HALOSEARCH: Searching for Unknown Halocarbons in the Atmosphere

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Agenda

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- Introduction: context, substances, measurement network
- Measurement method
- Data
- Identification method
- Example with CFC-11
- Take-home message

Vision

- To identify all trace gases in the atmosphere containing halogen, sulfur, silicon – relevant for environment, climate and public health

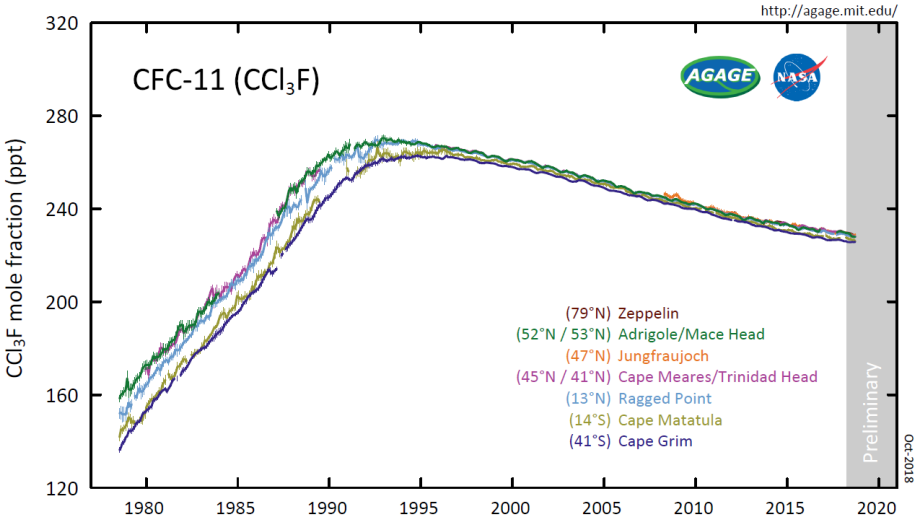
- To be prepared for target screening of expected pollutants *before* emissions to the atmosphere start

Need for global atmospheric measurement network

- E.g.: Montreal Protocol, monitoring of ozone depleting substances → protection of ozone layer




1978: Start of ALE (Atmospheric Lifetime Experiment)



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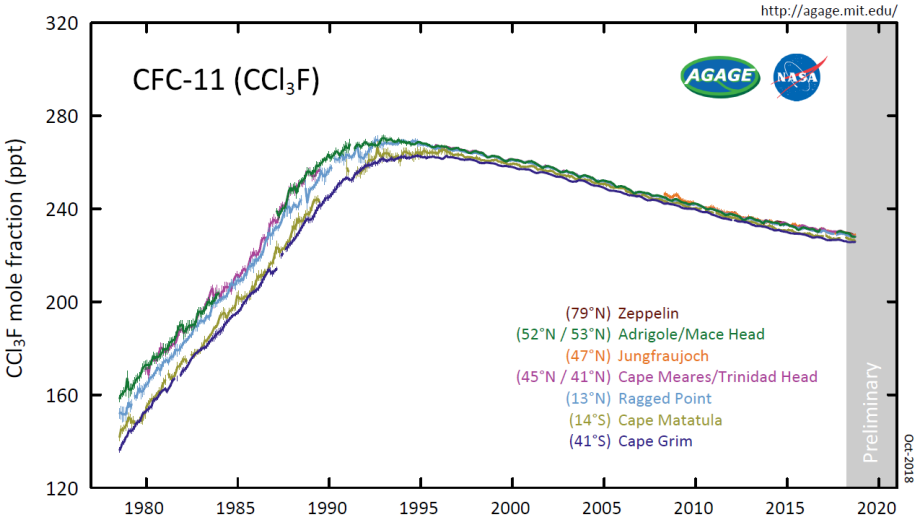
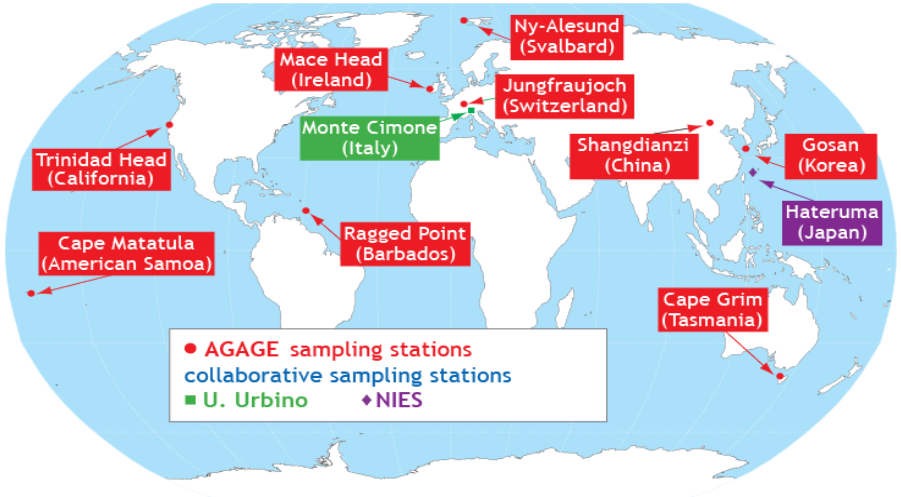


AGAGE in 2019



Four generations of halogenated compounds (simplified)

