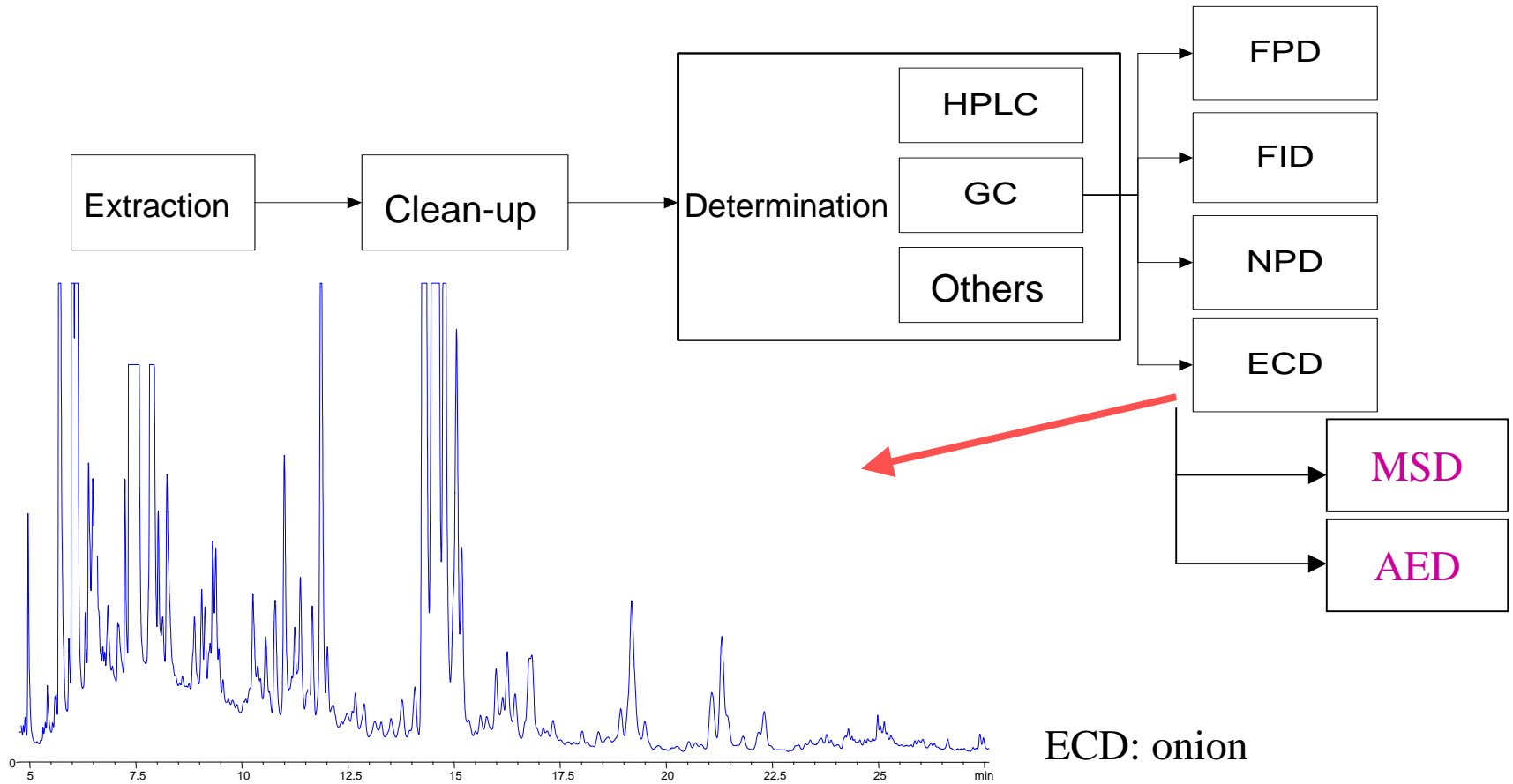


Simple identification of toxic substances in food through combination of GC-AED and GC-MS

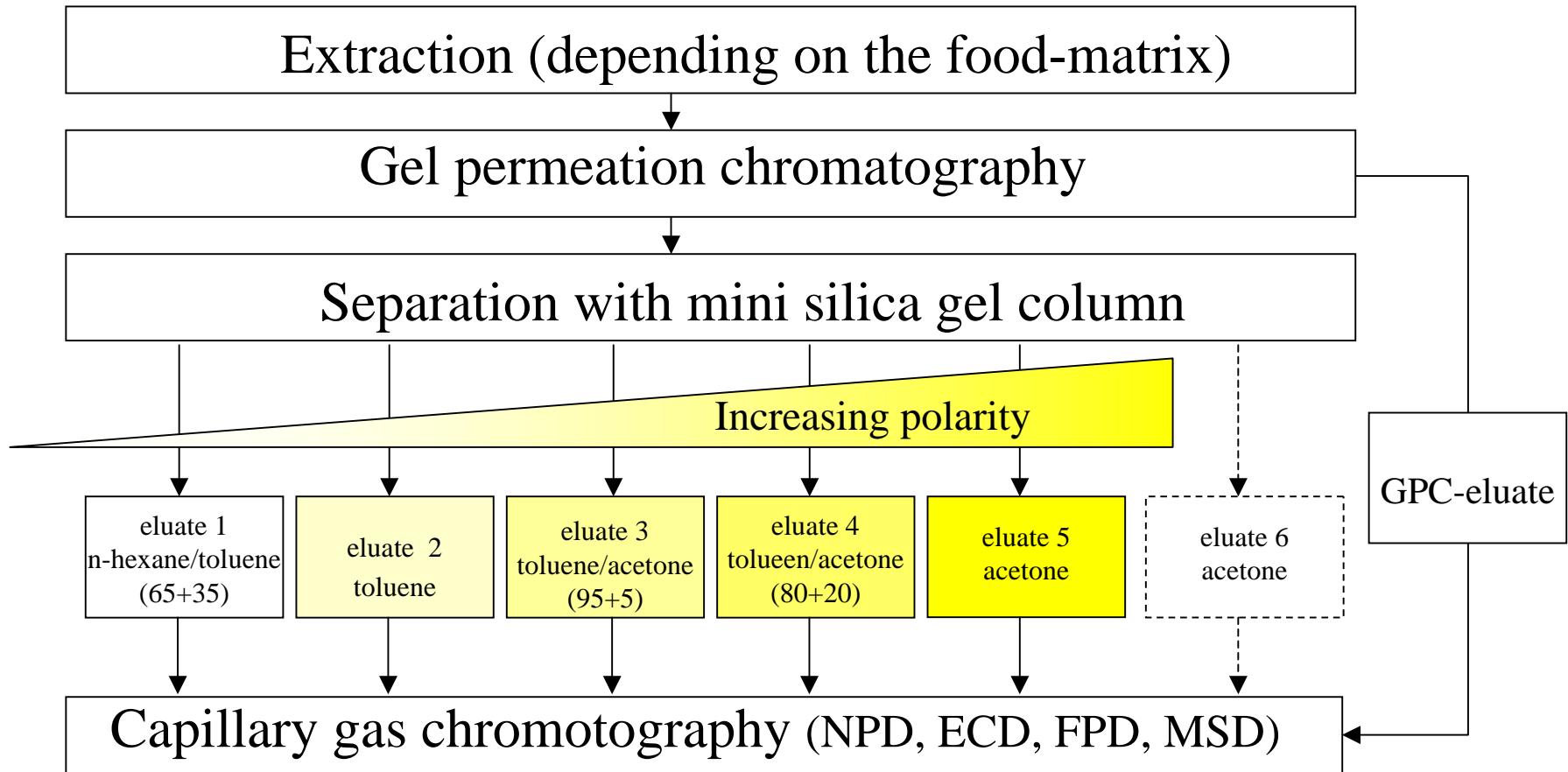
Katja Ziegenhals



Analysis



Analysis – modular multimethod S19



Analysis – modular multimethod S19

Gel permeation chromatography :

