HALOSEARCH: Searching for Unknown Halocarbons in the Atmosphere

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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)

http://agage.mit.edu/
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AGAGE in 2019

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Four generations of halogenated compounds (simplified)

<table>
<thead>
<tr>
<th>Generation</th>
<th>Example</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CFC</td>
<td>1</td>
<td>4'660</td>
</tr>
<tr>
<td>I</td>
<td>HCFC</td>
<td>0.05</td>
<td>1'760</td>
</tr>
<tr>
<td>II</td>
<td>HFC</td>
<td>0</td>
<td>&lt;4</td>
</tr>
<tr>
<td>III</td>
<td>HFO</td>
<td>0</td>
<td>1'300</td>
</tr>
</tbody>
</table>

- R11: Trichlorofluoromethane
- R22: Chlorodifluoromethane
- R134a: Tetrafluoroethane
- R1234yf: Tetrafluoropropene

Montreal-Protocol
1987 – 2010

Kyoto-Protocol
2004 – 2030

MP Kigali-Amendment
2019 – 2048

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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

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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

- 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

- 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

1. High resolution data
   6 Hz

2. Select expected
time window

3. Check presence of
expected mass fragments

4. Identification of
molecule
Find formula for each mass
-> knapsack!
Workflow: Knapsack algorithm

Weight: 100.936 ± 0.002 g/mol (U = 20 ppm)
Expected number of solutions

- Until mass 120, nb of solutions <1000
- Fast, exact and complete calculations possible
Expected number of solutions

![Graph showing the expected number of solutions versus mass of fragment (g/mol). The graph includes two plots: one showing the number of formula solutions on a log scale, and another showing the number of solutions for a specific mass range.]

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Expected number of solutions

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

- For each abundant isotopologue, generate rare ones (several)
- For each rare isotopologue, generate abundant one (just one)
Example: CFC-11

CFCl₃

CFC-11: Mass of fragment [g/mol]

Relative intensity

0 0.2 0.4 0.6 0.8 1

0 20 40 60 80 100 120 140
Example: CFC-11

CFCl₃

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Example: CFC-11

CFCl$_3$
Example: CFC-11

\[
\begin{align*}
\text{CFCl}_3 & \quad \text{100.936 g/mol} \\
B_2\text{Br} \text{ and CFCl}_2
\end{align*}
\]
Workflow: overview

High resolution data 6 Hz

Mass calibration: mass with uncertainty better than ~20 ppm

Determination of time of peak max intensity: RT estimate

List of co-eluting peaks with exact mass

Generate molecular formula matching measured mass

Calculate DBE - exclude unrealistic results

Generate isotopic pattern to check presence of Cl, Br, C, S, Si (O, N)

List of plausible molecular formulas for each co-eluting ion
Workflow: overview

High resolution data 6 Hz

Mass calibration: mass with uncertainty better than ~20 ppm

Determination of time of peak max intensity: RT estimate

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Generate molecular formula matching measured mass

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List of plausible molecular formulas for each co-eluting ion

List of plausible molecular formulas for the precursor ion

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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!

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