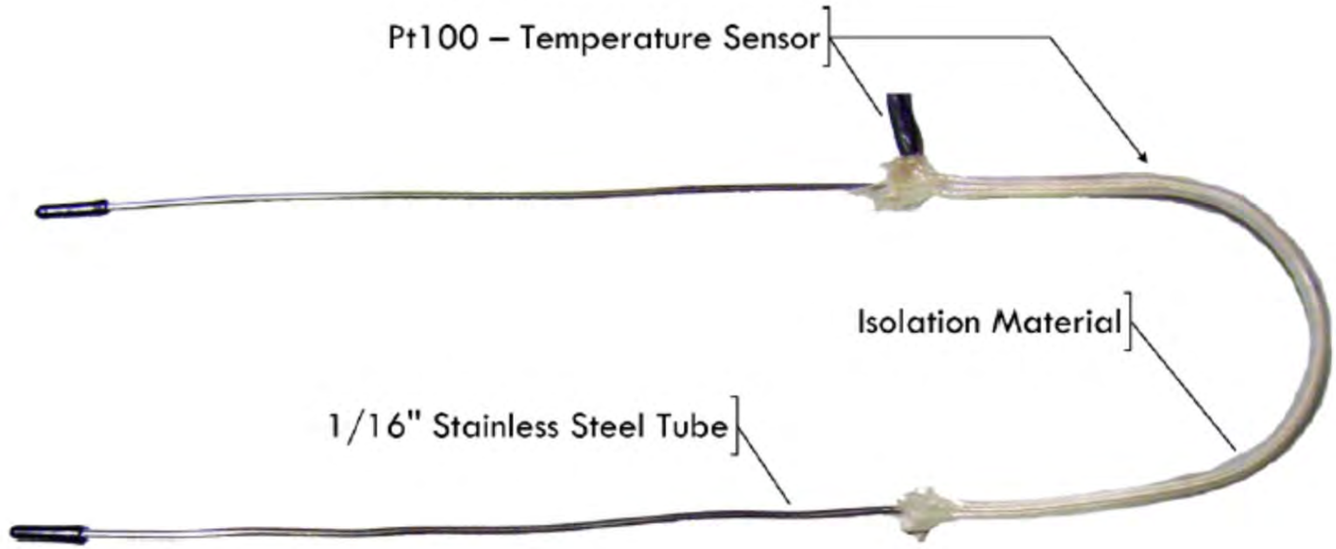


Sample loop with welded PT 100 sensor



Taunus Observatory: surrounded by Forests in the vicinity of Frankfurt

The need for Air-Archiving

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- **Only well-maintained and comprehensive long-term Air-Archive is from Cape-Grim in Australia.**
- **Some efforts to set up Northern Hemisphere air-archive are being undertaken.**
- **Especially for halocarbons the number of species in the atmosphere is huge; many new compounds identified during last decade.**
- **Purpose of an air-archive:**
  - To document the state of the Atmosphere, in particular with respect to long-lived gases with impact on radiative forcing or ozone depletion
  - To allow for retrospective analysis in search for species unknown or not investigated at the time of sampling.
- **Problem of classical air archive:**
  - Cost-intensive (tanks!)
  - Problem of sample storage (space and sample stability)
  - Production of aliquots is difficult; shipping of tanks is not possible (or not desired);

Stirling Cooler

- Different Stirling coolers tested, Twinbird and Global cooling in routine operation, sunpower not yet.
- **Twinbird cooler** (difficult to get; directly marketed from Japan): Model SC-TD08. Temperature down to -80°C, equilibrium at -60°C (depending on thermal load and duty cycle), rather cheap (1000€)
- **Global Cooling**, Athens, Ohio, Model M150: Operation down to about -130°C; Control electronics poorly documented; Special procedure for start-up necessary. Medium Price range, not available as stand-alone anymore
- **Sunpower CryoTel CT**: New, more powerful Stirling cooler tested successfully. Heat lift of 11W@77K. Allows operational temperatures down to -160°C or even further, weight 3.1 kg, good control electronics, more expensive (ab.10.000€).

The idea of a digital Air-Archiving

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- **What if we did not store air samples but the analytical result?**
  - i.e. store the GC/MS chromatograms instead of the samples
  - Will avoid costs for tanks and storage
  - Will avoid problems with sample stability
  - Product could easily be made available world wide
- **But …**
  - we will not benefit from improvements in analytical techniques, e.g. better detection limits
  - Species not measured by the GC/MS are not available:
    - (i) Either because the species was not trapped (pre-concentration device) or
    - (ii) It was not measured (because the MS-detector was not set up for this species) or
    - (iii) Because it co-elutes or is not properly separated or
    - (iv) because the detection limit was not sufficient
- **At least (ii) and partly (iii) and (iv) can be eliminated by using a *full scanning* and *high resolution* mass spectrometer with *sufficient sensitivity*!**
- **Time-of-flight mass spectrometers combine high sensitivity, high mass resolution and full scanning capabilities.**

Mass resolution for qualitative seperation

fragment	m	difference	Necessary Resolution (M/ΔM)
$CCl_2F_2^+$	84.966	0.136	625
$C_6H_{13}^+$	85.102		
CF_3^+	68.995	0.075	918
$C_5H_9^+$	69.070		
$C_2H_3Cl_2^+$	98.958	0.159	622
$C_7H_{15}^+$	99.117		

Overview

- **Limitations of QP MS systems**
- **Possible alternative mass spectrometric methods**
- **TOF instruments**
- **Setups and developments at University Frankfurt**
  - Sample preconcentration
  - Twin-MS instrument
  - FASTOF instrument
- **Mass resolution**
- **Limits of detections**
- **Linearities**
- **Reproducibilities**
- **Regular GC-TOF measurements as digital air archive**

Limits of detection (S/N = 3)

- QP MS run in SIM mode, detecting several ions simultaneously (up to 6), running at 4 Hz.
- H-TOF for nominal mass /accurate mass

	MSD / LOD [pg]			
Substance	5975 QP	QP Scan	H-TOF	BenchTof-dx
CFC-11 (CCl_3F)	0.35	2.1	0.08/0.03	0.17
CFC-12 (CCl_2F_2)	0.23	1.2	0.12/0.08	0.12
H1211	0.29	1.8	0.52/0.36	0.18

	MSD / LOD [ppq] (1 L preconcentration Volume)			
Substance	5975 QP	QP Scan	H-TOF	BenchTof-dx
CFC-11 (CCl_3F)	64	370	15/5	31
CFC-12 (CCl_2F_2)	48	241	25/17	25
H1211	43	276	78/50	27

Reproducibilities from multiple measurement: BenchTOF-dx / QP /H-TOF

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	QP [%]	BenchTOF [%]	H-TOF [%]
CFC-12	0.22	0.23	0.22
CFC-11	0.14	0.16	0.28
Halon 1211	0.60	0.55	1.0

Reproducibility based on 1 l. preconcentration volume (divided 2:1 between TOF and QP)

H-TOF uses other preconcentration device (build on the same principle).