Clean-up with gel chromatography using a polystyrol gel (Bio Beads S-X3) with cyclohexane/acetic acid ethylester

→ GPC-eluates

Purification with a mini silica gel column:

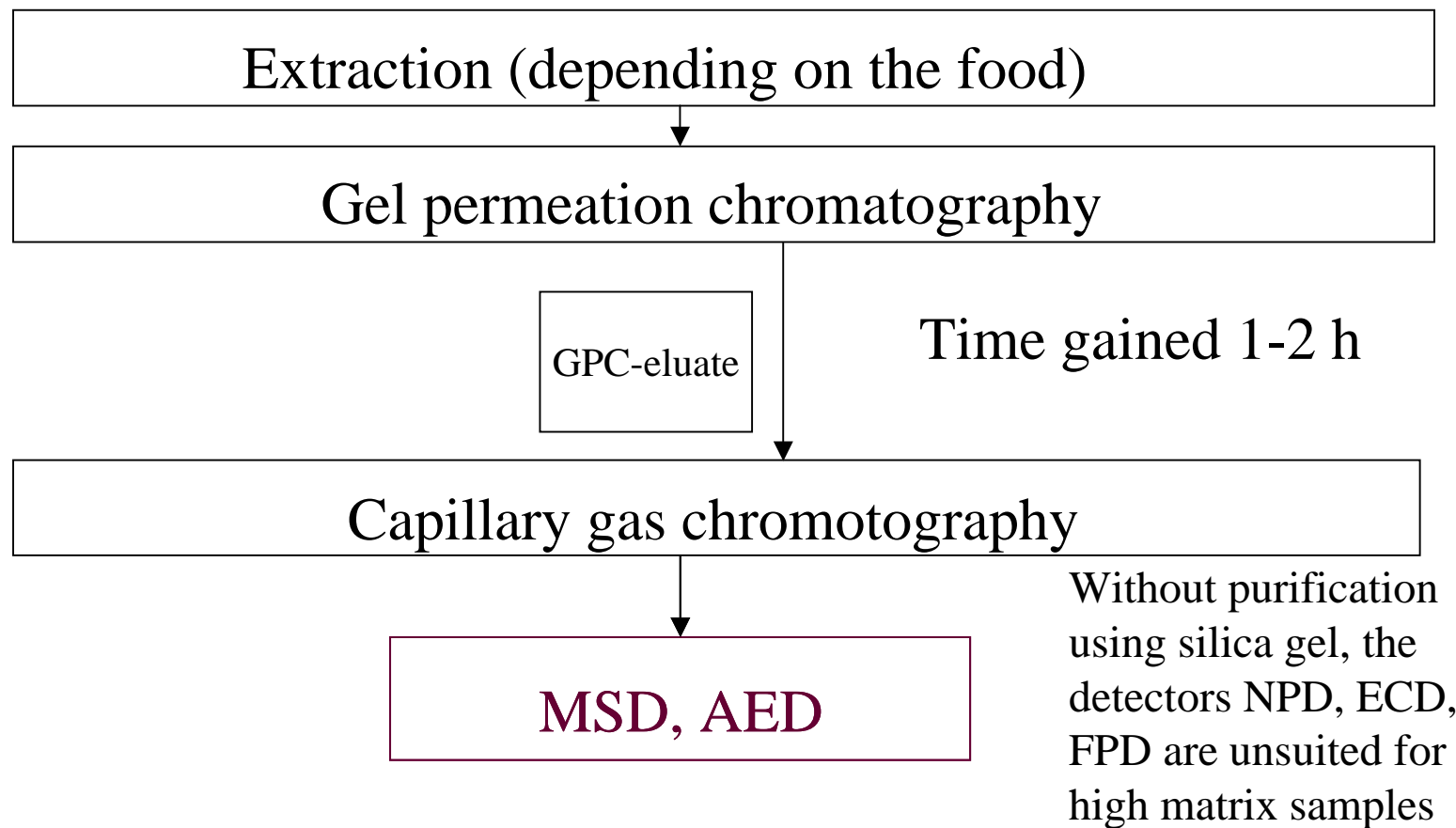
GPC-eluate is eluted on a mini silica gel column with solvents or solvent mixtures of increasing polarity.

- More than 700 active substances are distributed along the eluate according to their polarity
- Removal of interfering matrix components

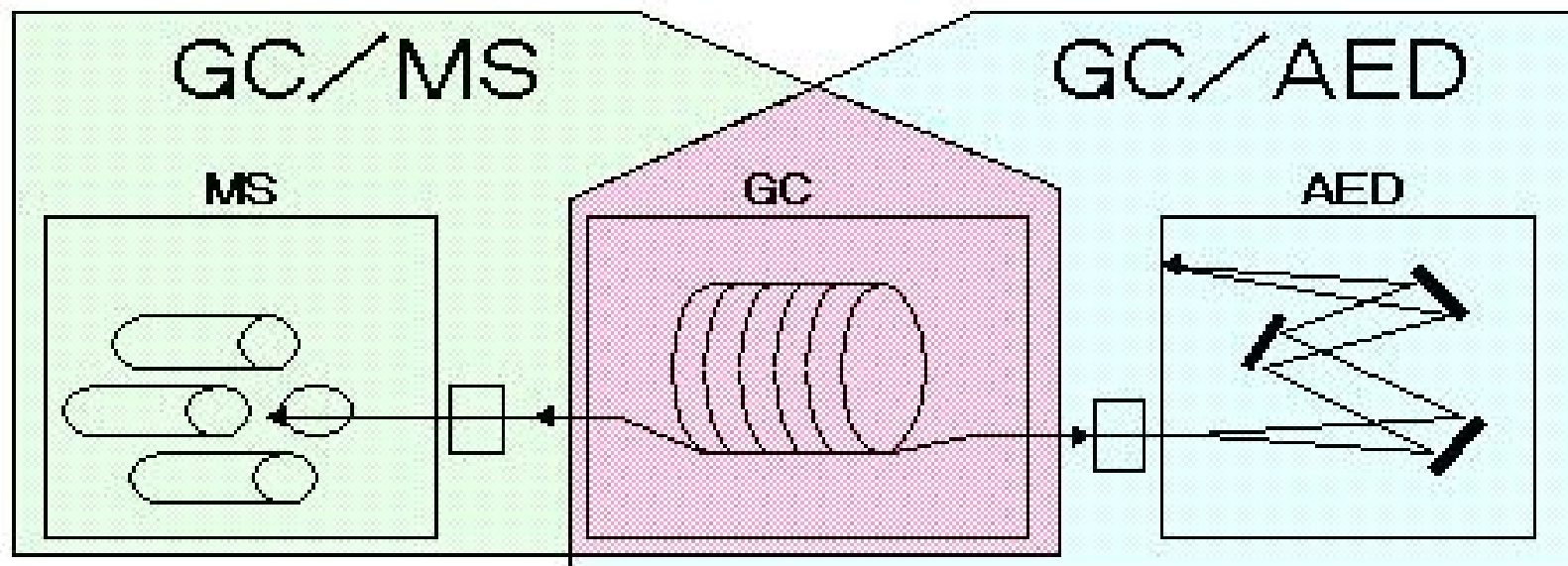
GPC-eluate and individual eluates must be injected into each detector (NPD, ECD, FPD)