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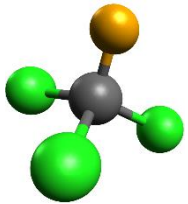
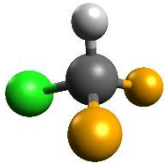
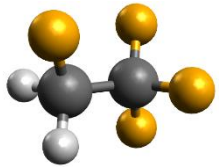
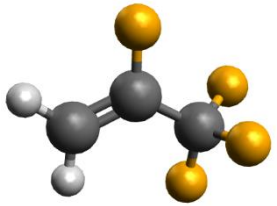
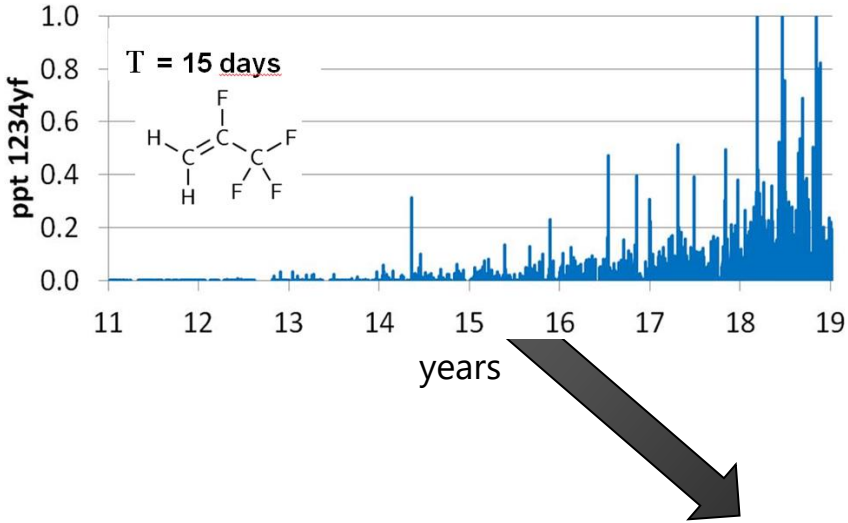
Generation	I	II	III	IV
	CFC **c**hloro**f**luoro**c**arbon	HCFC **h**ydro**c**hloro**f**luoro**c**arbon	HFC **h**ydro**f**luoro**c**arbon	HFO **h**ydro**f**luoro**o**lefin
Example	R11 Trichlorofluoromethane	R22 Chlorodifluoromethane	R134a Tetrafluoroethane	R1234yf Tetrafluoropropene
				
ODP GWP	1 4'660	0.05 1'760	0 1'300	0 <4
Phase-out	Montreal-Protocol 1987 – 2010	Montreal-Protocol 2004 – 2030	Kyoto-Protocol MP Kigali-Amendment 2019 – 2048	

Justification: environment, public health, safety

- HFO-1234yf: used in air conditioners of new cars
- Unknown environmental/health effects of new substances / by products / decomposition products
- Strength of AGAGE network: implementation of worldwide target screening of newly detected substance can happen in < 1 year

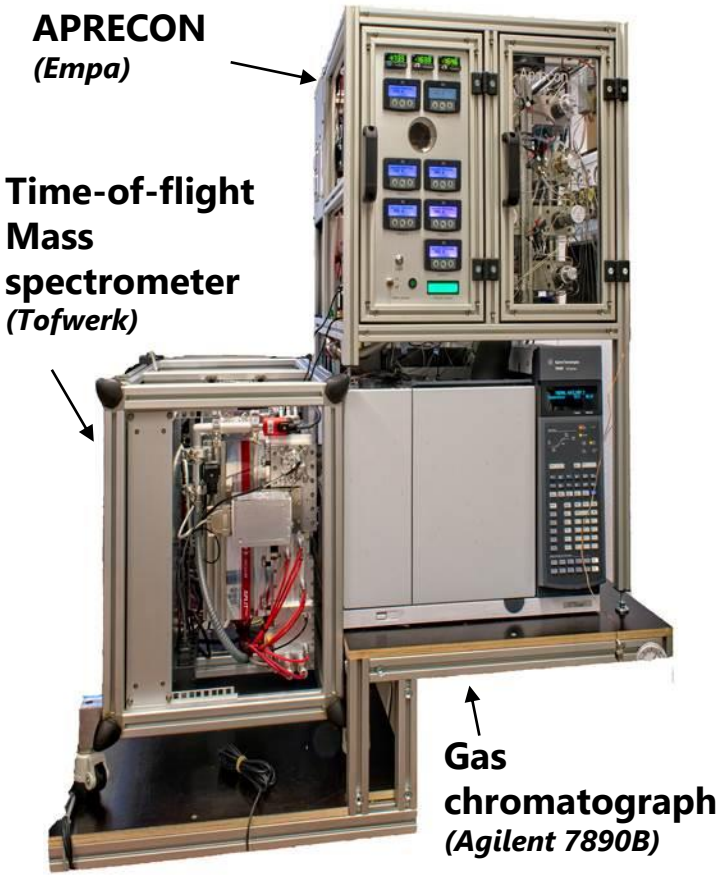


Data from Jungfraujoch, CH

HFO-1234yf catches fire at Mercedes

Measurement method

- APRECON-GC-MS: advanced preconcentration – gas chromatograph - time of flight mass spectrometer
- Data acquisition: preconcentration + analysis 1h10 min
- File size: 500 MB



Atmospheric data

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- Mass range of molecules: 26 (ethyne) to < 300
- Mass range of fragments: 24 ($C_2H_2^+$) to 293 ($C_7F_{11}^+$)
- Small masses → Use TOF-MS instrument (not e.g. Orbitrap)
- Number of atoms per fragment: 1 (Cl^+,…) to 18 ($C_7F_{11}^+$)
- Many isomers: identification by fragments → hard ionisation, EI
- Many isotopologues with clear pattern (with Cl, Br, C, O, S, N)

Molecule identification: Route

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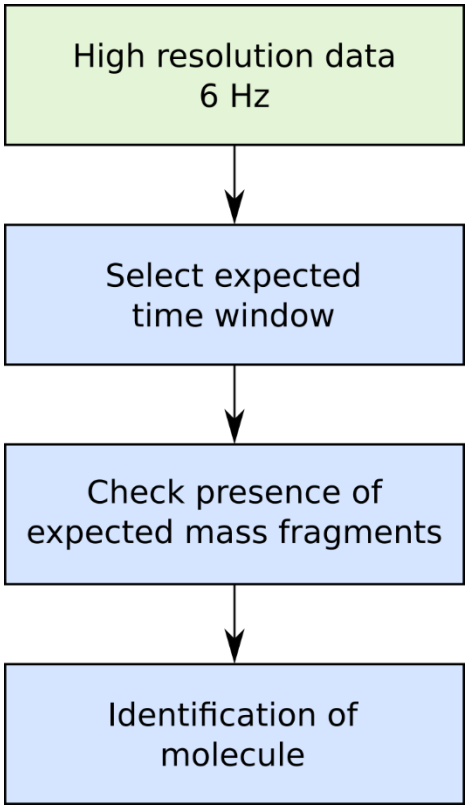
- Automated identification
- Automated quality control on identification
- Confidence estimate
- Efficient data processing – in less time than needed for acquisition!
- Intelligent process: robust with varying sample properties
- Programming language: Python

