

# Features of a micro GC based on Sorptive Extraction and Microchip Plasma Emission Detection (PED) for the Analysis of Harmful and Toxic Substances in Air



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## Goals

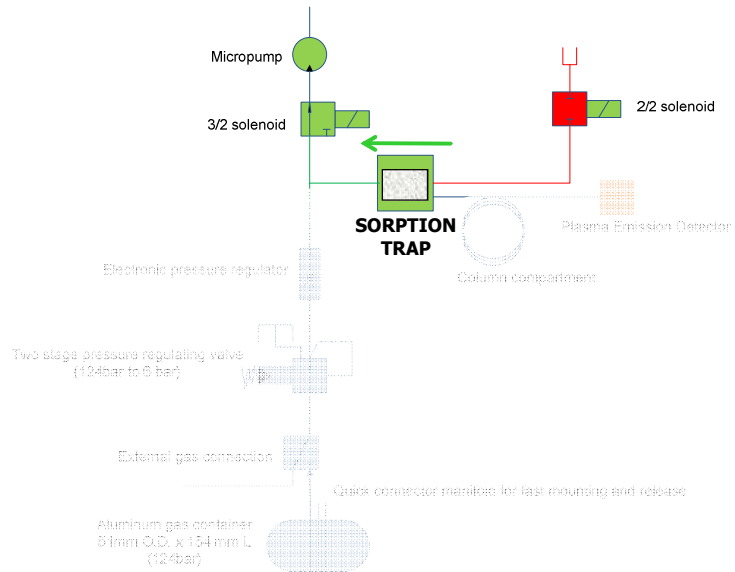
- Miniaturization
- Independant operation
- Flexibel configuration
- Robustness



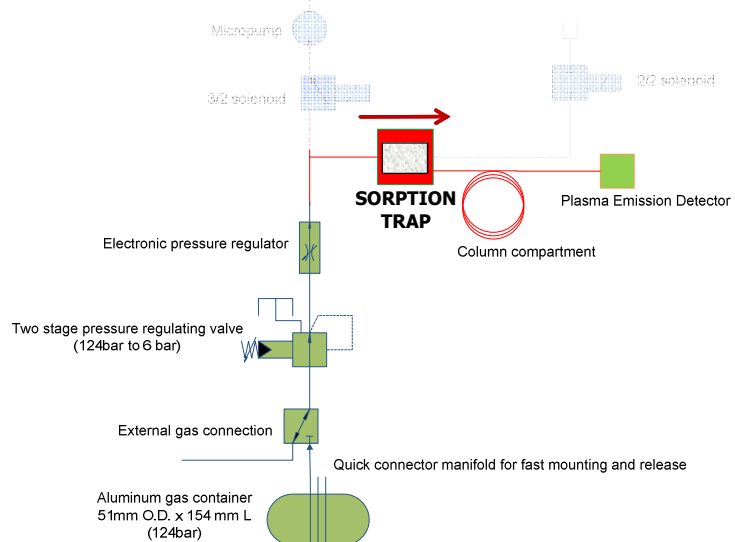
**RIC** | Research Institute  
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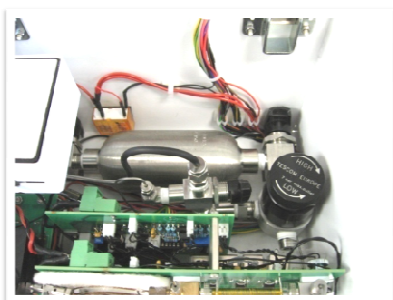
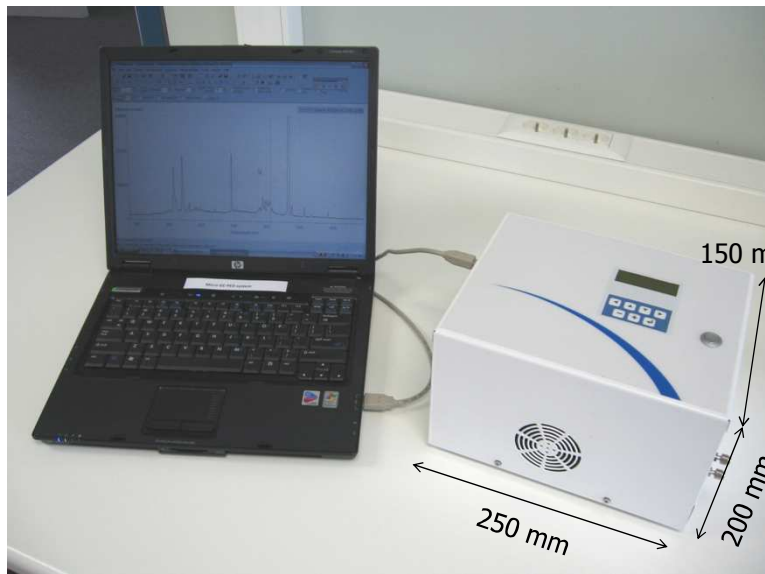
## Sampling