Analysis



Coupling of GC-MS and GC-AED



Similar retention times → Comparison of chromatograms

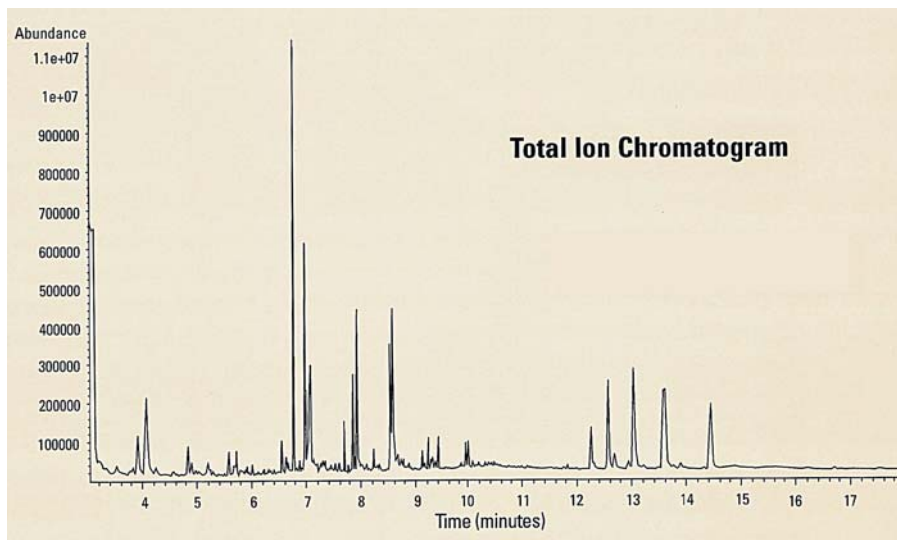
→ Reduction of matrix effects

→ More information, confirmation

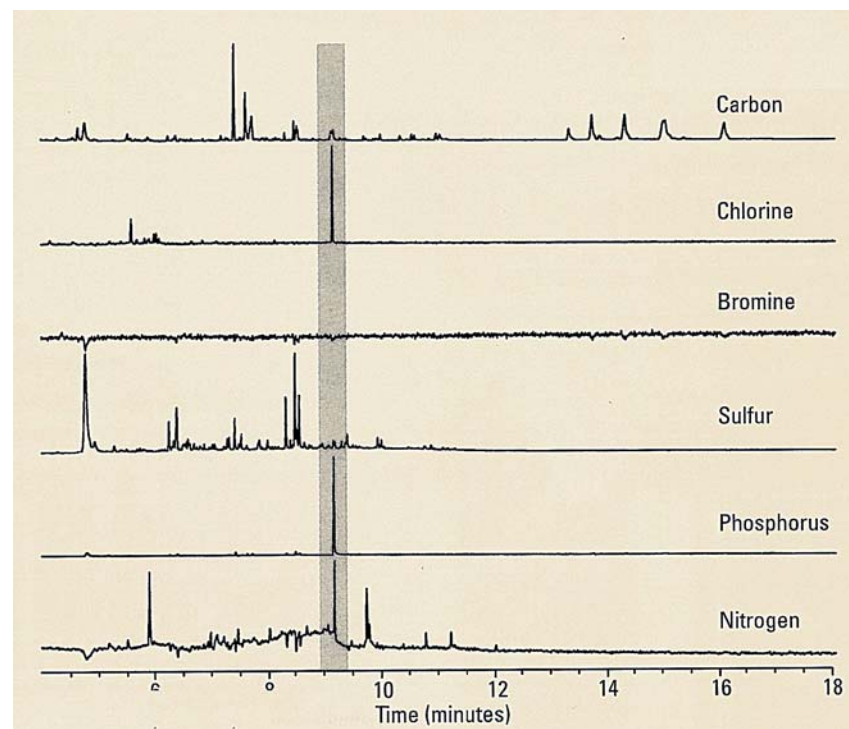


Coupling of GC-MS and GC-AED

TIC-chromatogram



AED-traces

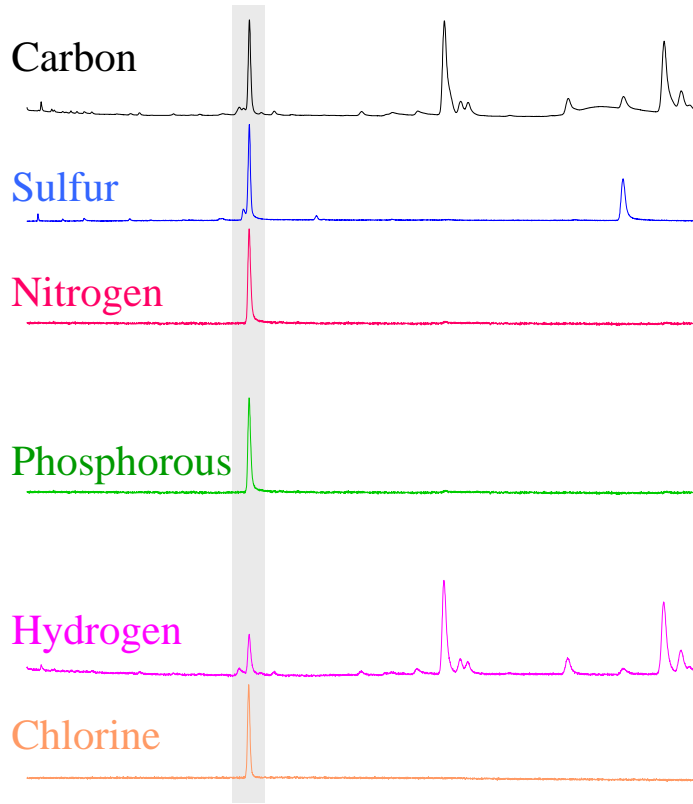


Information on traces of elements and spectra

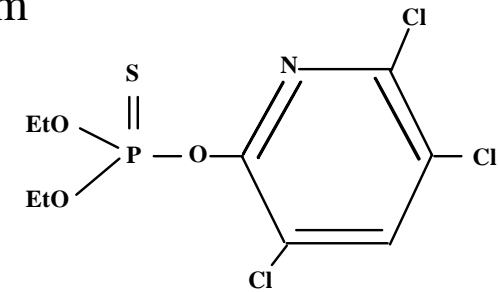
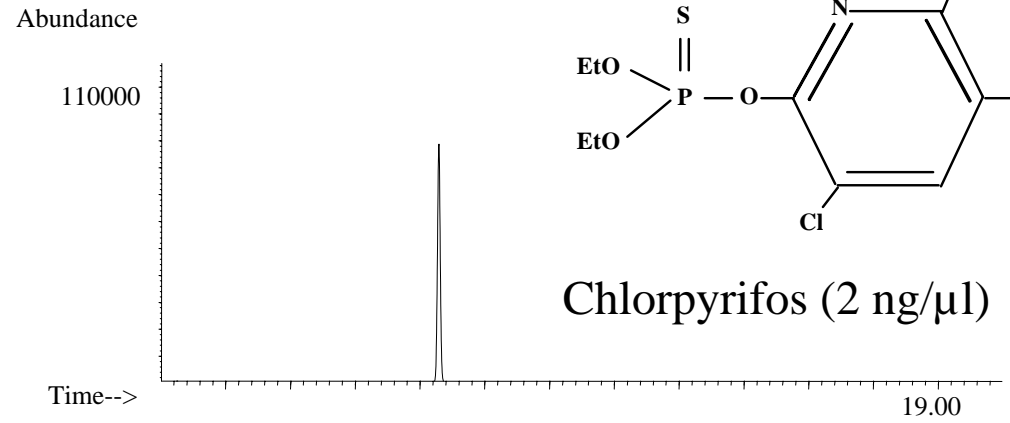