Workflow

Target analysis



Workflow

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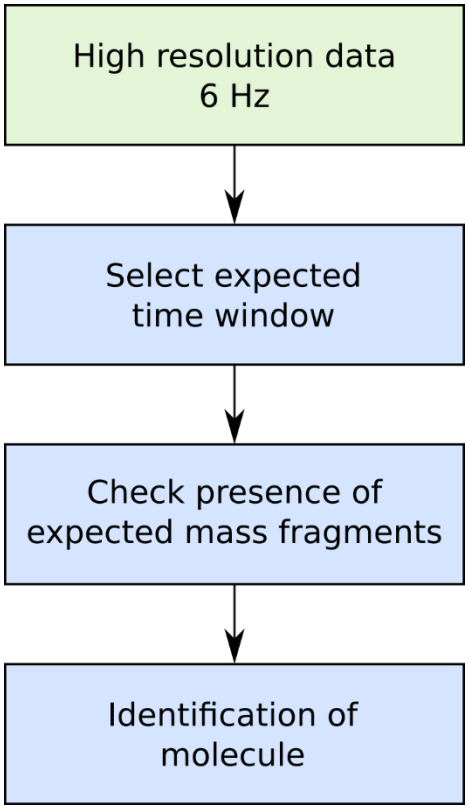
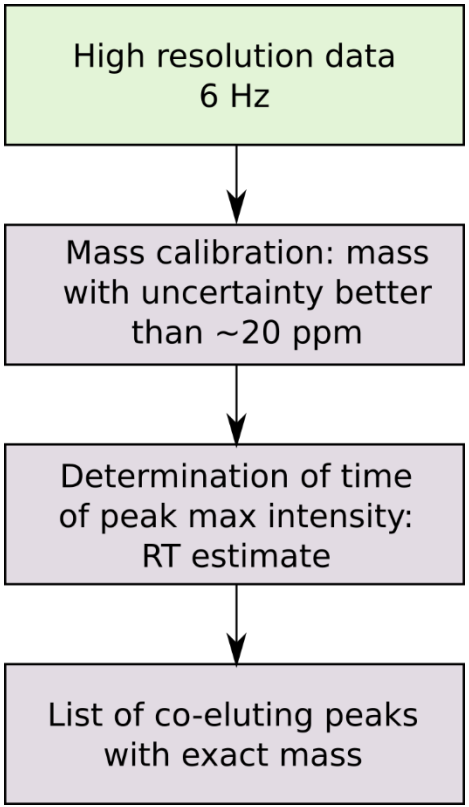
Target analysis



Non-target analysis



Find formula for each mass
-> knapsack!

Workflow: Knapsack algorithm

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Weight: 100.936 ± 0.002 g/mol (U = 20 ppm)

Expected number of solutions

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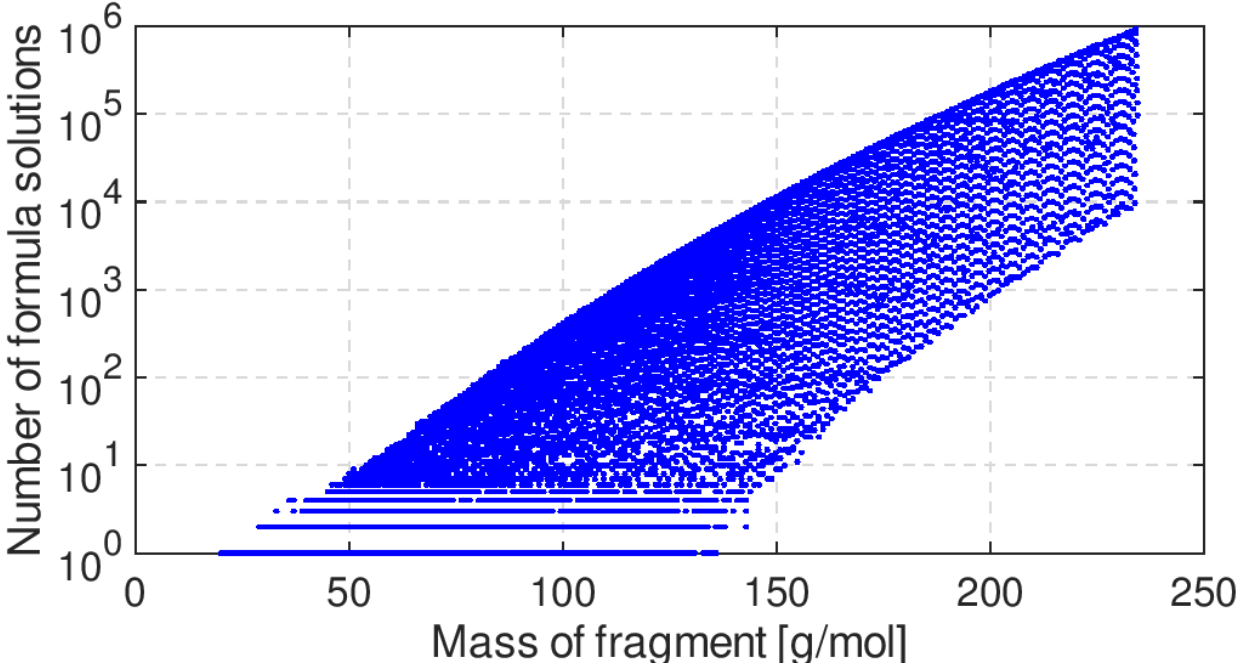
- 22 atoms: H, B, C, N, O, F, Si, S, Cl, Br, I + stable isotopes
- Until mass 120, nb of solutions <1000
- Fast, exact and complete calculations possible