## Thermal desorption - detection



# $\mu$ CAD (Micro Chemicals-in-Air Detector)



**Plasma chip detector**

Cooling fan

Display and microcontroller

**Temperature controlled column heater**

**Chemical trap**

Sample IN  
Calibration IN

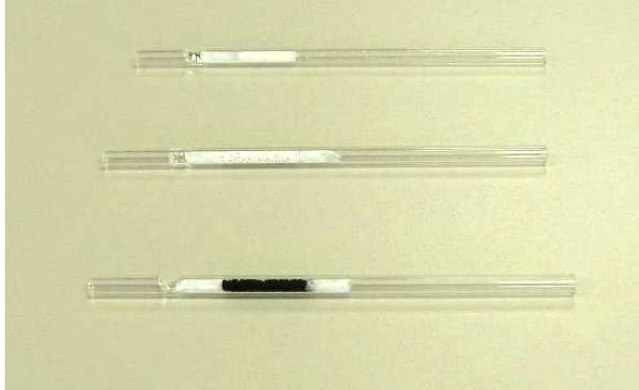
Manifold

**Miniature pump**



## Different types of miniaturized chemical traps

- PDMS (novel)
- Tenax
- Carbotrap B

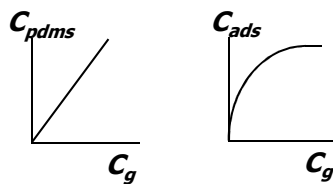


Traps only contain minimum amount of sorption material: 15-20 mg

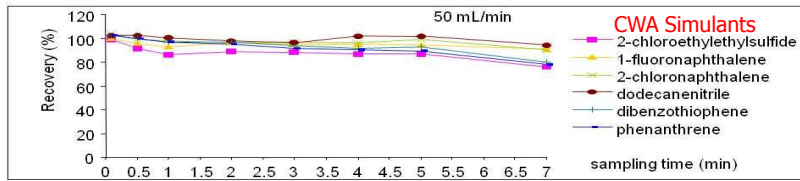
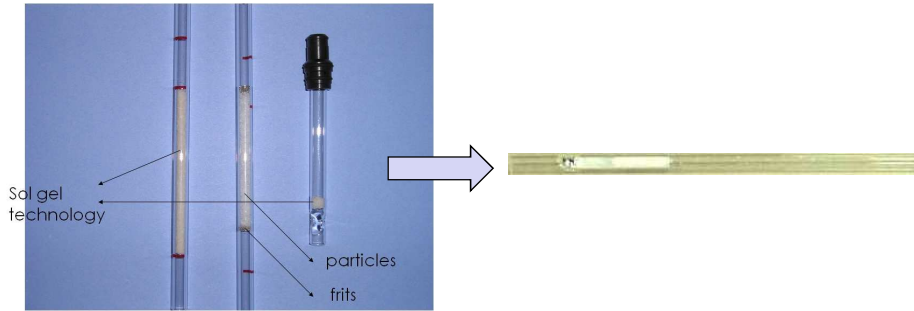


## PDMS trap based on (ab)sorptive extraction

- Compounds partition from the sample into the bulk of a polymeric retaining phase
- Bulk retention instead of surface adsorption
- (one of the) advantages of sorption:

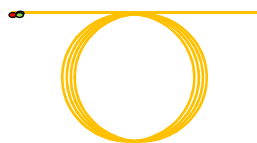


## Application range PDMS trap



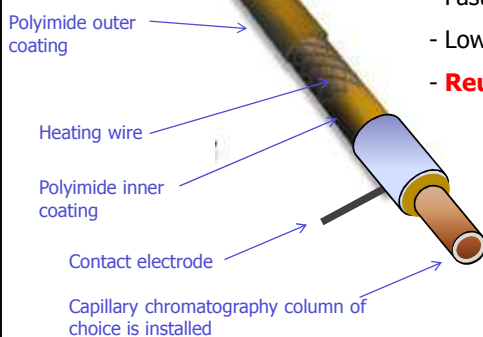
Typical boiling poing range = 150-350°C

## Novel capillary column heating technology



### Advantages

- Chromatographic column of choice installed
- Compact heating jacket
- Flexibel
- Rapid heating (100°C/min)
- Fast cooling
- Low power consumption
- **Reusable**

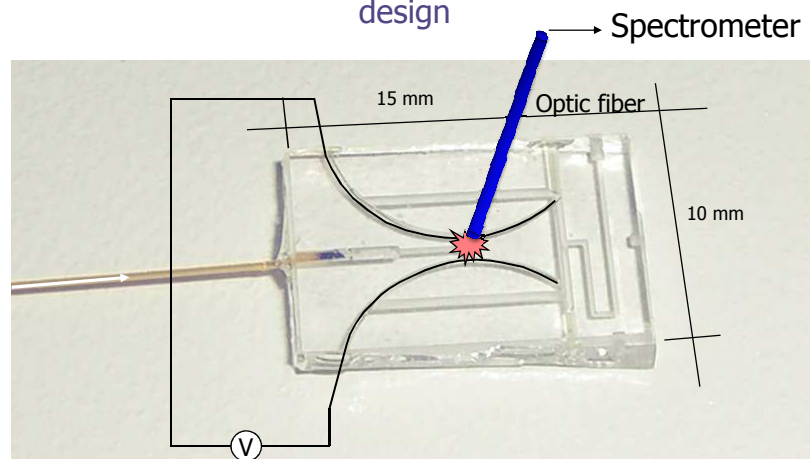


# Miniature detector 1

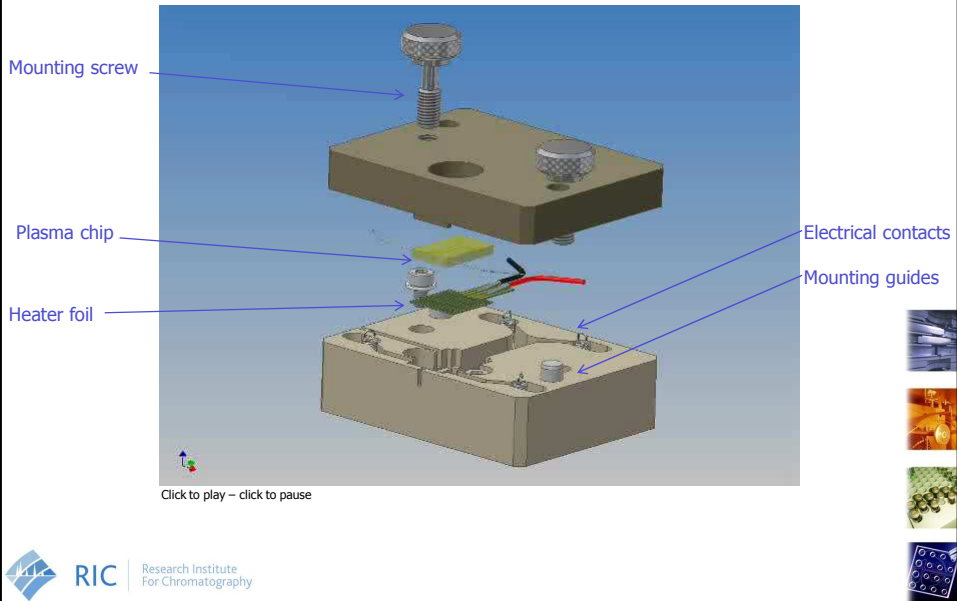
## Plasma Emission Detector Chip (novel)