Coupling von GC-AED und GC-MSD

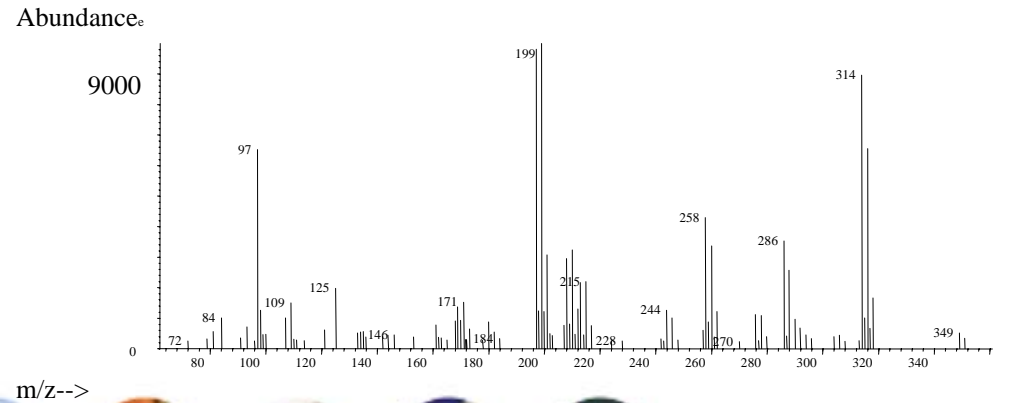
AED-traces



TIC-chromatogram



Chlorpyrifos (2 ng/μl)



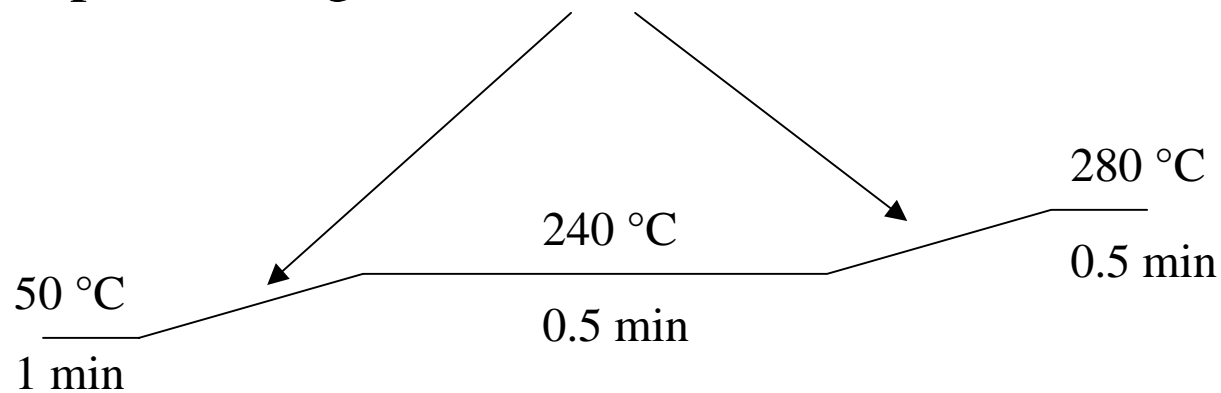
Coupling of GC-MS and GC-AED



Injector type

PTV (UNIS) → pulsed splitless
temperature variable injector

- rapid heating (500 °C/min)



- 2 min splitless

- liner: quartz liner for UNIS multi restriction (JAS 90307L)



Configuration of the column

DB-5ms

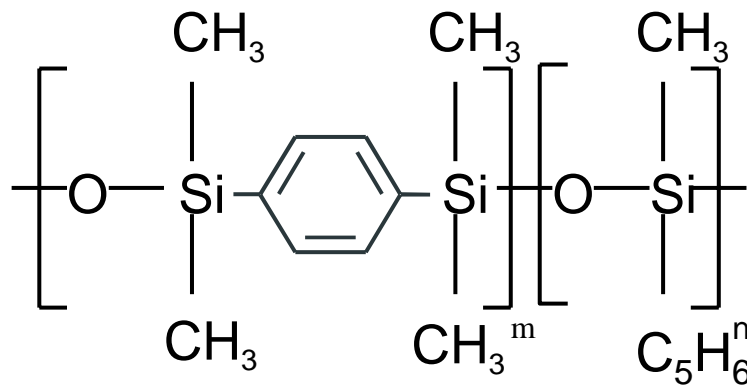
- 30 m length
 - 0.32 mm inner diameter
 - 0.25 μm film thickness
-
- low bleed phase
 - unpolar
 - higher upper temperature limits (350 °C)



Configuration of the column

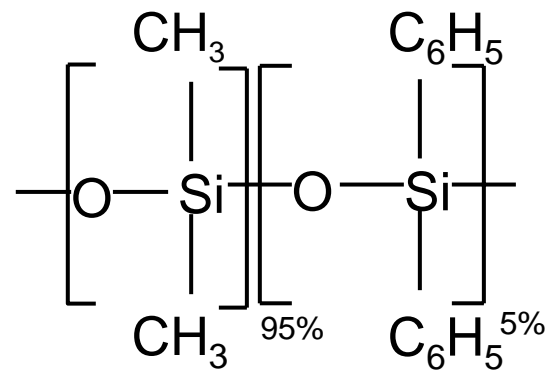
DB-5ms

- low bleed phase
- unpolar
- high temperature limits



HP-5ms

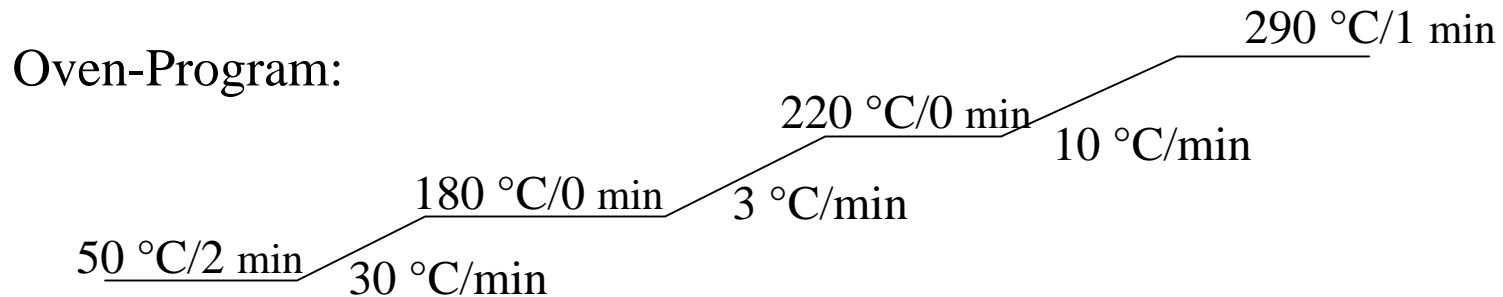
- low bleed phase
- unpolar
- high temperature limits