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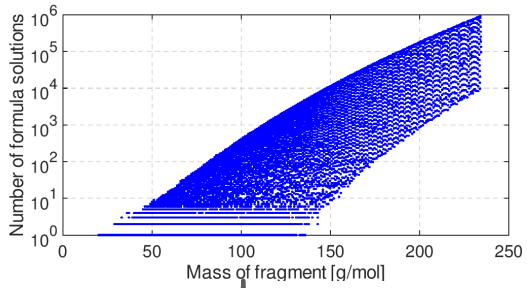

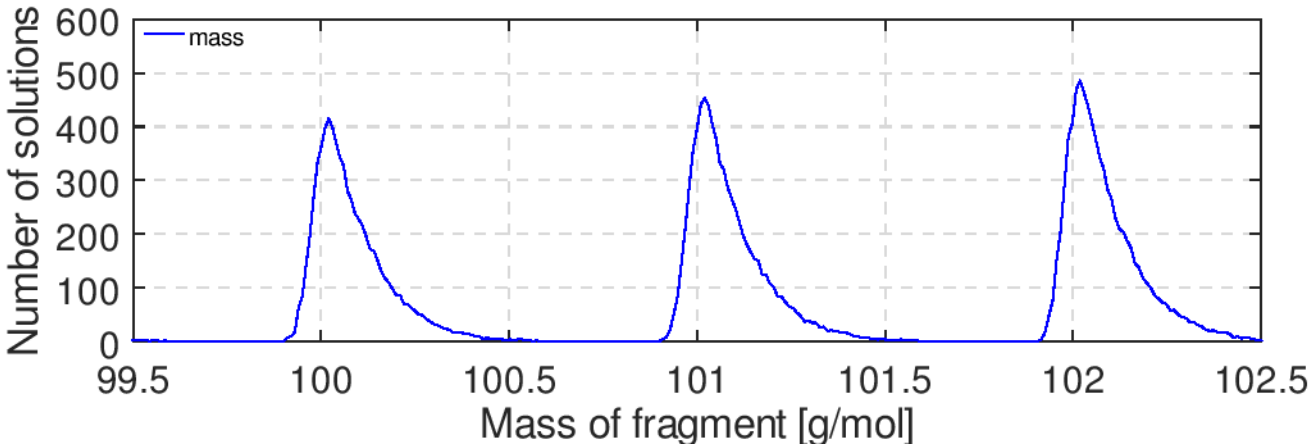

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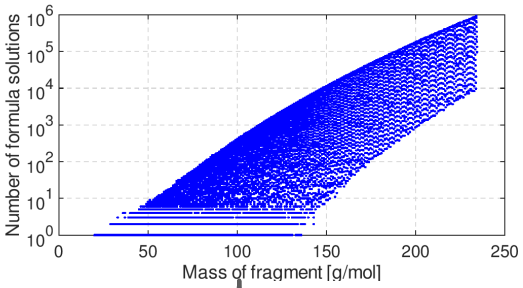
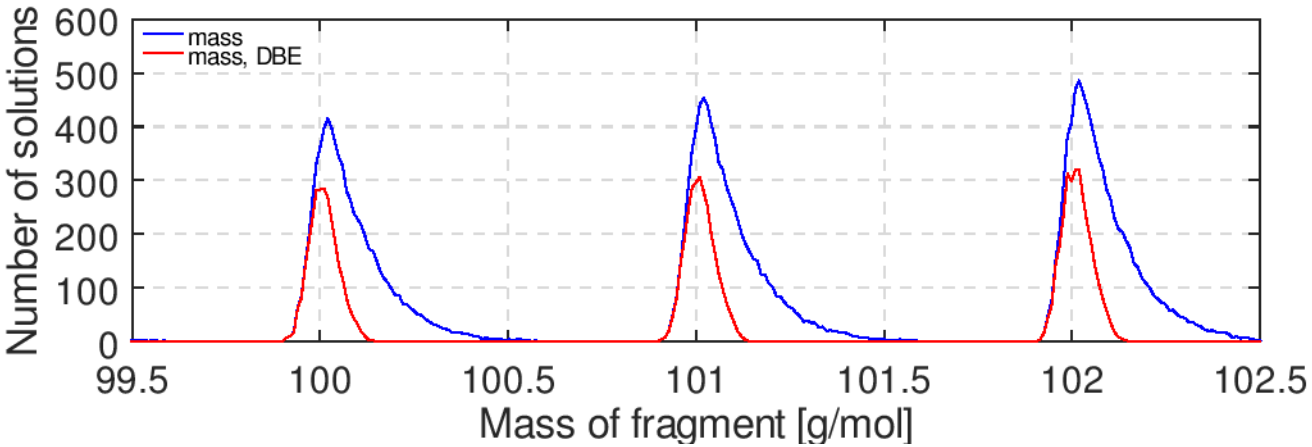


- DBE: double bound equivalent, ‘chemistry rule’

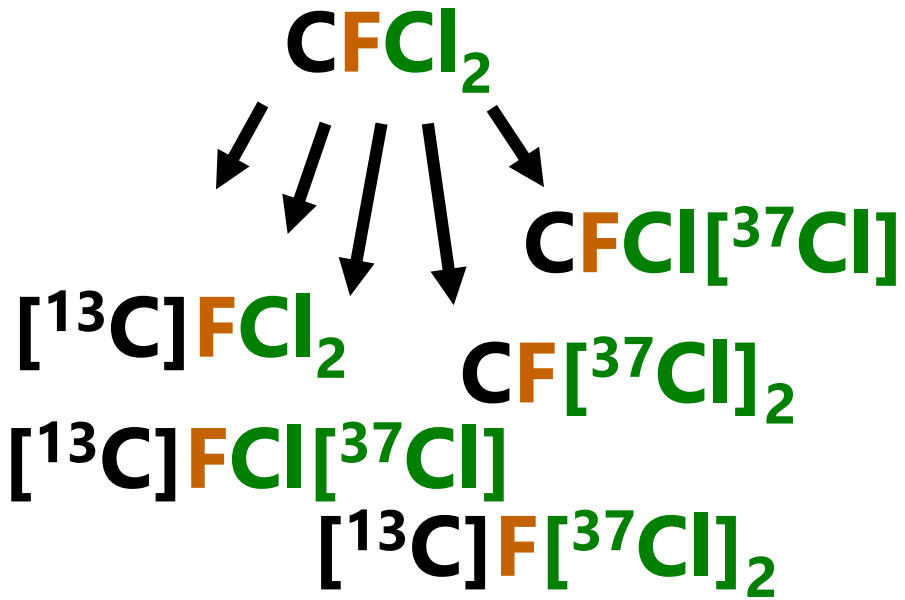
$$DBE = 1 + 0.5 \sum N_i \, (V_i - 2)$$

- All formula with DBE < 0 eliminated



Real data: Number of solutions – with mass, DBE and isotopes

- For each abundant isotopologue, generate rare ones (several)