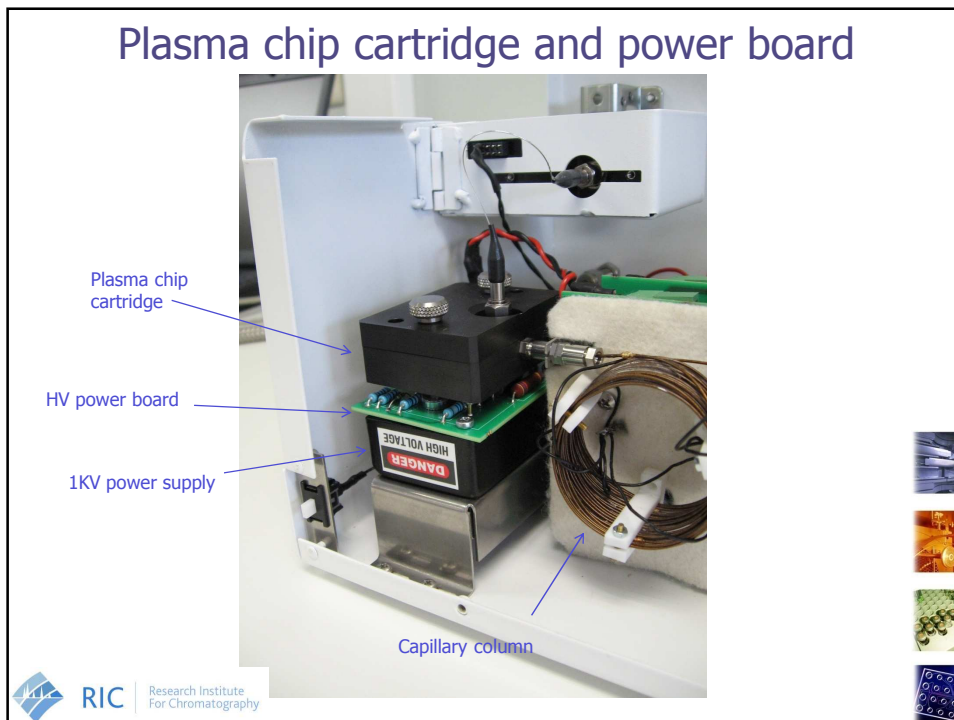
### Plasma Emission Detector design



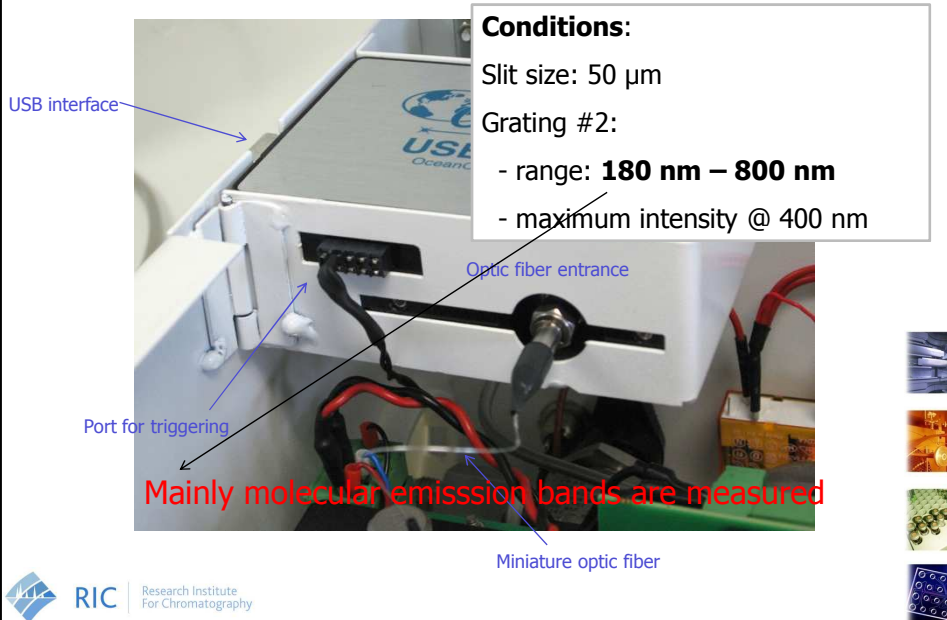
## Assembly and mounting of the plasma chip cartridge



## Plasma chip cartridge and power board

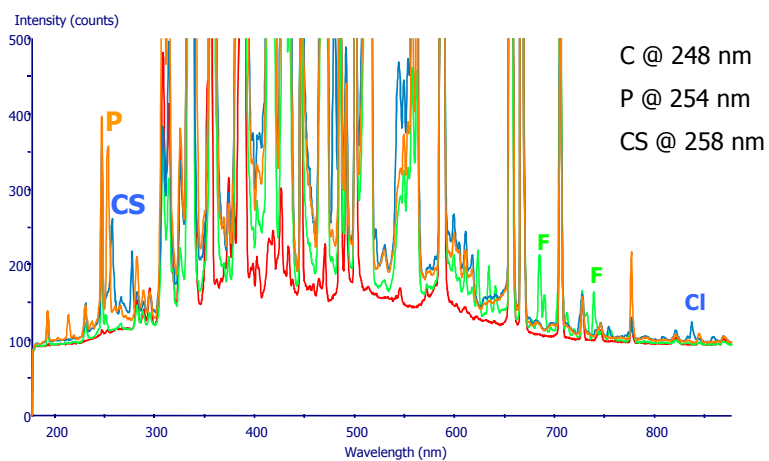


## Miniature diode array spectrometer



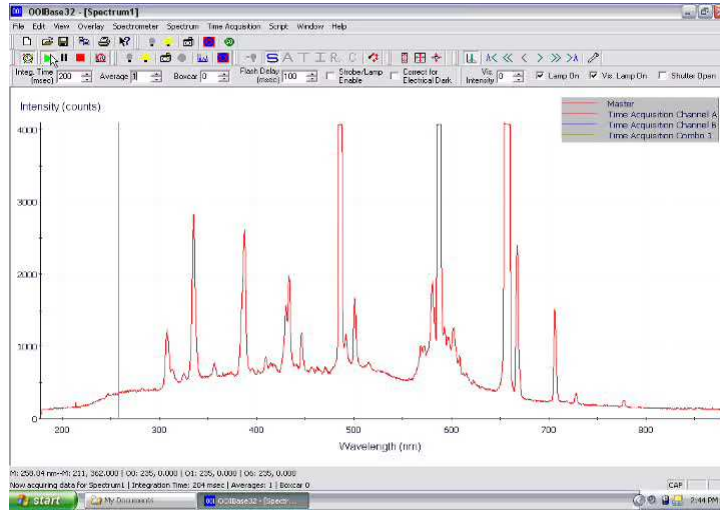
## Typical spectra

Helium (99.9%) / Hydrogen (0.1%)