Limitations of Quadrupole Mass Spectrometers

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- **Quadrupole is a mass filter**
  - Only selected ions pass, most ions are lost
  - Usually in SIM mode for necessary sensitivity

- **Limited mass resolution**
  - About unit mass resolution, imlying $M/\Delta M$ of about 50-200 for typical mass ranges

fragment	m	difference
$CCl_2F_2^+$	84.966	0.136
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$C_2H_3Cl_2^+$	98.958	0.159
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- **Rather slow mass spectrometer**
  - Dwell times needs to be distributed to different ions (qualifier, quantifier)
  - Typically 4 Hz time resolution can be achieved (depending on the number of ions and the necessary sensitivity (dwell time)

Alternative Mass Spectrometers

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- **Magnetic sector instruments**
  - Expensive, big, very sensitive, very high mass resolution, no full scan information
- **Ion Trap Mass spectrometers**
  - High mass resolution possible (depending on scan speed)
  - Rather poor absolute mass accuracy and quantification (linearity, preciscion)
  - Best suited for high masses
- **Time-of-Flight mass (TOF) spectrometers**
  - Used to be big and expensive
  - Have become much more affordable and compact (reflectron technology)
  - Extremely fast (20.000 spectra per second, up to 1 kHz extractable)
  - Intrinsic full-scan information available
  - Reasonable to high mass resolution (800- 12.000)

But are TOF MS sufficiently

- sensitive,
- reliable and easy to operate,
- reproducible and
- linear?

Examples for mass resolution: H-TOF, resolving power 4.000 (m/z=87,$C^{37}ClF_2$)

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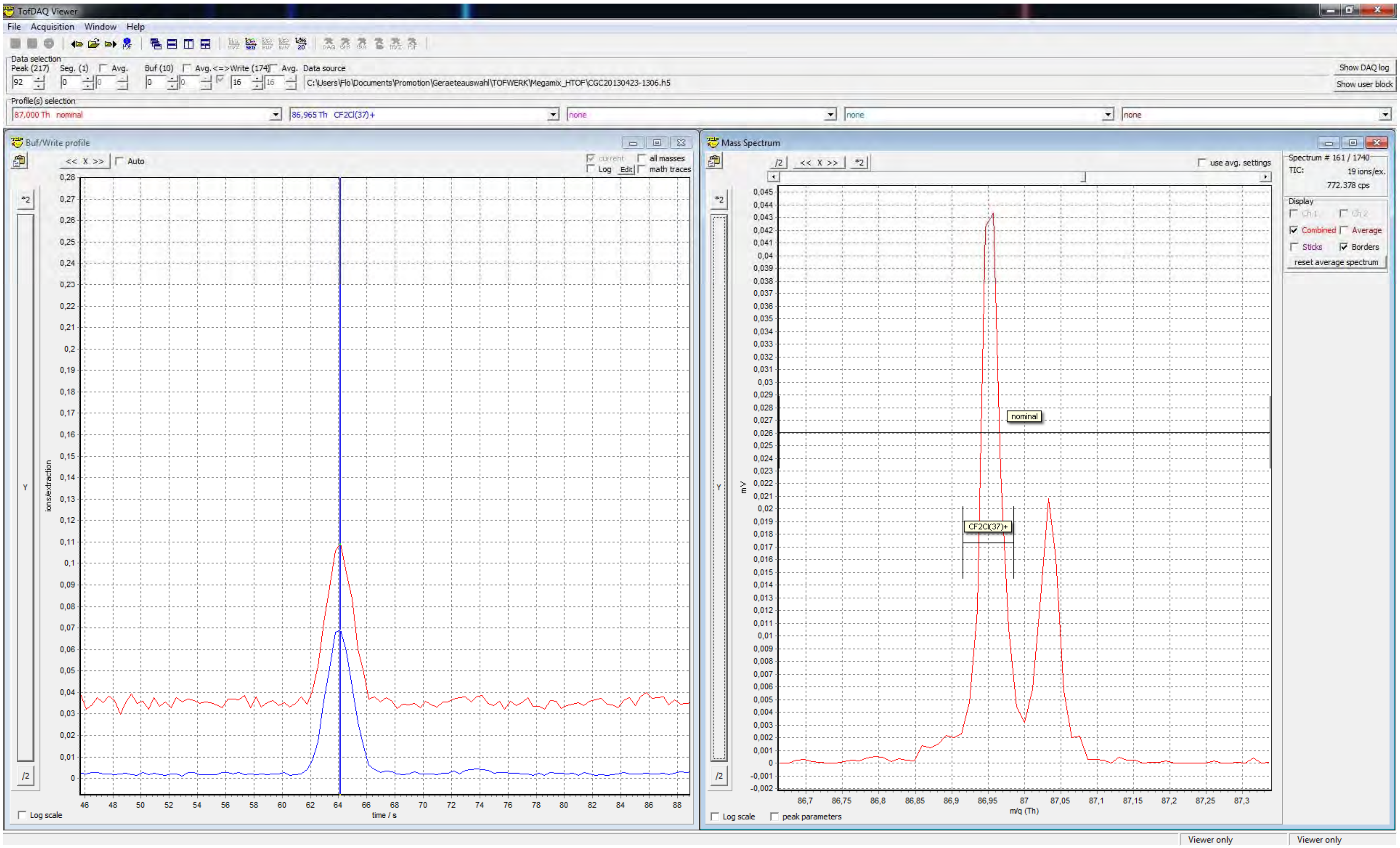
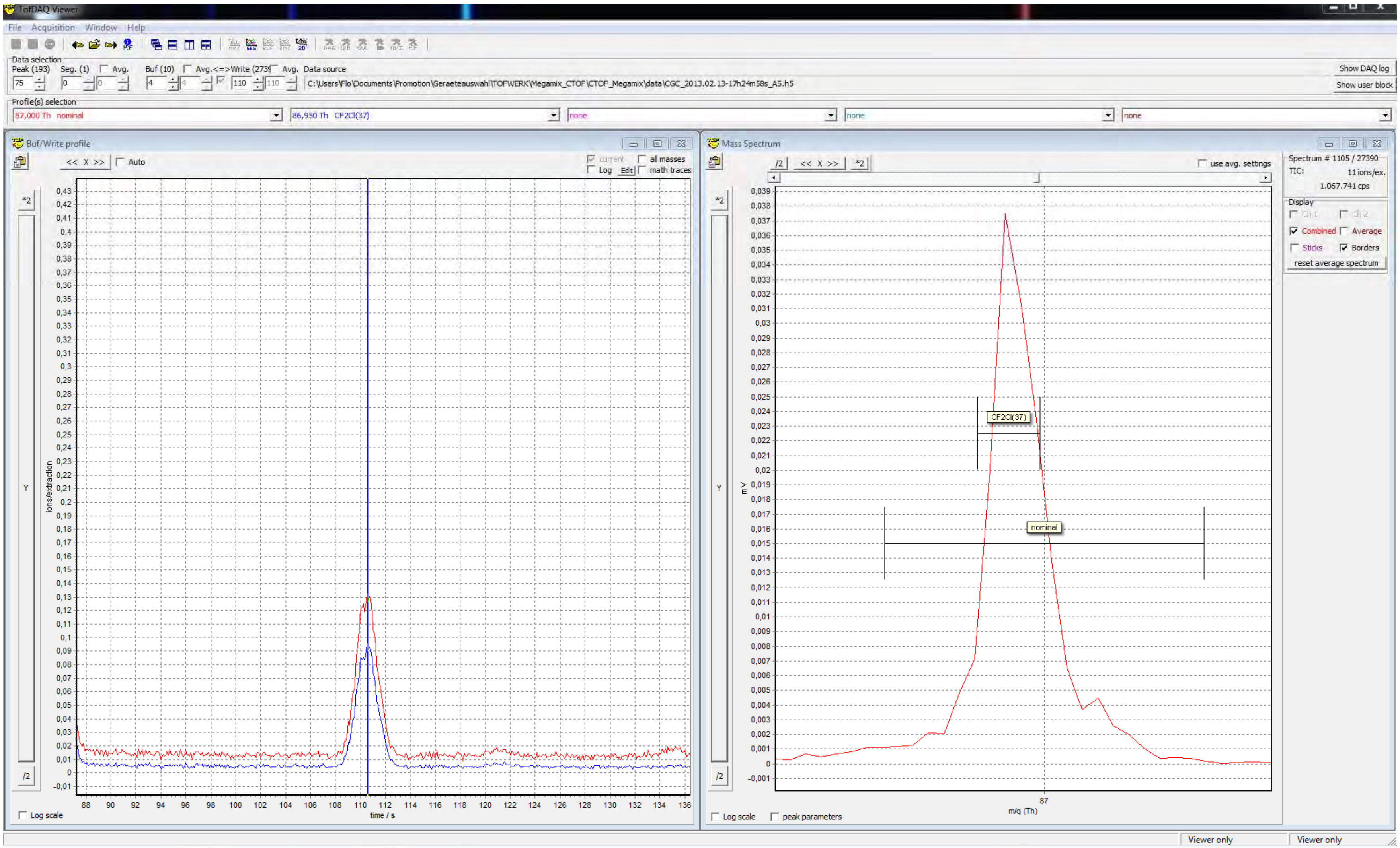