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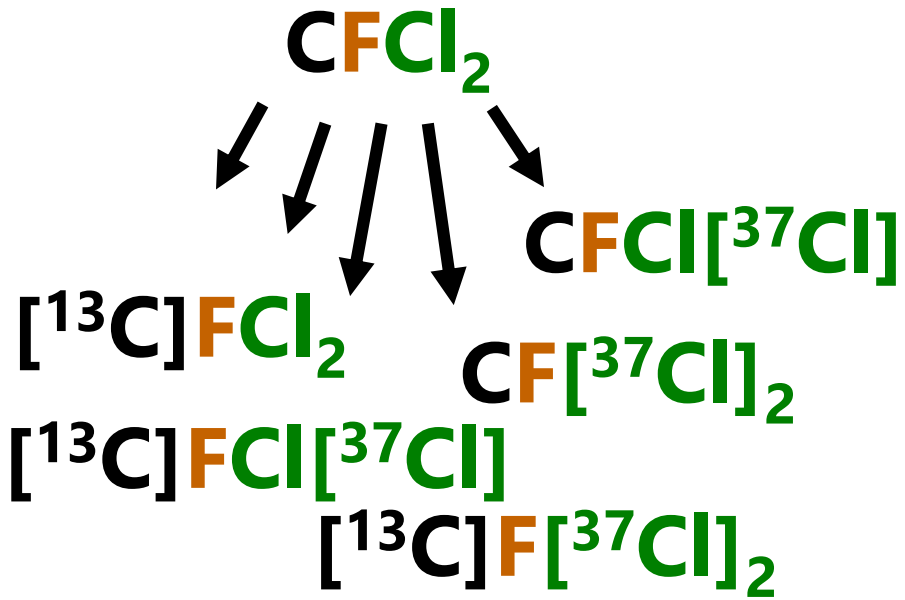
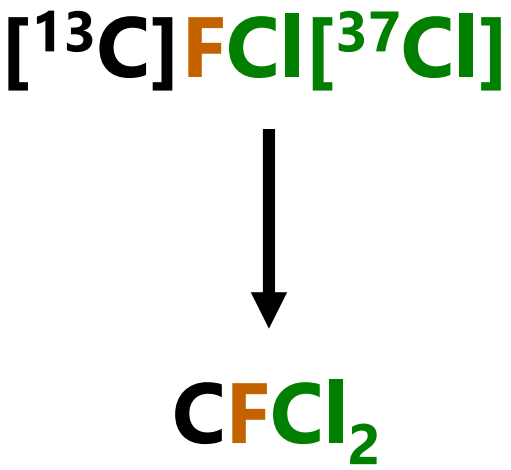
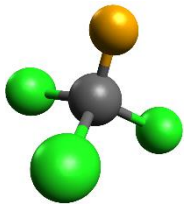


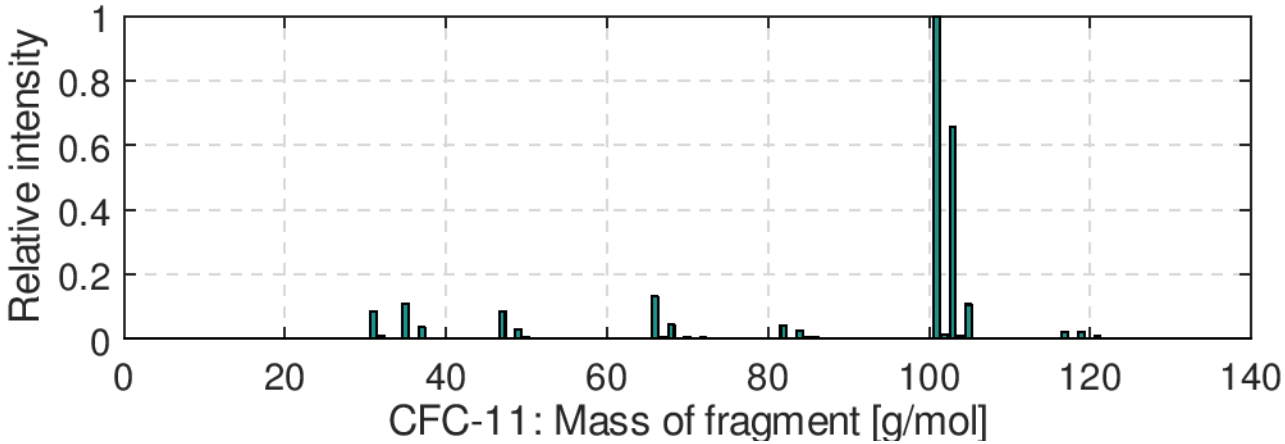
- For each rare isotopologue, generate abundant one (just one)



Example: CFC-11



$CFCl_3$



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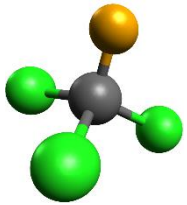