# Spectral change in function of time

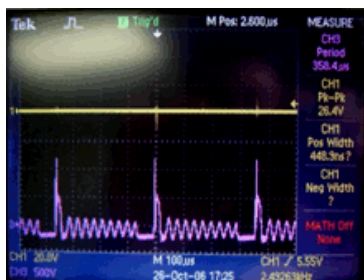


Tri-ethylphosphate: P-band @ 258 nm



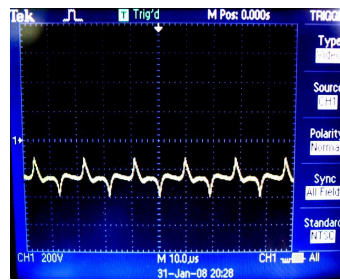
# (Pulsed) DC power supply for PED

## Line transformer based pulsed DC



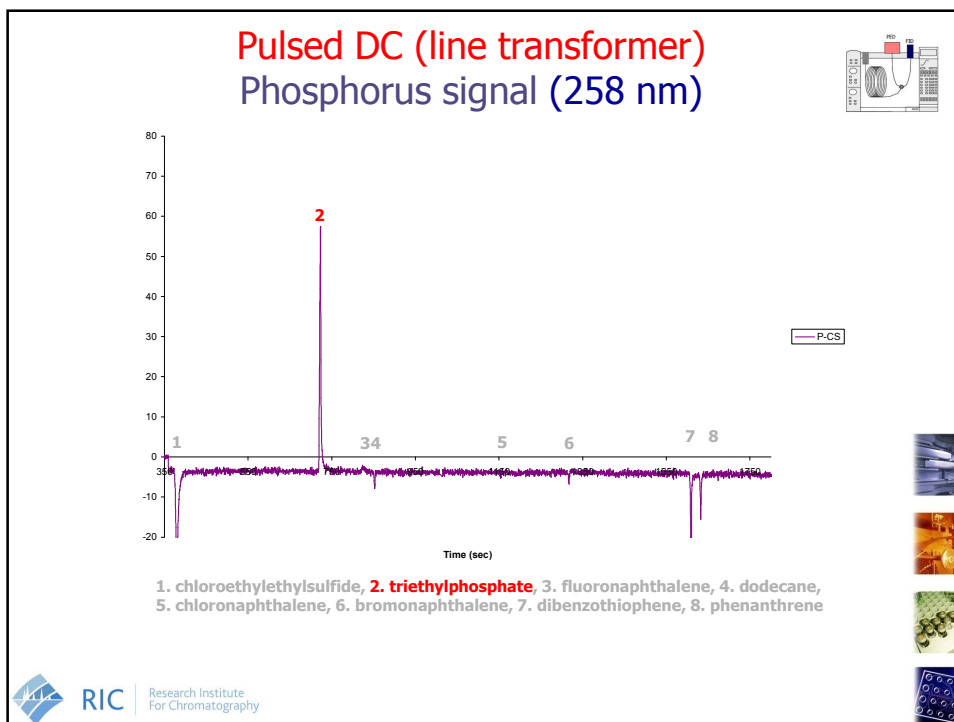
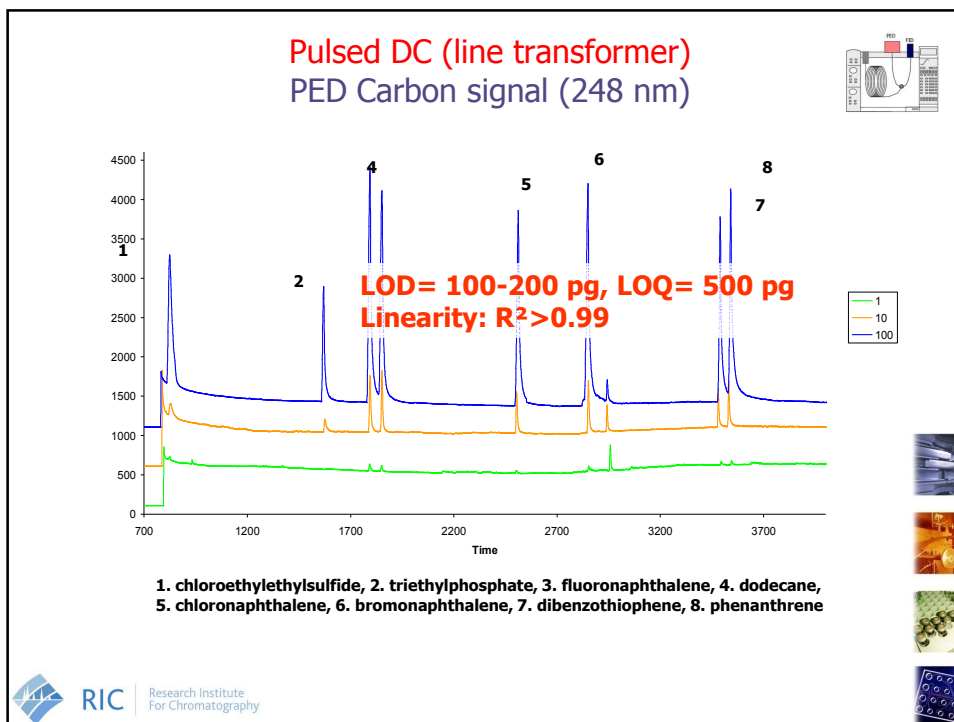
1350 V DC pulse  
 50 µs pulse width  
 cycle of 350 µs