Examples for mass resolution: C-TOF resolving power 800 (m/z=87; $C^{37}ClF_2$)



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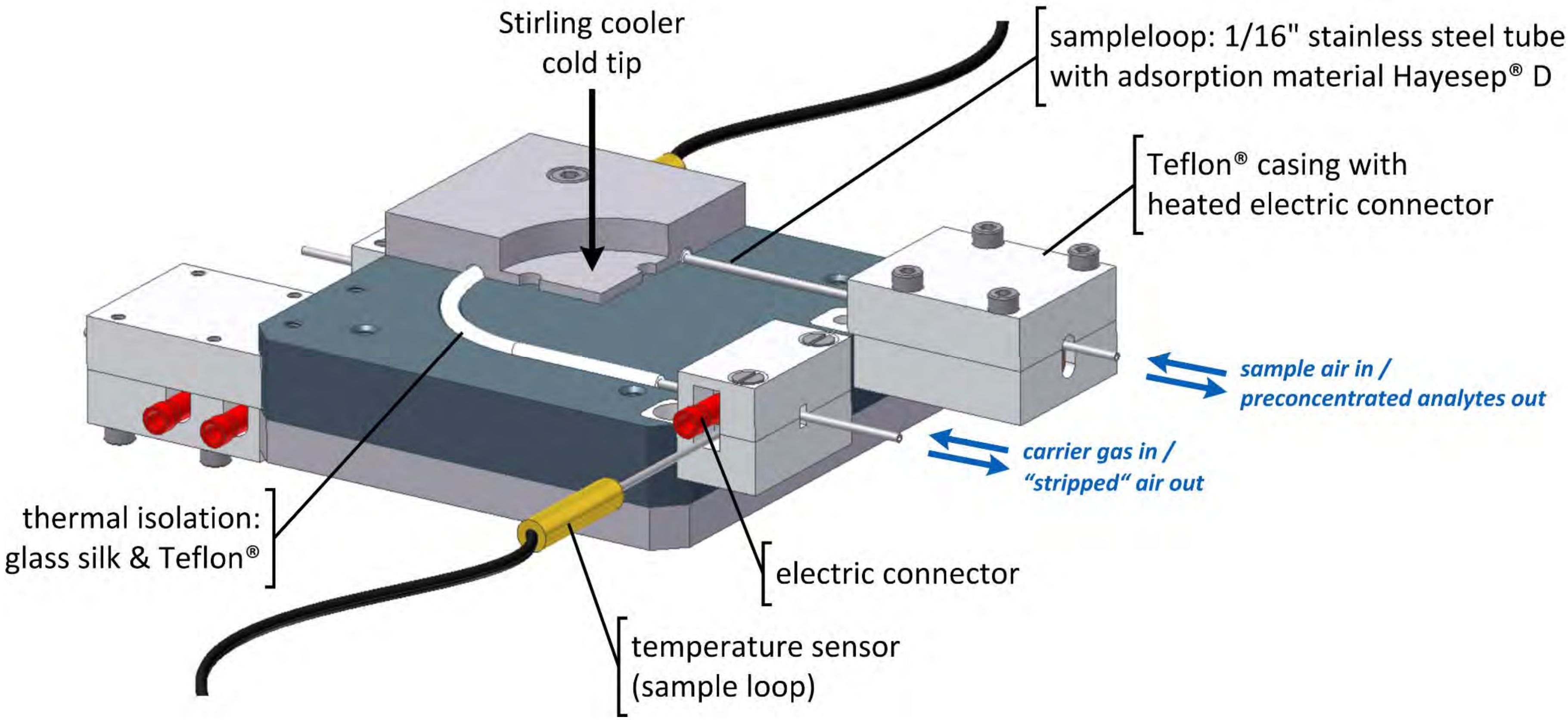
- **Rather slow mass spectrometer**

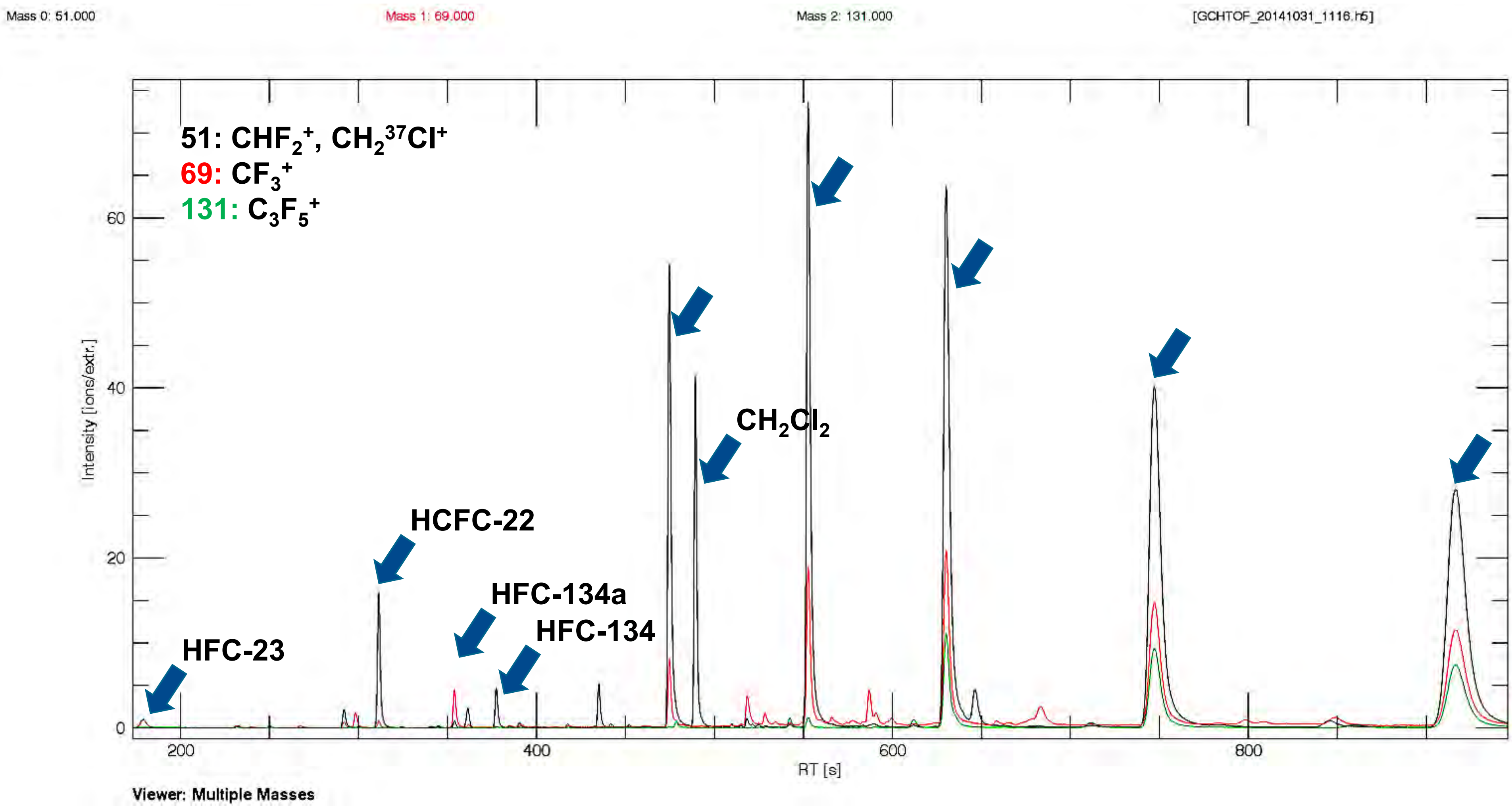
- ► **Time of Flight (TOF) MS is an alternative offering higher mass resolution, full scan information and acquisition rates of 100 Hz and more.**