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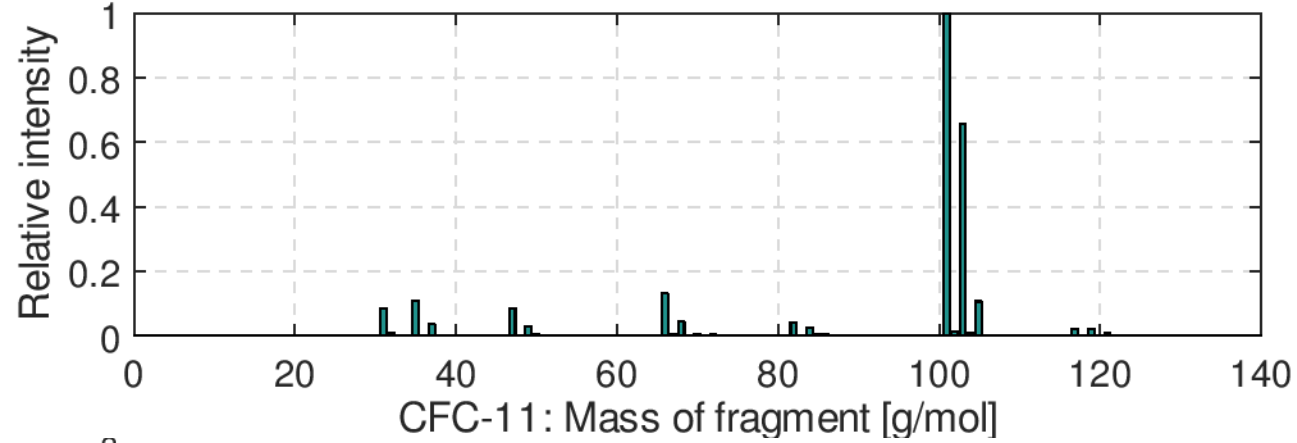

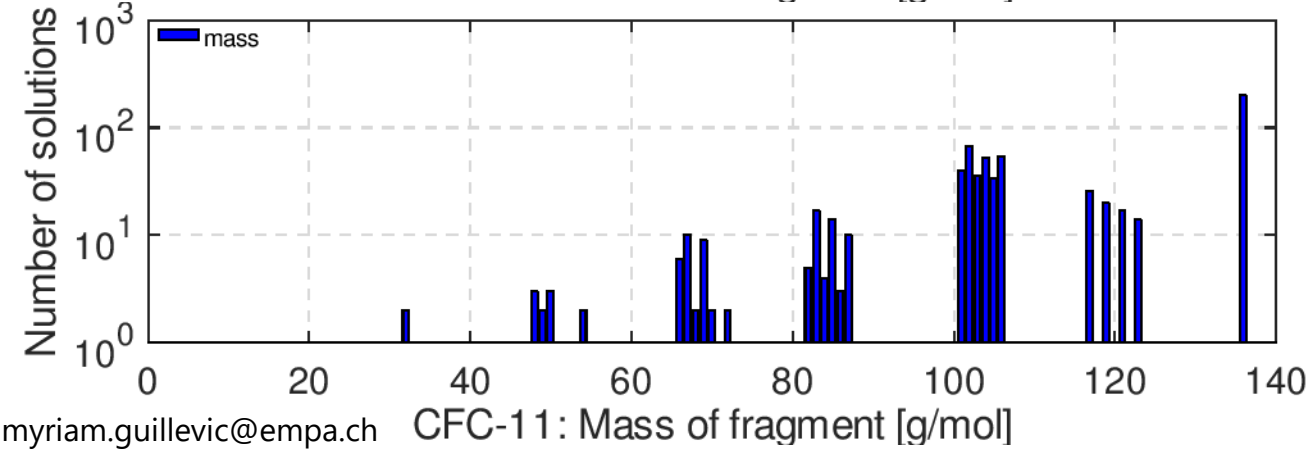

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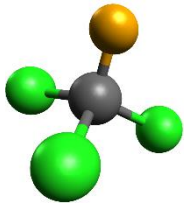

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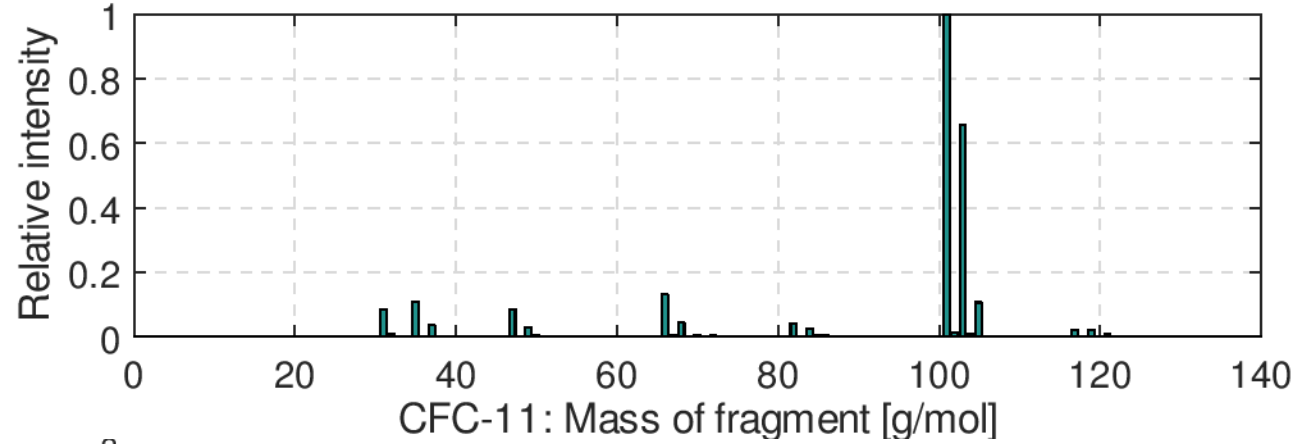