→ different polarities



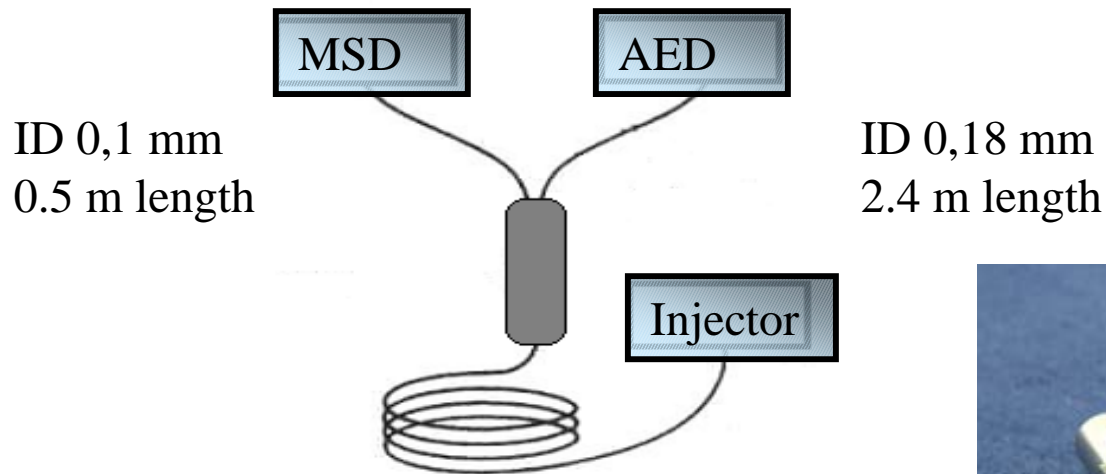
Parameters



- const. flow 2.9 ml/min
→ DB-5ms (ID 0.32 mm)
- Run time 28 min
- Carrier gas: Helium
- Injection volume: 2 μ l
- const. pressure 55 kPa (Agilent)
→ HP-5ms (ID 0.25 mm)
- Run time 41 min
- time difference for 3 runs → $3 \times 13 \text{ min} = 39 \text{ min}$



Restriction

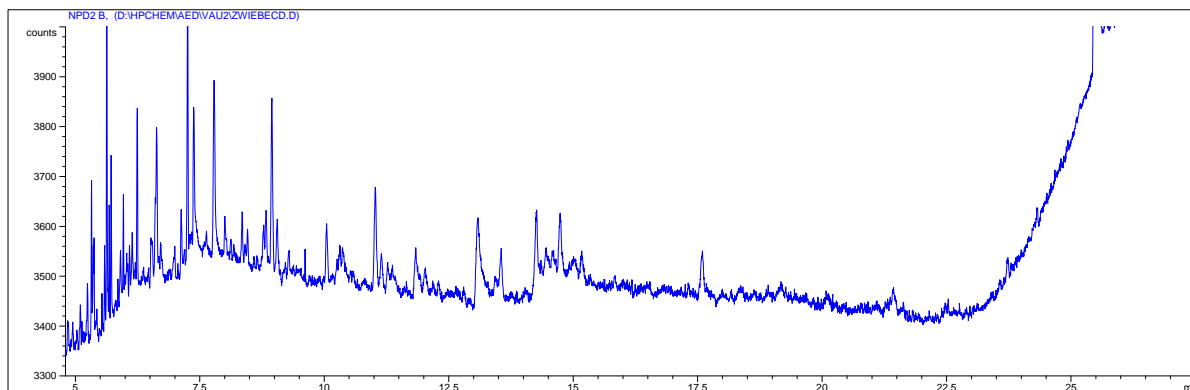


splitter

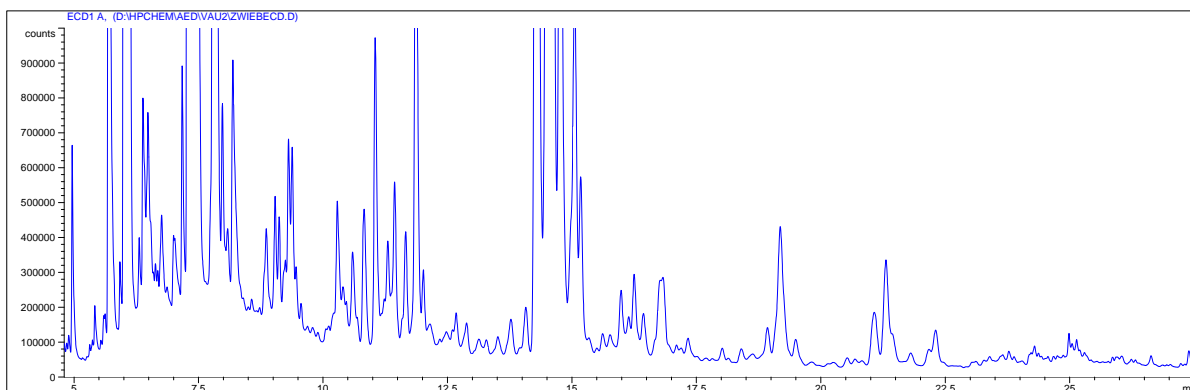
- split ratio 1:2
- very similar retention times



Sample demonstration - onion



NPD



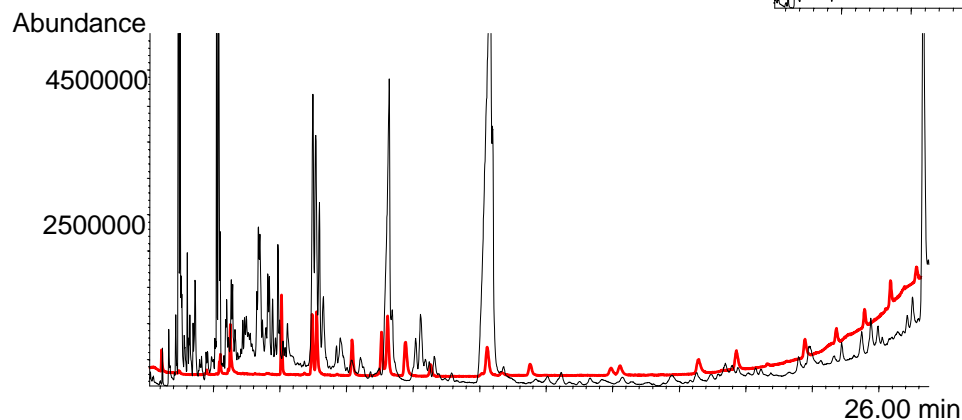
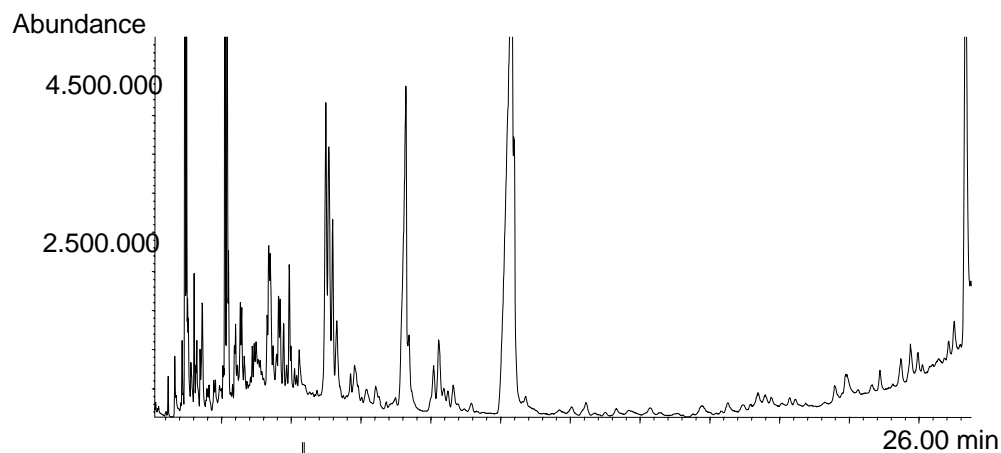
ECD