Stirling-cooler based pre-concentration for two sample loops

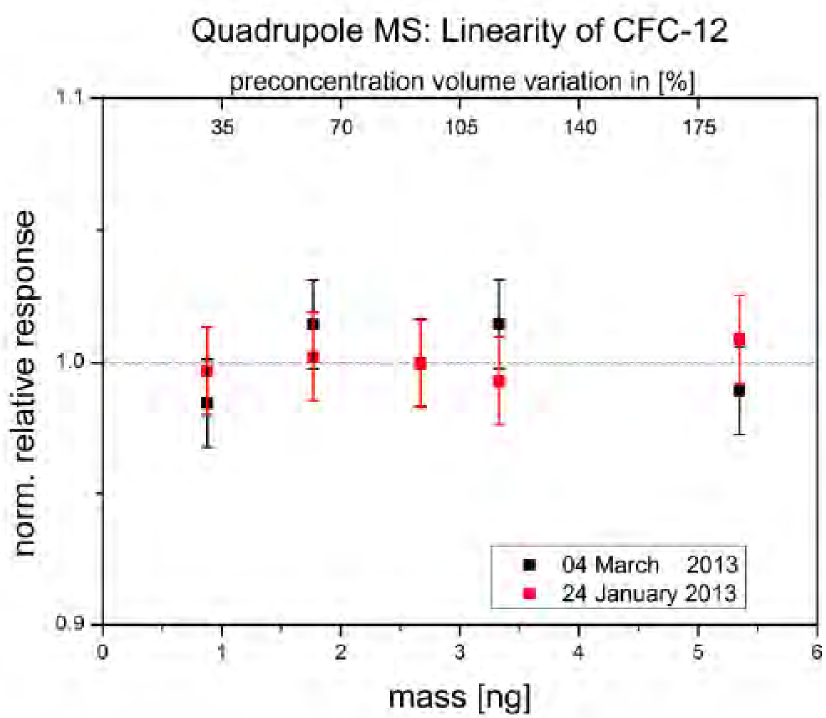


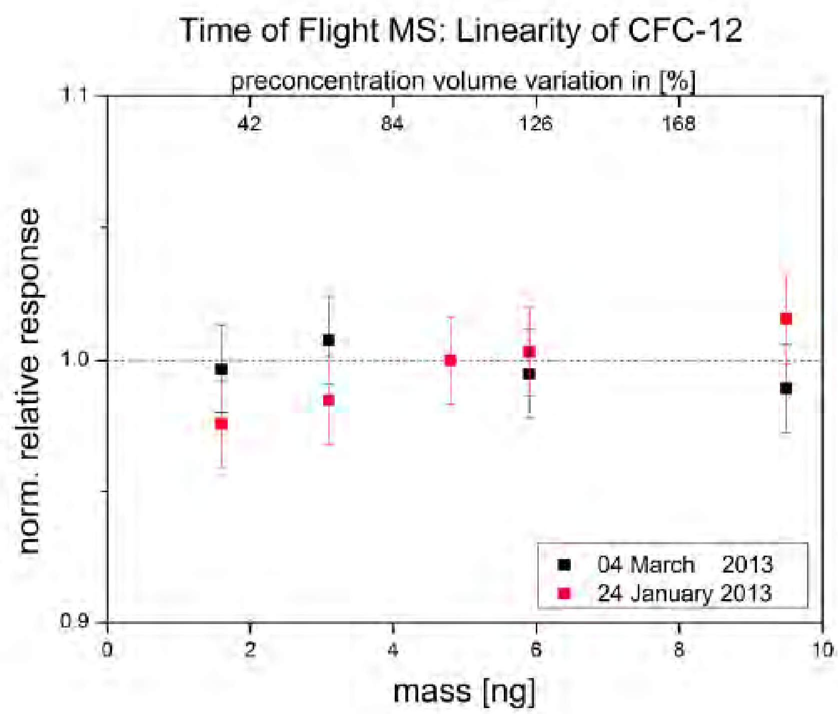
GC/HTOF instrument: full-scan mass information

- **Making use of full mass range spectra: identification**



Linearity: BenchTOF-dx and Quadrupole





all error bars are 3 sigma standard deviations

Examples of GC/TOF (BenchTOF) measurements: HFC-142b at Mace Head; comparision with NOAA

NOAA GC/MS flask data taken from ftp://ftp.cmdl.noaa.gov/hats; courtesy of Steve Montzka and Jim Elkins; scaled to AGAGE scale.

Examples of GC/TOF (BenchTOF) measurements: Halon 1211 at TO; comparison with GC/QP