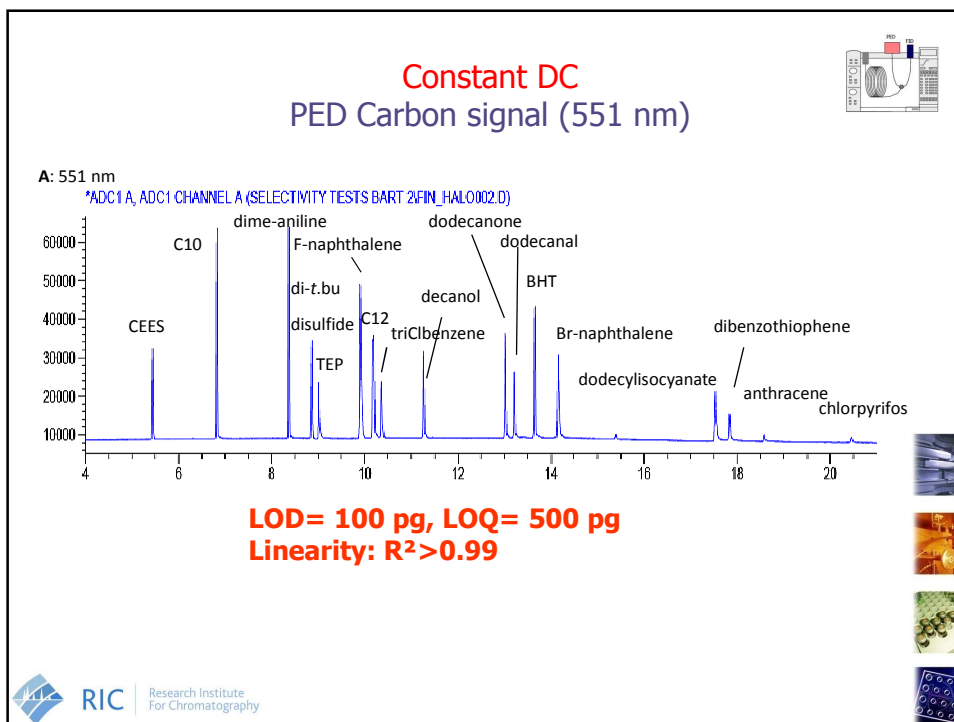
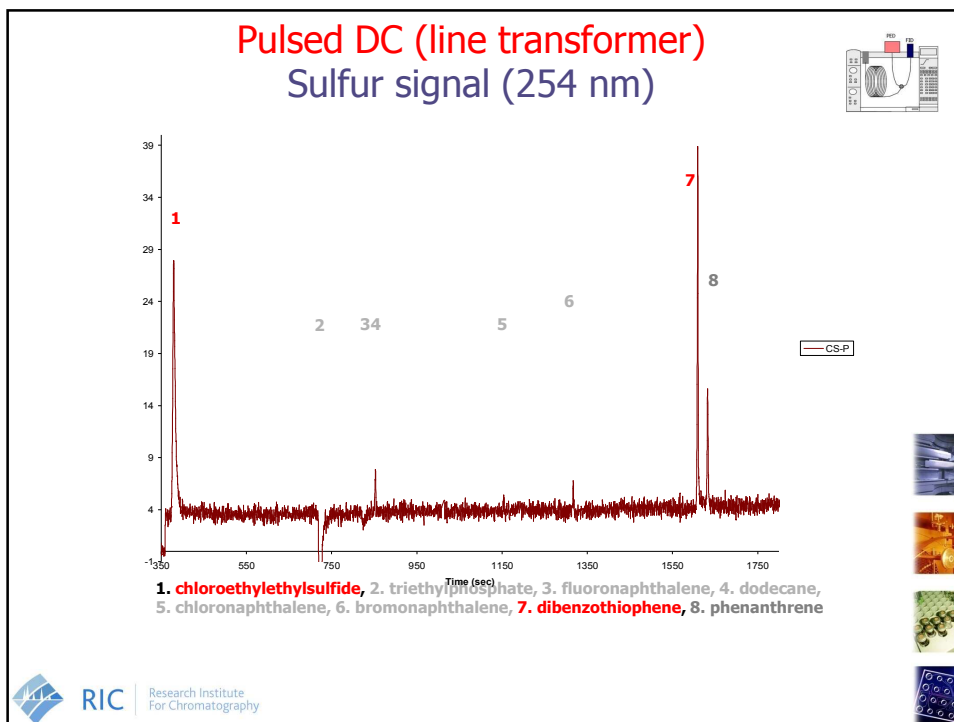
## Constant DC ('self induced' DC pulse)