→ Residues remain hidden



Sample demonstration - onion

MSD - SCAN



Residues remain hidden

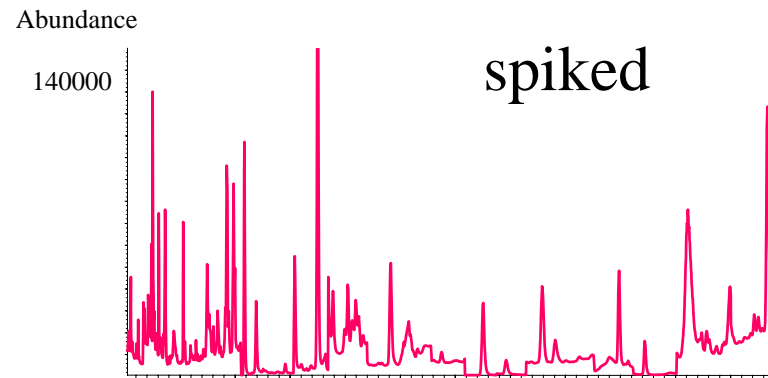
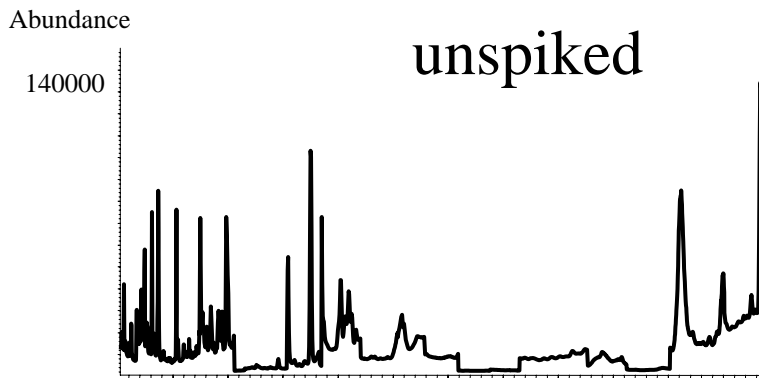
Standard-Mix (2.5 ng/μl)

→ 0.5 mg/kg (in onions)



Sample demonstration - onion

MSD – SIM-Mode



SIM-mode is not capable to compensate for all matrix effects

→ depend on characteristic masses



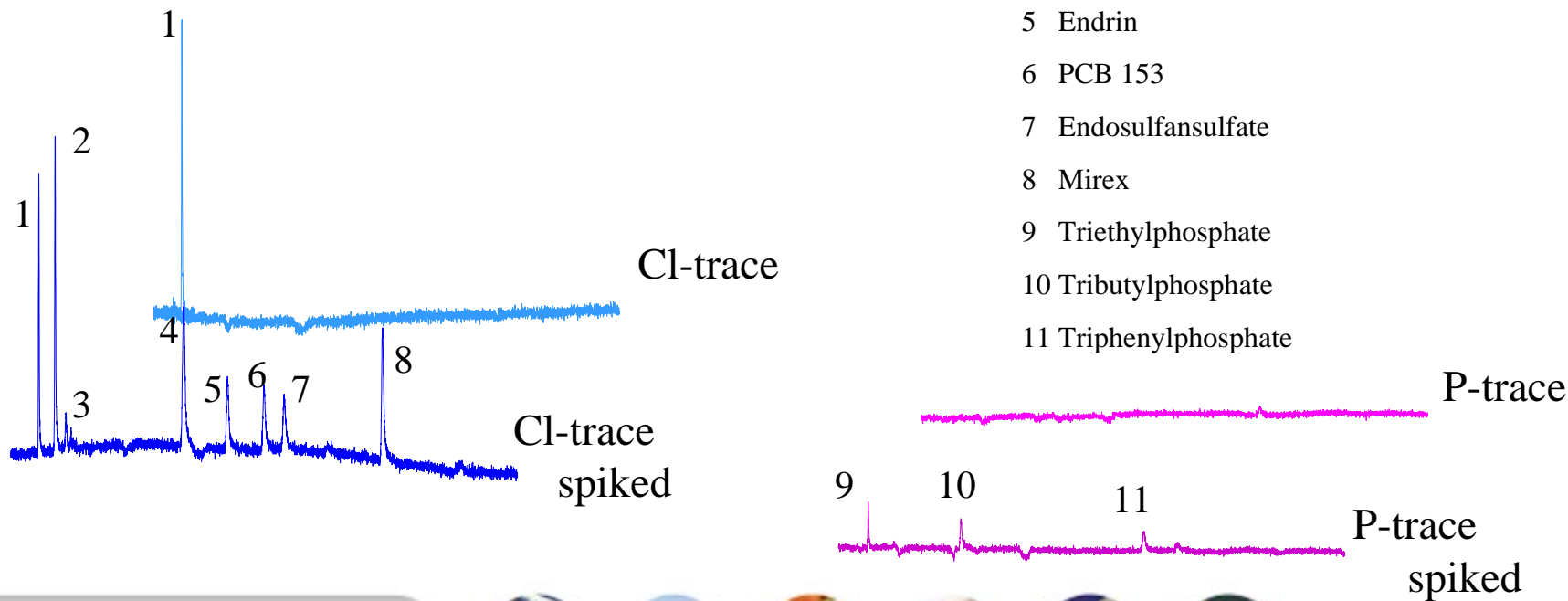
matrix calibration, standard addition



Sample demonstration - onion

AED

Cl-trace and P-trace: no matrix-coelution interfered



- 1 Tetrachlorxylol (ISTD)
- 2 HCB
- 3 Atrazin
- 4 PCB 101
- 5 Endrin
- 6 PCB 153
- 7 Endosulfansulfate
- 8 Mirex
- 9 Triethylphosphate
- 10 Tributylphosphate
- 11 Triphenylphosphate