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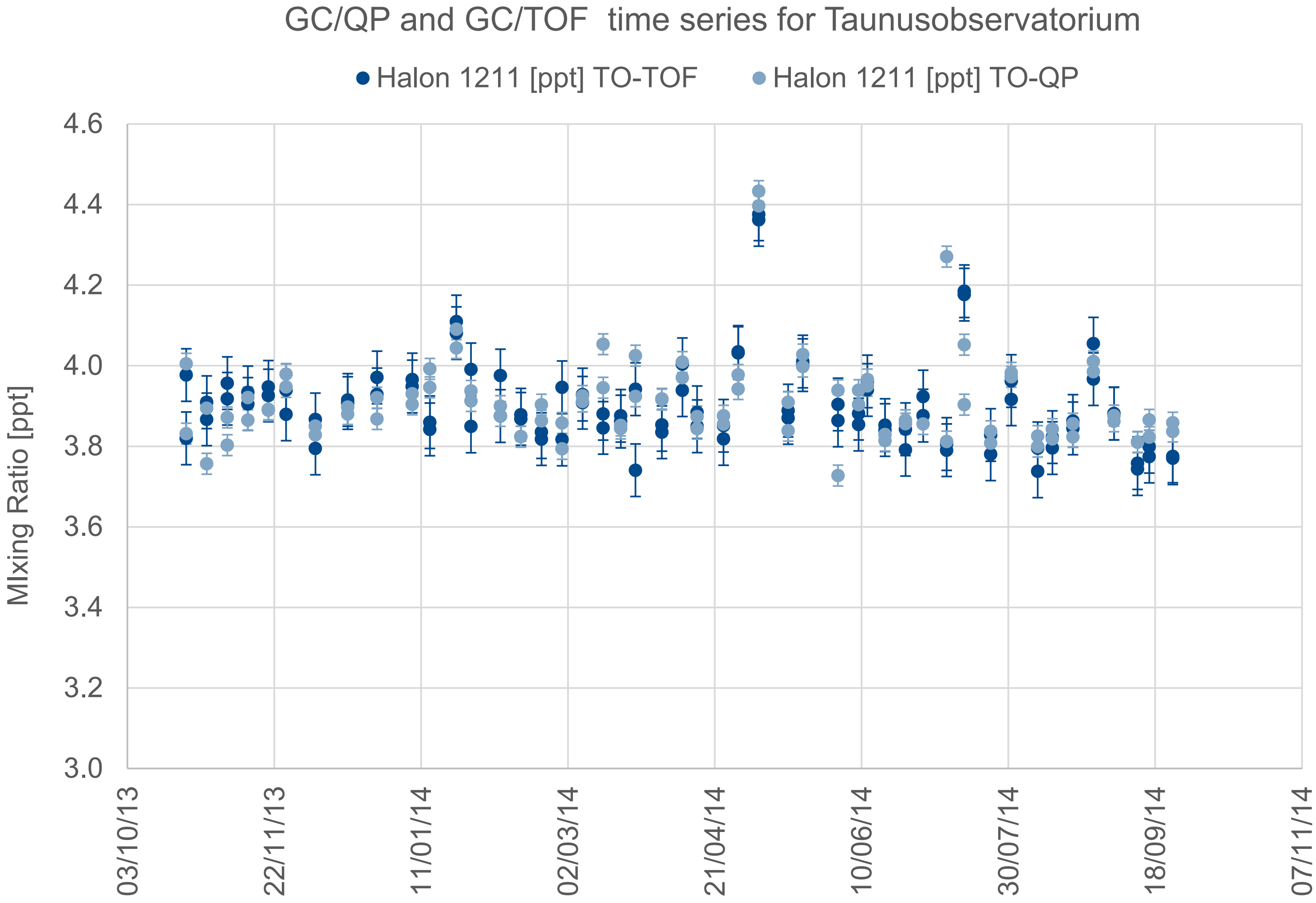

Examples of GC/TOF (BenchTOF) measurements: CFC 11 at TO; comparison with GC/QP

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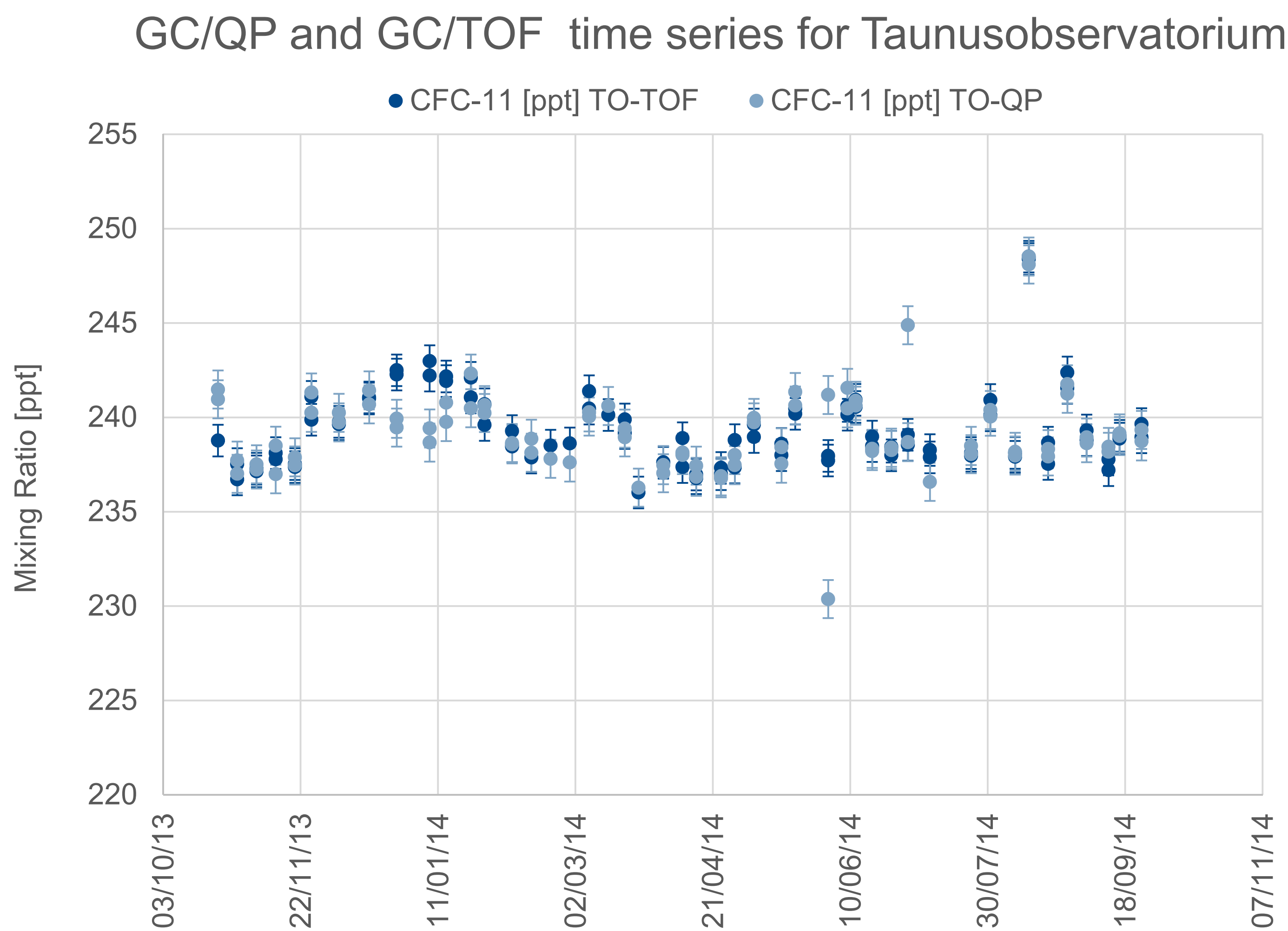

Examples of GC/TOF (BenchTOF) measurements: HCFC 142b at TO; comparison with GC/QP