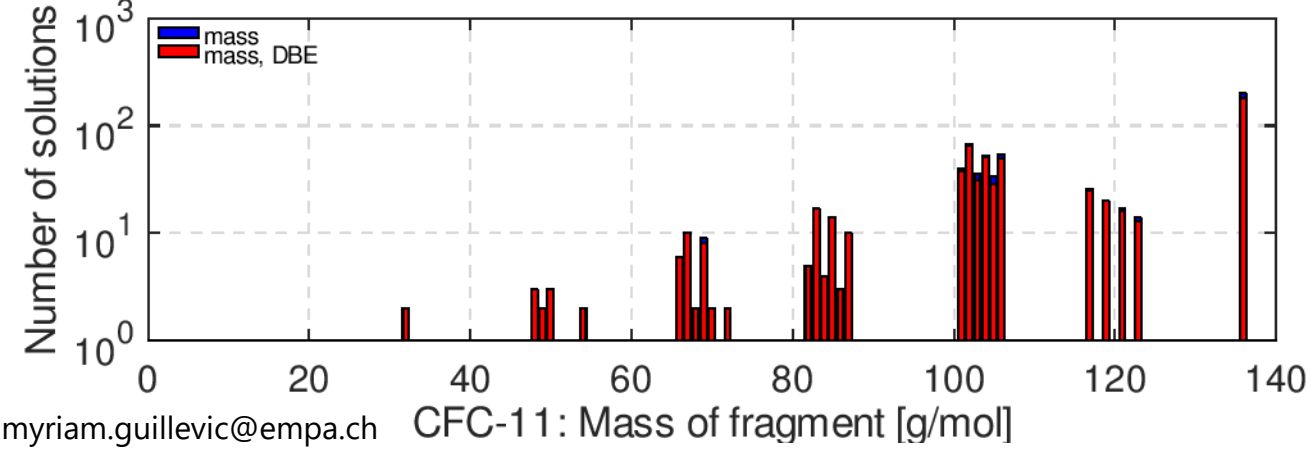

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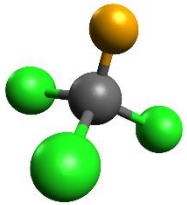

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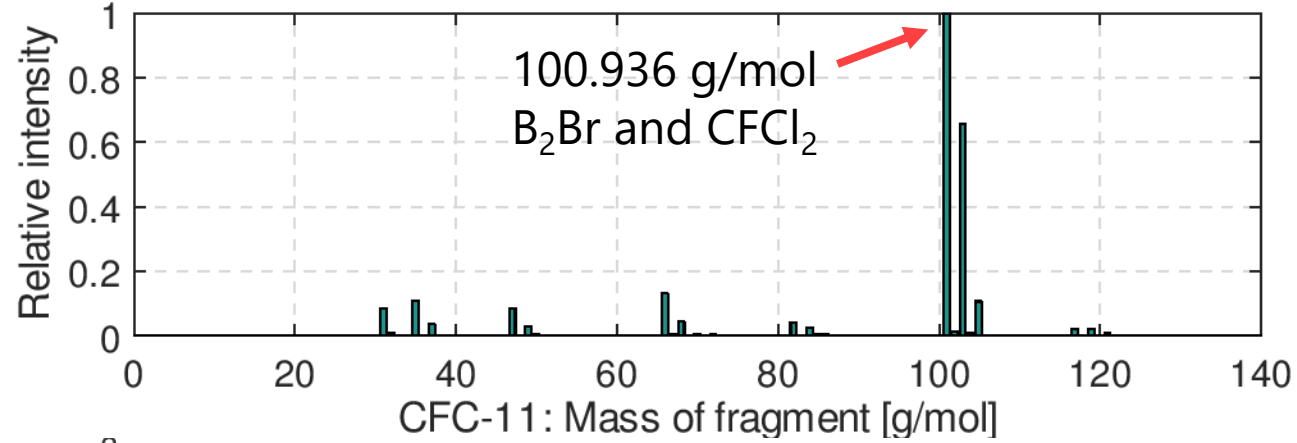
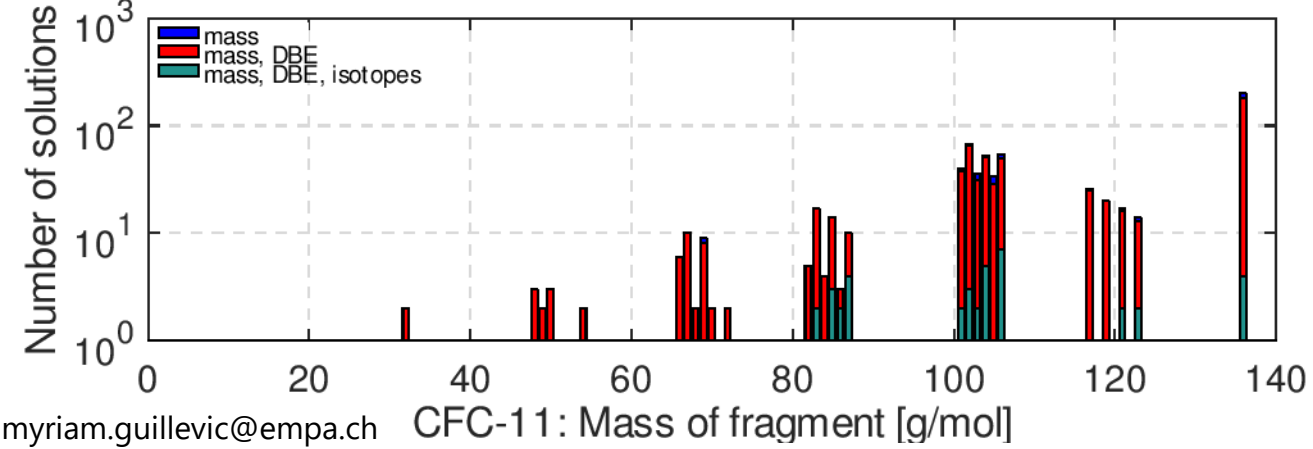
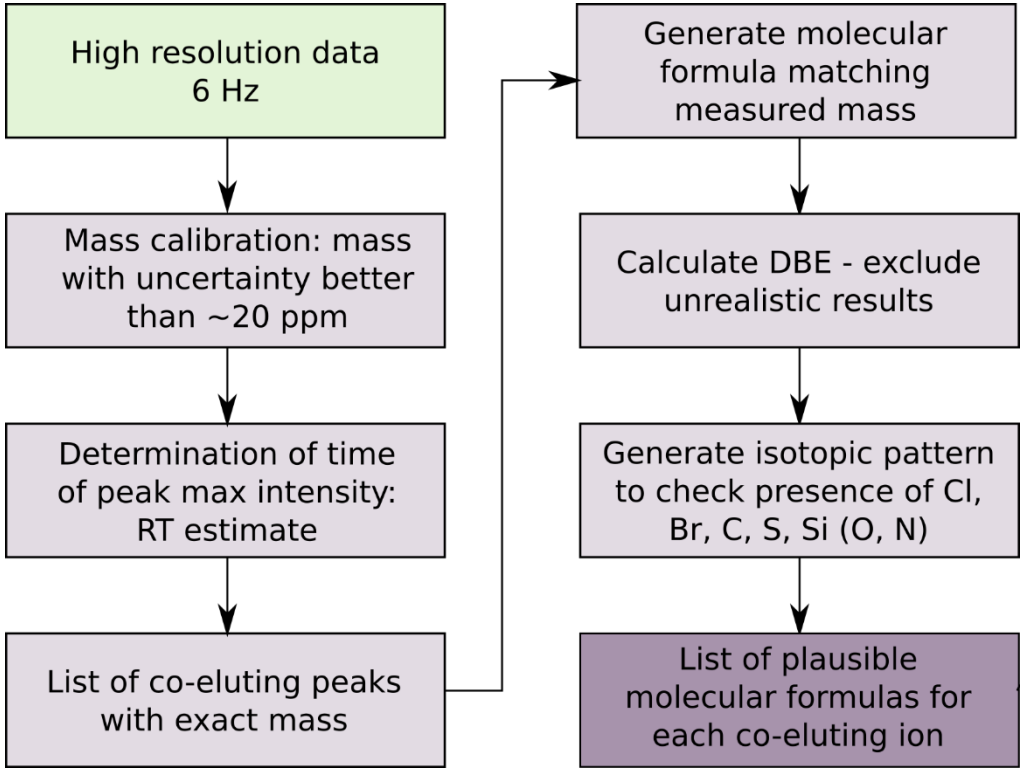