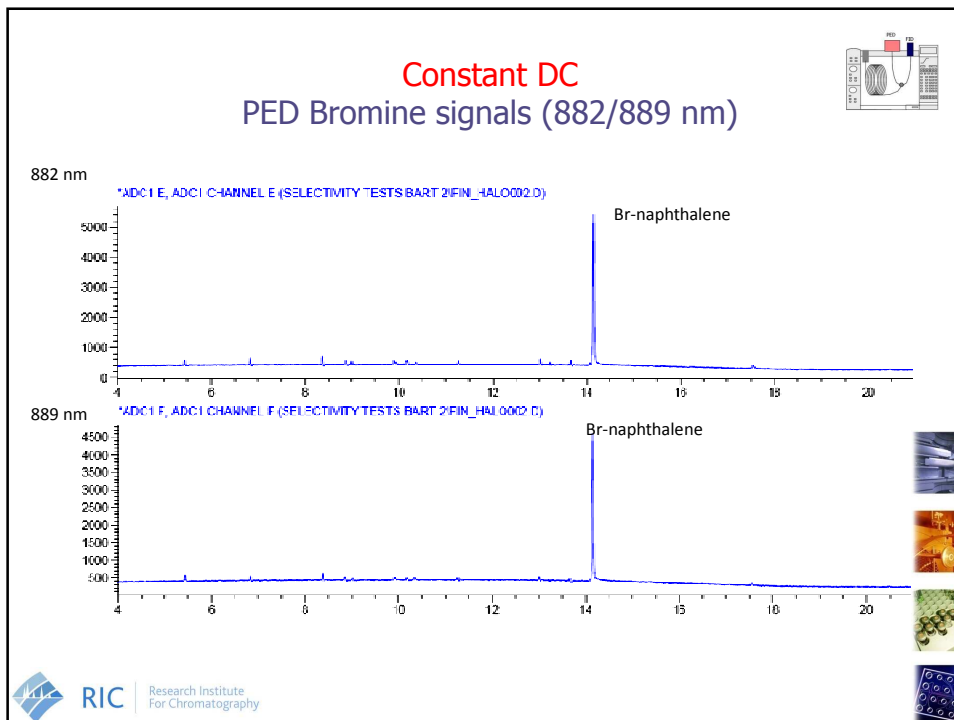
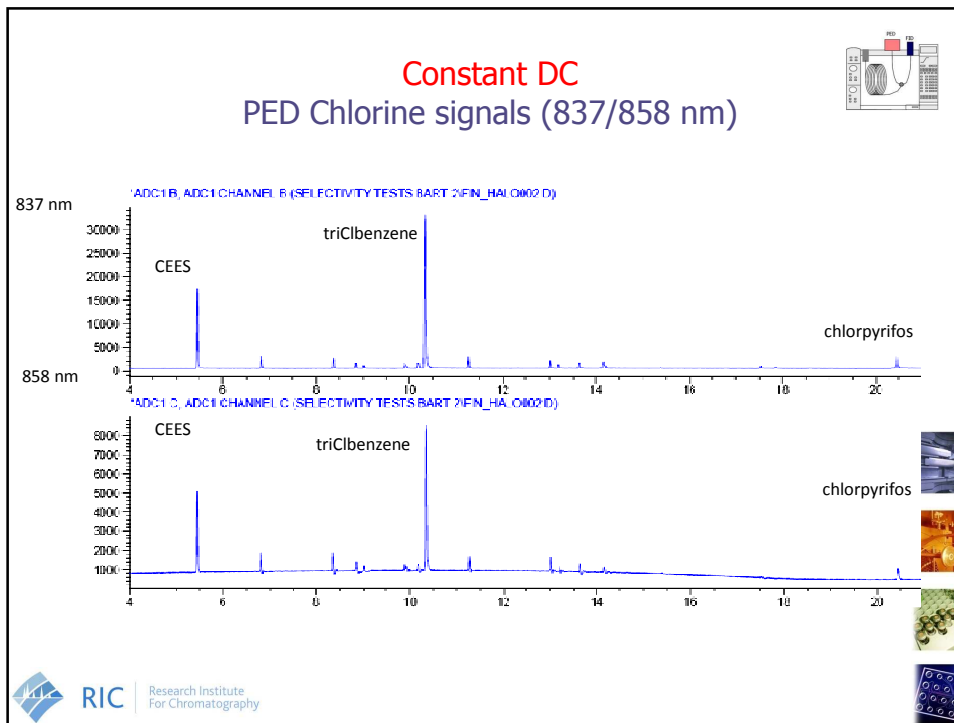


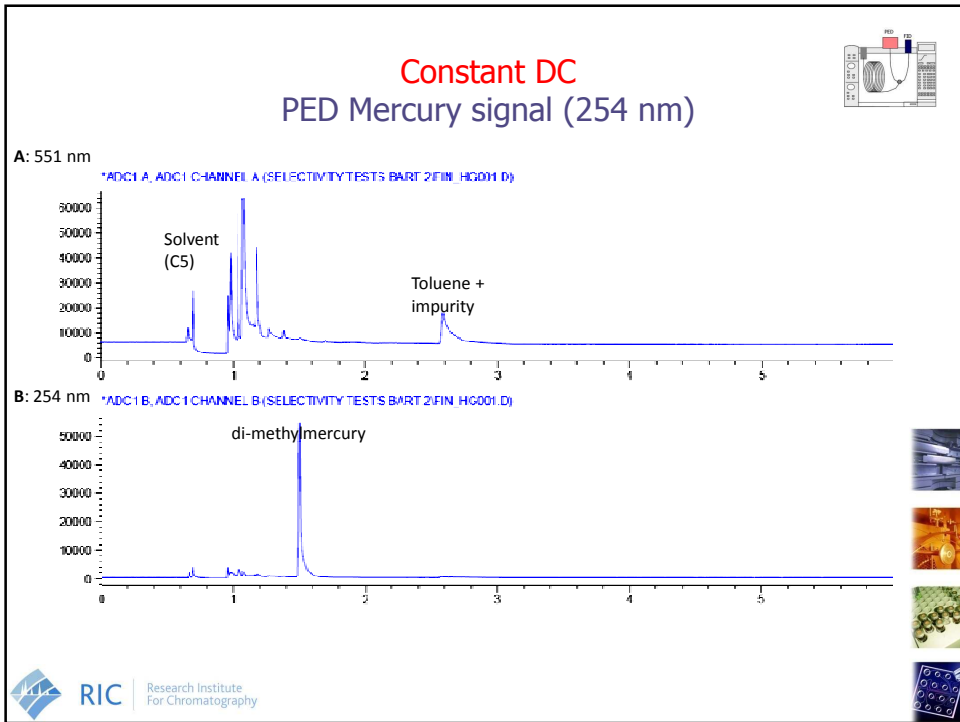
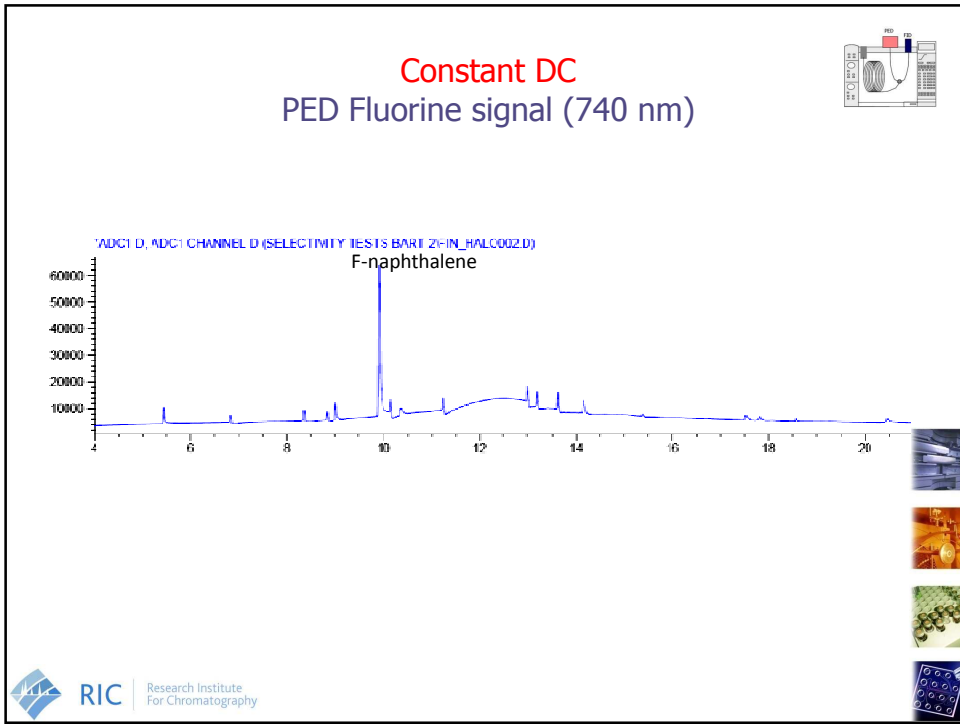
1kV DC power supply (EMCO, Sutter Creek, CA, USA)  
 voltage pulse of 350 V superposed 230 V DC  
 2 µs pulse duration  
 20 µs cycle time