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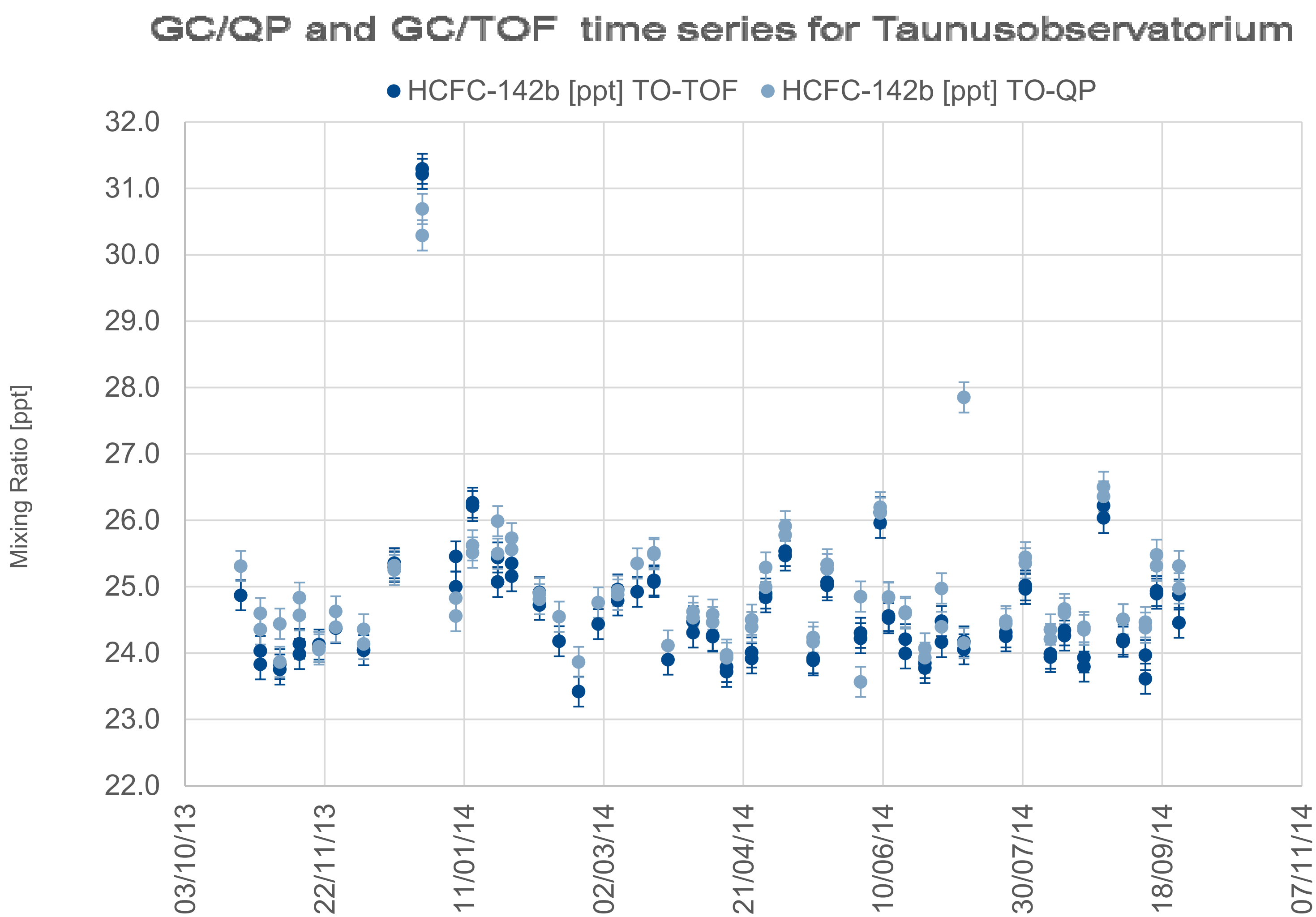
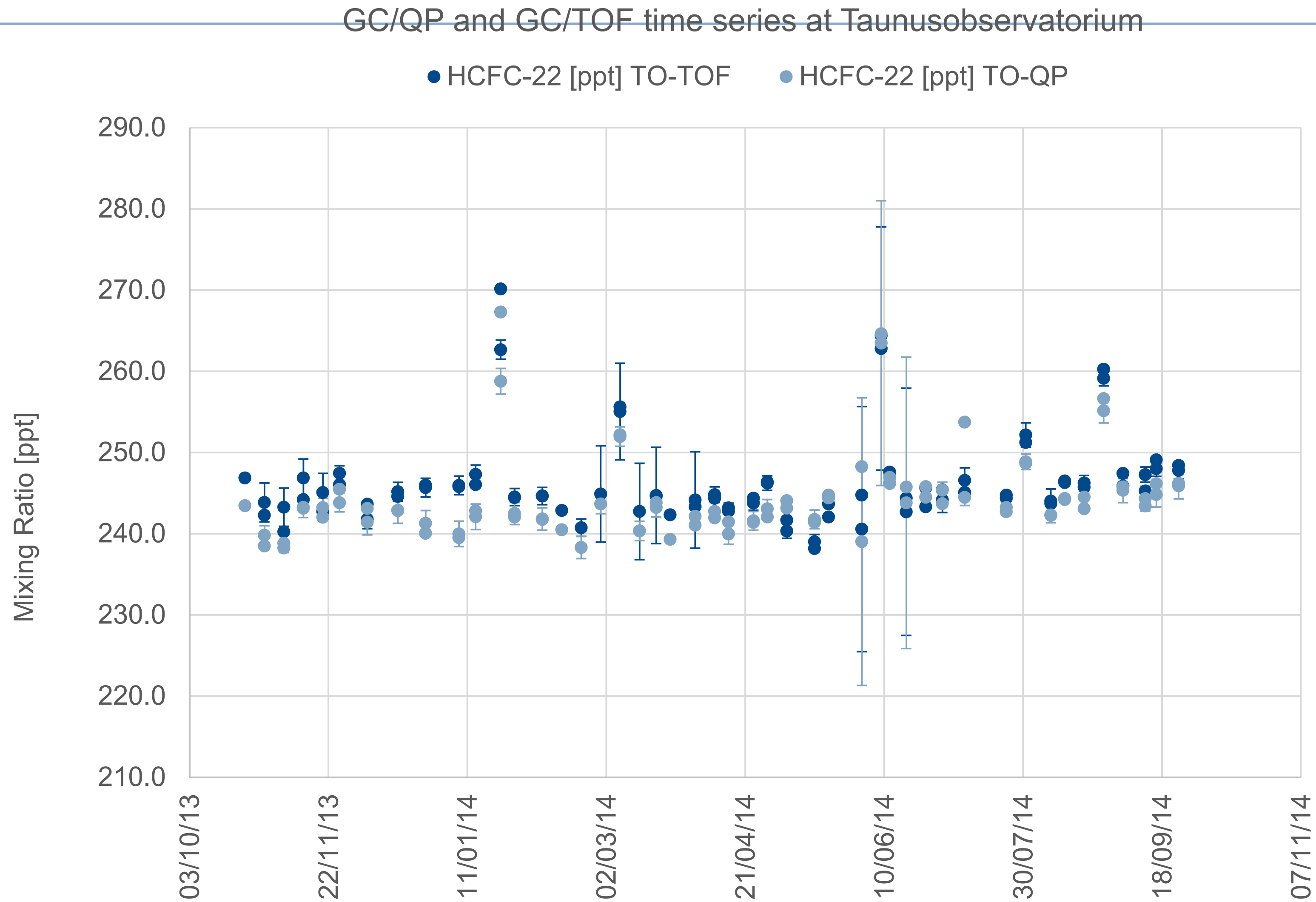