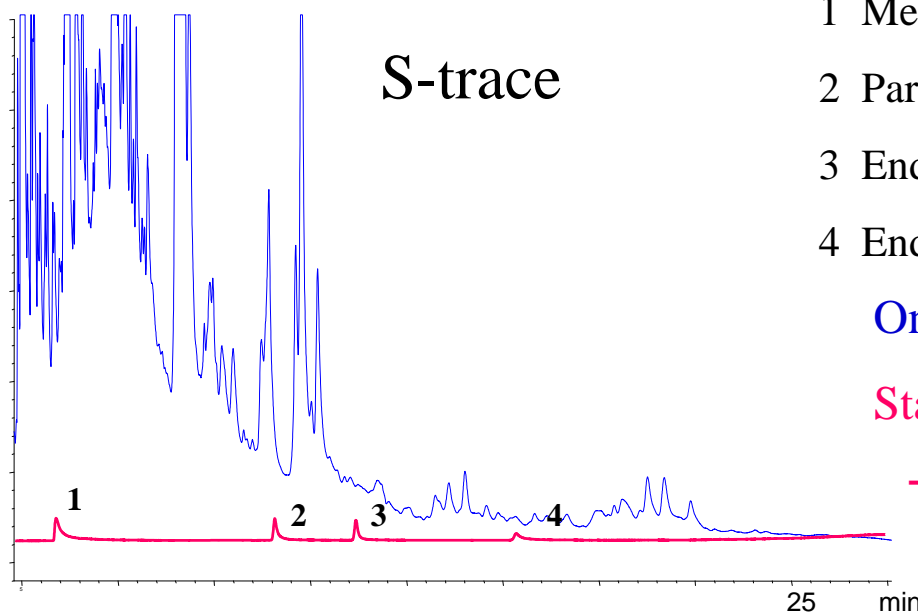
Sample demonstration - Onion

AED

Counts

500

S-trace



1 Methamidophos

2 Parathion

3 Endosulfan, alpha

4 Endosulfan sulfate

Onion without additives

Standard-mix (10 ng/μl)

→ corresponds to 2 mg/kg (in onions)

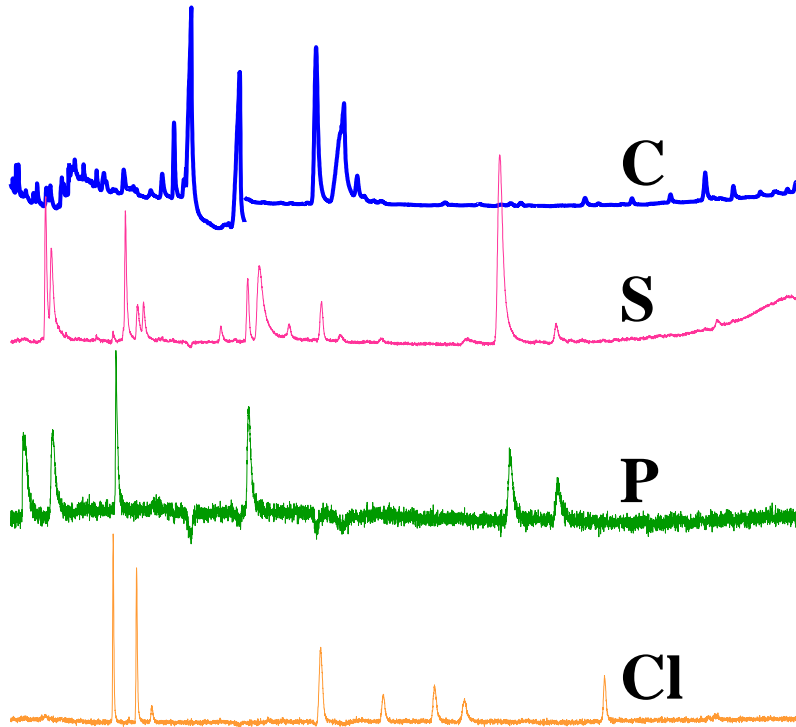
➤ Because of the onion's sulfur containing components, the S-trace can not be used for analysis.



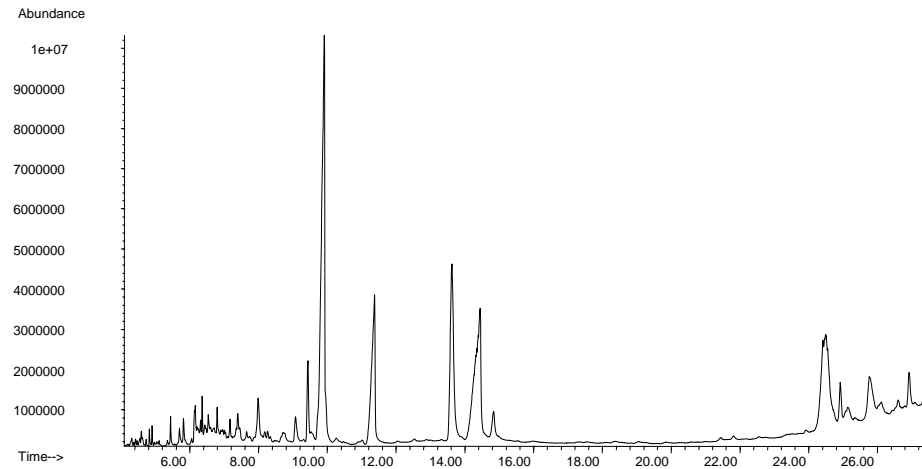
Coupling of GC-MS and GC-AED

AED-traces

Matrix black tea



TIC-chromatogram



Screening →

Confirmation



Use of MSD for complicated matrices

- SIM-Mode: - increased sensitivity (10 fold)
 - however, limited number of residues per run
- Unspecific in SCAN during the analysis of complicated matrices
- Precise structural information: Retention time and spectra
- Confirmation through special structure data bases (NIST, Wiley)
- Databases and retention-time libraries (RTL, Maurer and Pflieger)
- Quantification of single characteristic fragments
- Applications dependent on matrices



Use of AED for complicated matrices

- Elementspecific
- Less sensitive than selective detectors (except for sulfur traces)
- Especially Nitrogen 174 nm
 - Improved by measurement at 388 nm
- Determination of the element ratios
- Compound-dependent and independent calibration
- Reduction of influences from interfering matrix compounds
- Multiple injections



AED – N (388 nm)

- Instead of N (174 nm)
- Measurement of the CN-band at 388 nm
- Conditions: auxiliary gas methane (99,999 %) 344 kPa