## Constant DC Selectivity/sensitivity data

Element (X)	Selective wavelengths (nm)	Element to carbon selectivity (g X / g C)	Sensitivity (absolute qty)	Compounds tested
C	551, 558*, 430 (CH)	n.a.	100 pg	alkanes, aromatics
Cl	837*, 858	10-30	100 pg 100 pg 500 pg	2-chloroethyl ethylsulfide (CEES) 1,2-dichloroethane 1,3-dichloro-2-propanol Trichlorobenzene chloronaphthalene chlorpyrifos
Br	882*, 889	10	1 ng	1,2-dibromoethane bromobenzene 1-bromonaphthalene
F	740*	200	100 pg	Fluorobenzene 1-fluoronaphthalene 4-ethoxytrifluoro-3-butenone
Hg	254*, 365	>>	100 pg	di-methylmercury

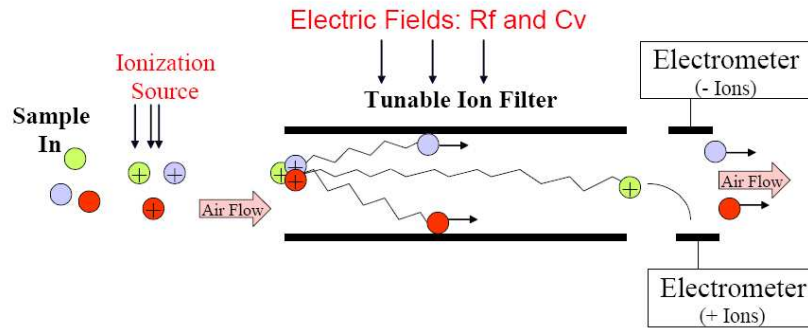


## Miniature detector 2

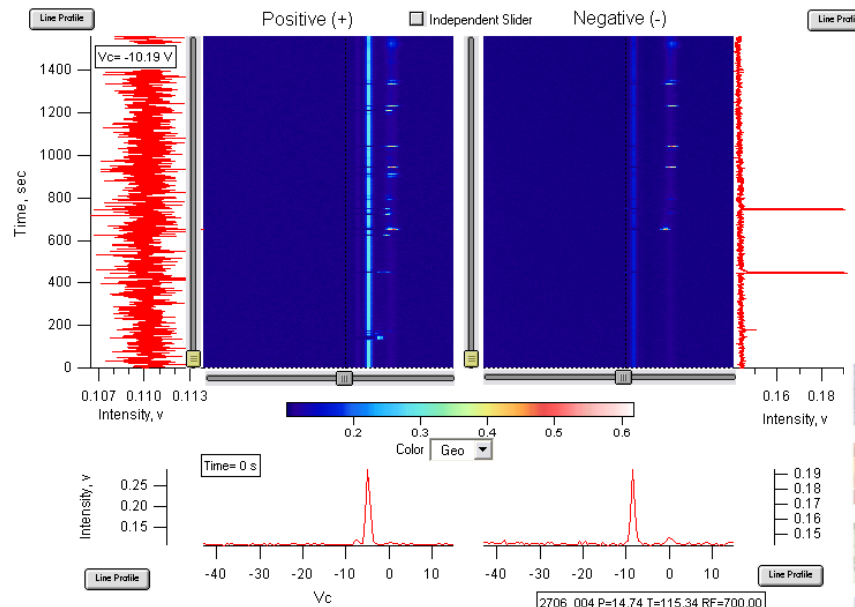
### Differential Ion Mobility Spectrometer