Examples of GC/TOF (BenchTOF) measurements: HCFC-22 at TO; comparison with GC/QP



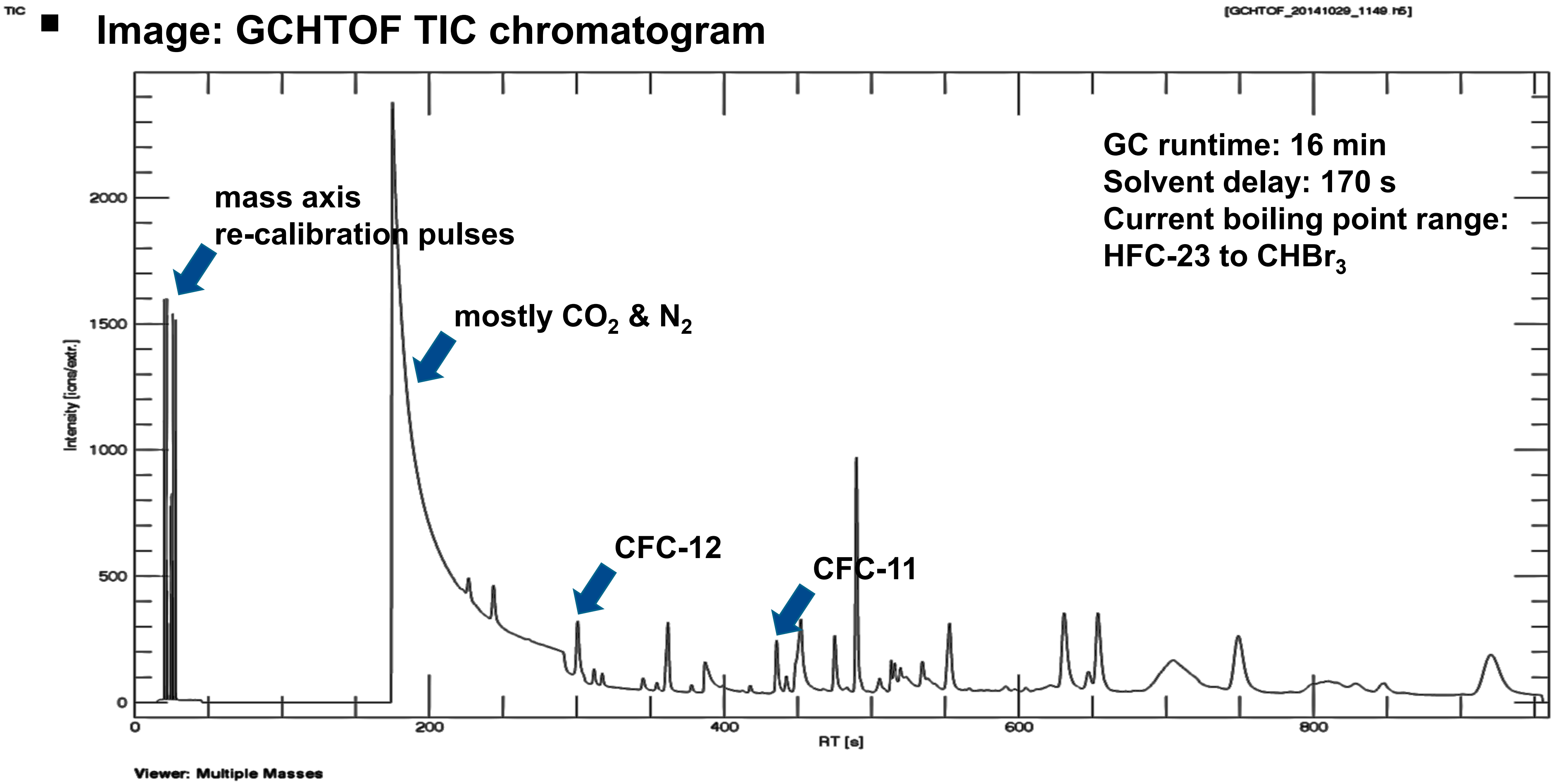
Limits of detection (S/N = 3) Alte Werte!!

- QP MS run in SIM mode, detecting several ions simultaneously (up to 6), running at 4 Hz, except *: only 1 ion measured
- C-TOF and H-TOF based on high concentration standard

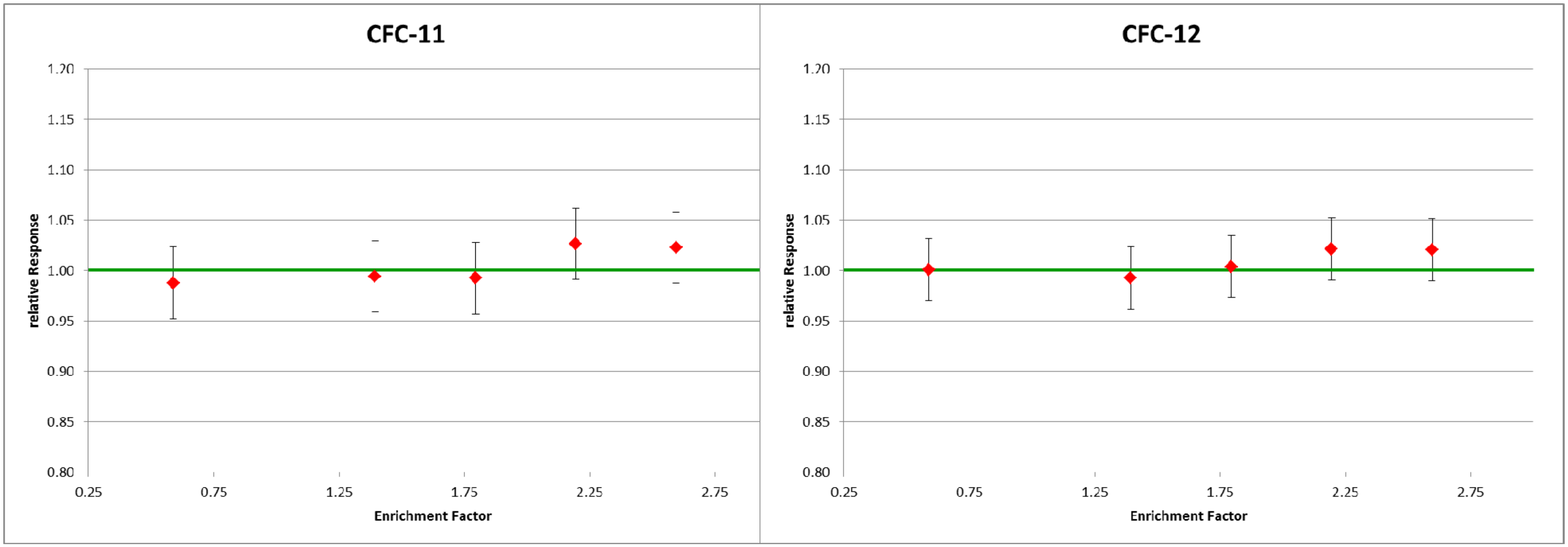
	MSD / LOD [pg]			
Substance	5975 QP	C-TOF	H-TOF	BenchTof-dx
CFC-11 (CCl_3F)	0.3*	0.15	0.16	0.15
CFC-12 (CCl_2F_2)	0.1*	n.d.	n.d.	0.10
CFC-113 ($C_2Cl_3F_3$)	1.69	0.25	0.19	0.32
CFC-114 ($C_2Cl_2F_4$)	1.60	0.23	0.13	0.19
Methylbromide	0.61	0.19	0.17	0.14
Dichloromethane	0.73	0.38	0.55	0.66
Methyliodide	0.09*	0.04	0.06	0.07
Tetrachloroethene	0.49	1.18	0.09	0.10
Tetrachloromethane	1.17	0.61	0.12	0.43
Chloroform	0.59	0.61	0.26	0.18

GC/HTOF instrument

- Assembly & construction phase finished in Oct 2014
- Current phase: instrument characterization
- Image: GCHTOF TIC chromatogram