Workflow: overview



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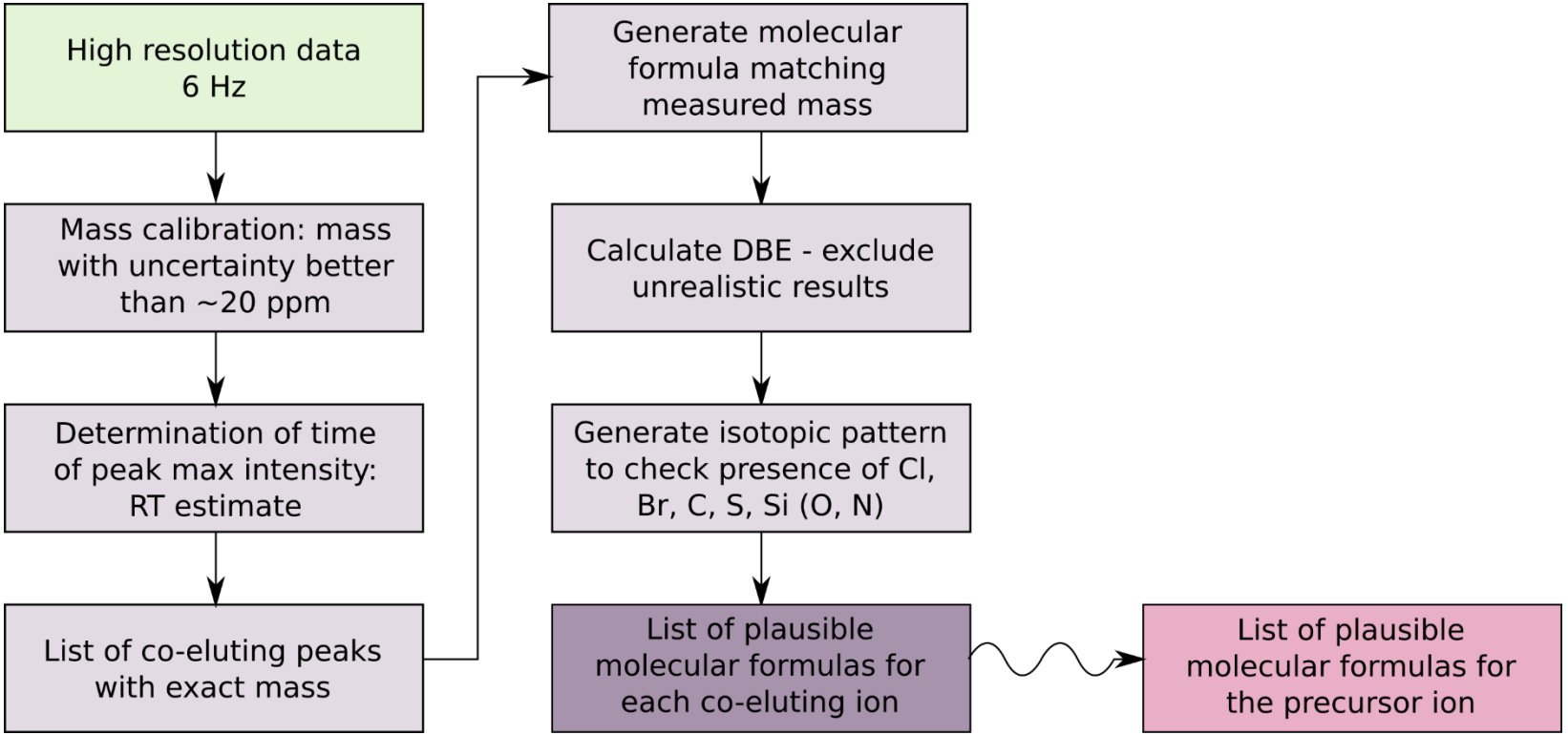

Take-home message

- Trace gases in the atmosphere: small molecules
- Many exact calculations are possible
- Fragment identification: using TOF exact mass, DBE, isotopic pattern
- Molecule identification: in progress
  - Build molecule from fragment
  - Soft ionisation
  - Retention time
  - Comparison to NIST data converted to high resolution
- Any inputs welcome!

Thank you for your attention!

We acknowledge Tofwerk and Aerodyne for technical support

Contact: myriam.guillevic@empa.ch