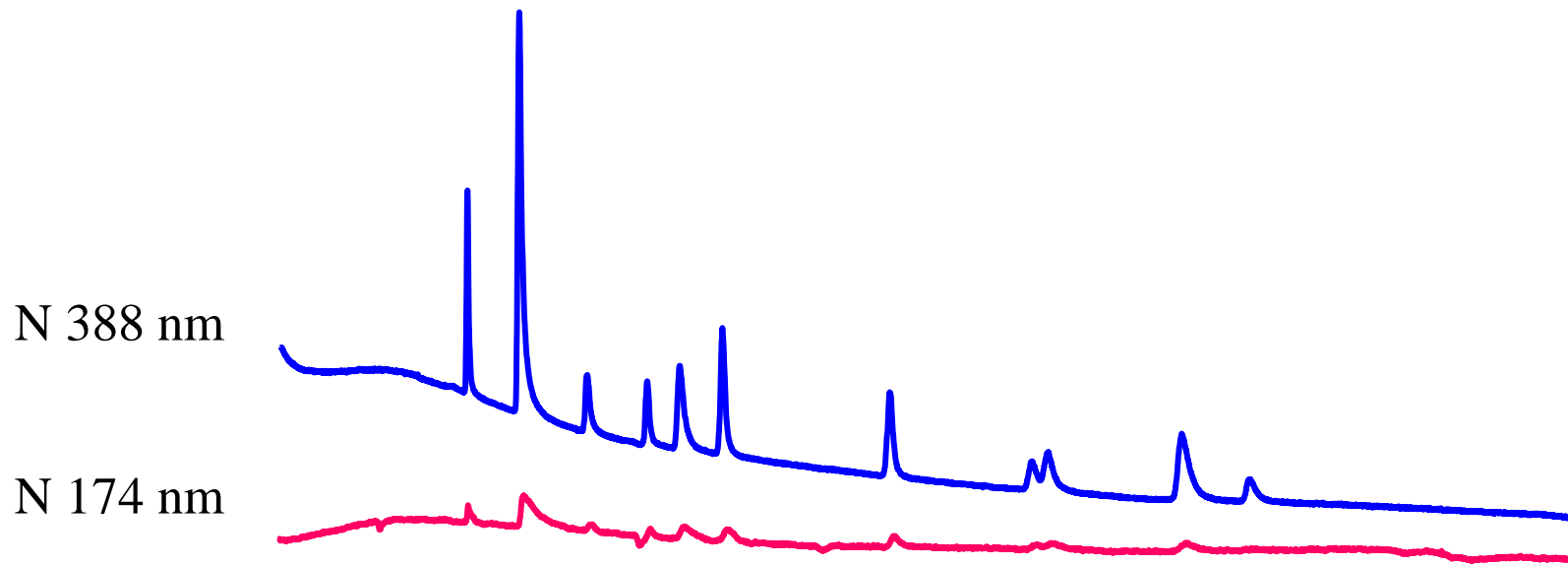
make-up flow	230 ml/min
oxygen	344 kPa
hydrogen	207 kPa
purge vent	10 kPa (35 - 40 ml/min)

- Additional injection



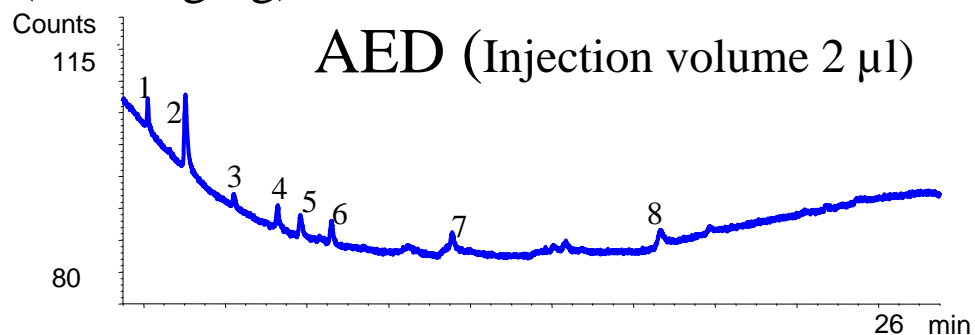
AED – N (388 nm)

➤ Improved sensitivity (10 fold)

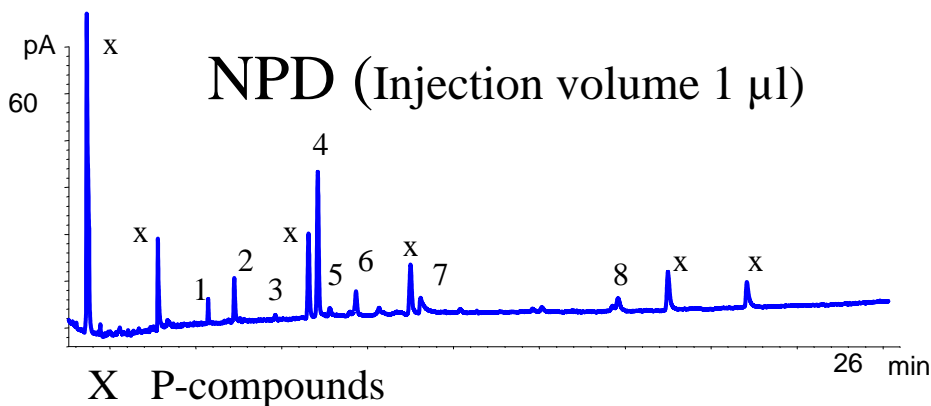


Comparison between NPD and AED (N 388 nm)

Matrix clementines spiked with mix of active substances
(0.15 mg/kg)



- | | |
|----------------|----------------|
| 1 Tebutam | 5 Tetraconazol |
| 2 Terbutylazin | 6 Tolyfluanid |
| 3 Vinclozolin | 7 Binapacryl |
| 4 Chlorpyrifos | 8 Iprodione |



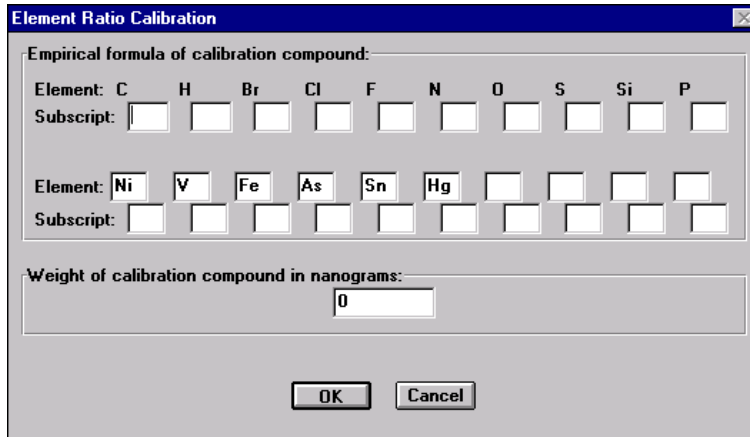
Element selective detektor
↓
Increased sensitivity



CIC – Compound Independent Calibration

Calibration with any standard compound

Condition: Calibration substance must contain the elements which are to be analysed.



Element Ratio Calibration

Empirical formula of calibration compound:

Element: C H Br Cl F N O S Si P
 Subscript:

Element: Ni V Fe As Sn Hg
 Subscript:

Weight of calibration compound in nanograms:

OK Cancel

- Quantification
- Element-ratios
- Empirical Formula



CIC – Compound Independent Calibration

- Response-factors depend on concentrations
 - Unsited for residue analysis
- One standard for several unknown compounds
- MSD → Information on molar mass and confirmation
 - ↓ supplementation
 - Quantification with any standard (AED)



Conclusion

- Complicated matrices → **Method of choice**
- Multiple injections take time
 - Additional injections can be used for SIM-Methods
- Confirmation (MSD), Empirical Formular (AED)
- Combination to identify unknown compounds
 - AED (Screening) → MS (Confirmation)**
- Reduced sample preperation
 - **Economization** of the clean-up with mini silica gel column
 - **Economization** of injecting several eluates on several element-selective detectors
- Better informational value (heteroatoms, structure)
- Sensitivity depends on the active substances and the matrix



Simple identification of toxic substances in food by coupling of GC-AED and GC-MS



AED- atom-emissions detector