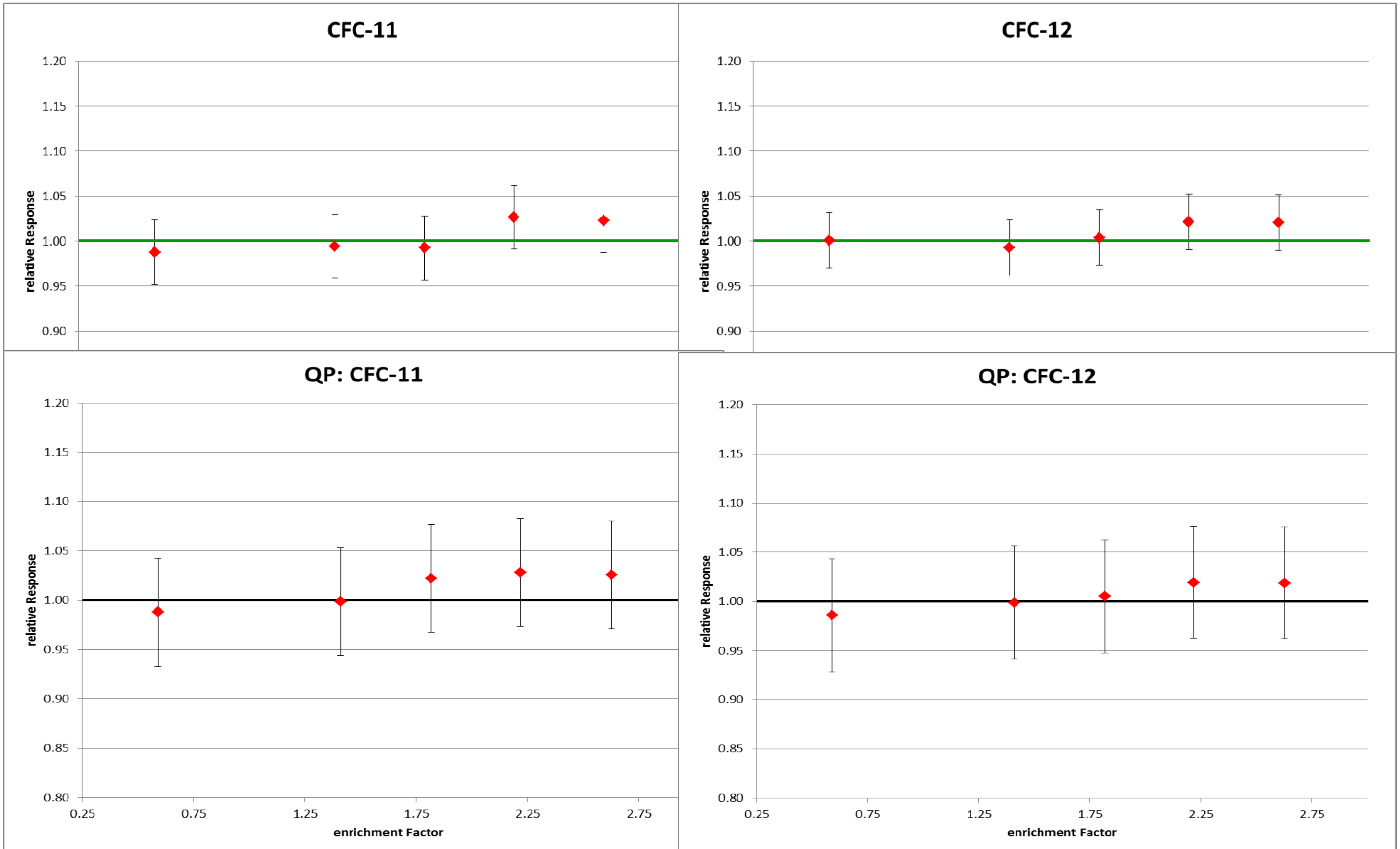


Linearity C-TOF

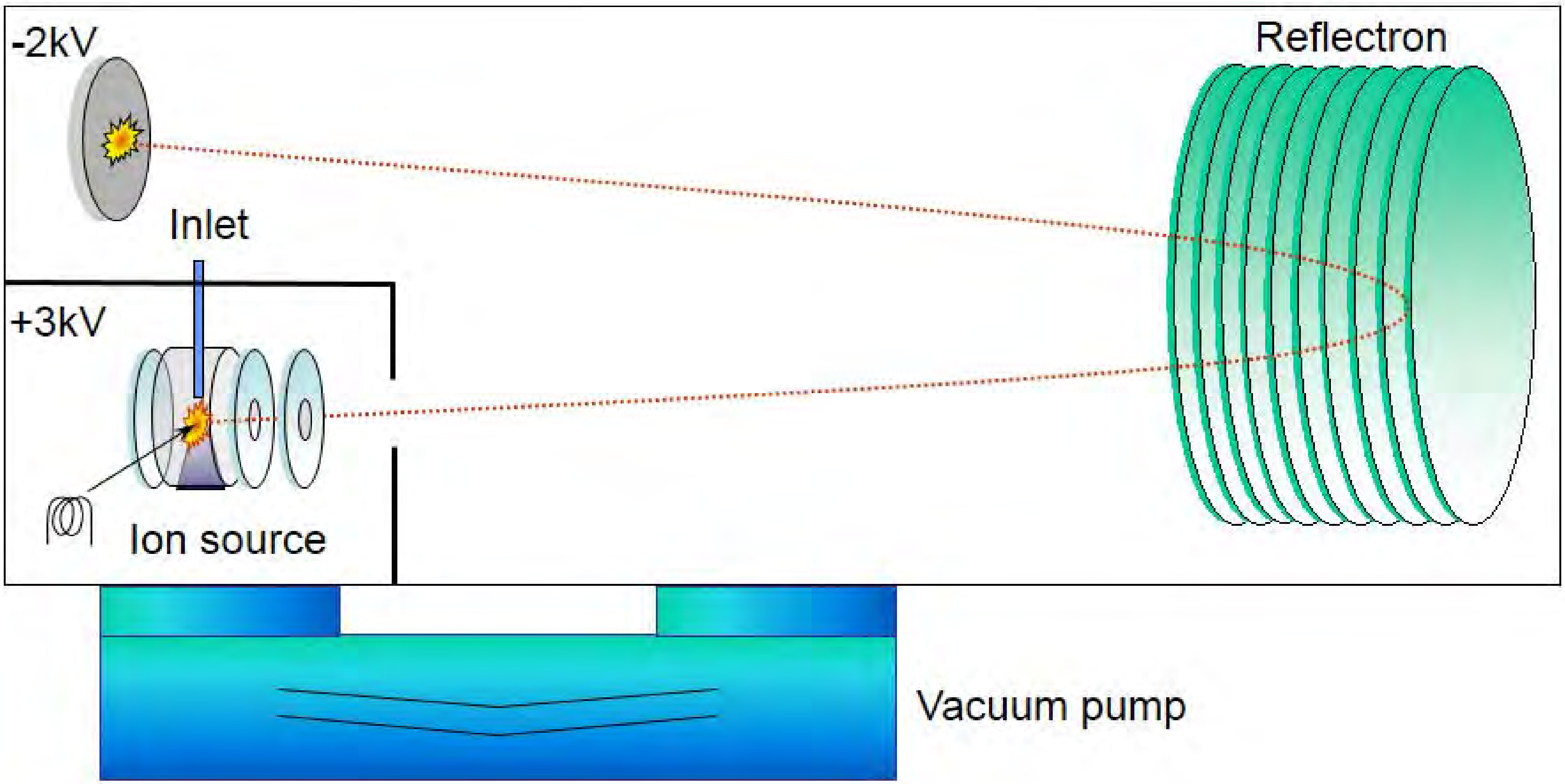


- all error bars are 3 sigma standard deviations; measurements performed at Tofwerk using mobile GC-MS system.
- Linearity is very similar to quadrupole: deviations from 1 are probably not an MS-effect.

Linearity C-TOF



The BenchTOF-dx: direct extraction



The H-TOF (and C-TOF) instrument: orthogonal extraction