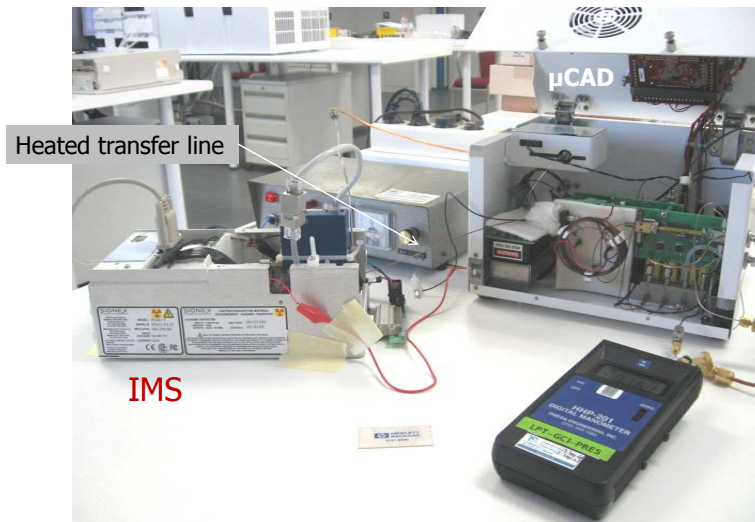
# IMS principle



# IMS output



## $\mu$ CAD-IMS set-up



## Application 2

### BTEX in air



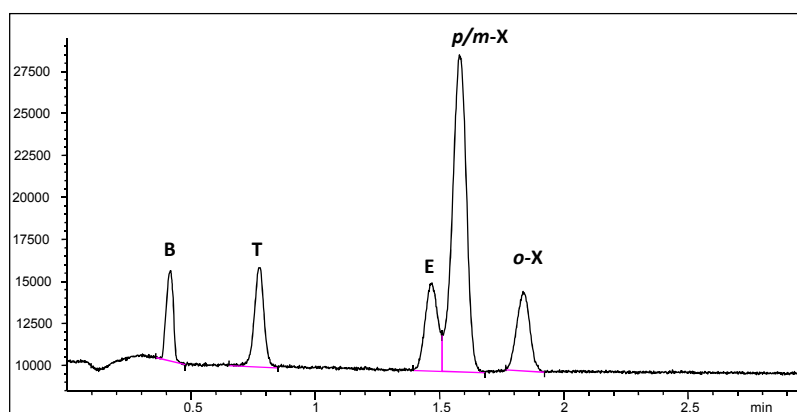


## $\mu$ CAD conditions

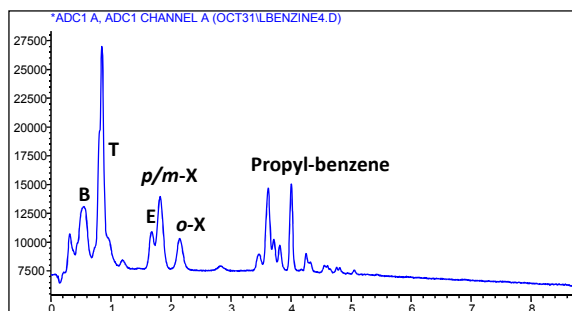
Sample	- 0.66 $\mu$ g/L B, T, E, m-X, o-X in air
Sampling	30 sec @ 110 mL/min (vial 1.1 times flushed)
Chemical trap	<b>Carbotrap B</b>
Thermal desorption	200°C (40 sec)
GC column	<b>5 m x 250 <math>\mu</math>m I.D., 1 <math>\mu</math>m df HP1-MS</b>
Carrier gas	Helium, constant pressure @ 7.5 psi (52 kPa)
GC column temp	<b>35°C (3 min)</b>
PED	Time acquisition: CH A 8nm, CH B 558nm, CH C 254nm, CH D 258nm, CH E 833nm, CH F 685nm, USB4000 Integration time 50 msec, Avg 1/10



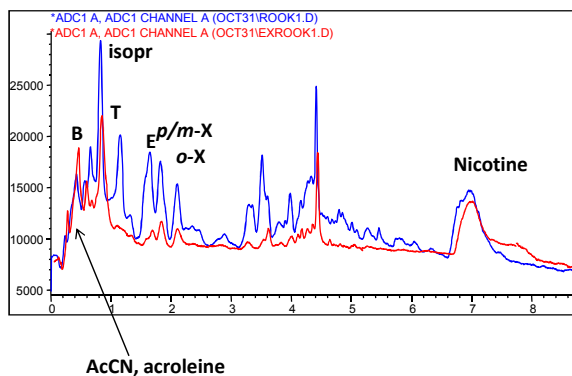
## $\mu$ CAD-PED Standard mixture in air (0.66 $\mu$ g/L)



## Air at petrol station (lead-free fuel)



## Cigarette smoke – exhaled smoke



## Application 3

### Chlorinated compounds in air

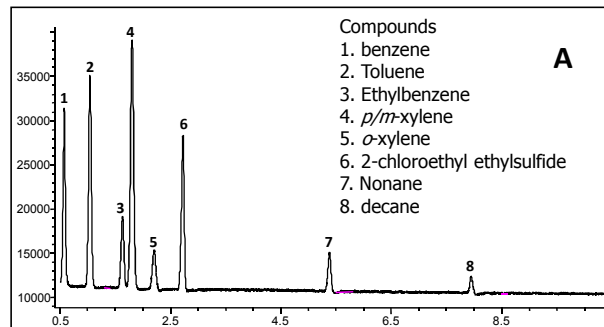


### $\mu$ CAD conditions

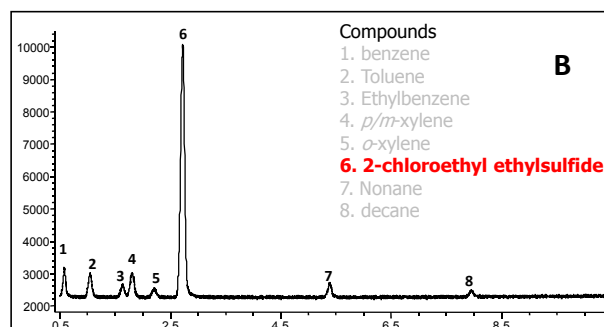
Sample	- 10 $\mu$ L per compound injected in 20 mL vial and equilibrated at 80°C - 10 $\mu$ L vapor injected in heated (150°C) 10 mL sampling valve
Sampling	10 sec @ 200 mL/min (sample vial 2 times flushed)
Chemical trap	<b>Tenax TA</b>
Thermal desorption	200°C (40 sec)
GC column	<b>5 m x 250 <math>\mu</math>m I.D., 1 <math>\mu</math>m df HP1-MS – connected to FID/PED/IMS/<math>\mu</math>ECD</b>
Carrier gas	Helium, constant pressure @ 7.5 psi (52 kPa)
GC column temp	<b>35°C (3 min) – 5°C/min – 150°C</b>
FID	280°C, air 350mL/min, H2 35 mL/min
PED	Time acquisition: 248nm, 558nm, 254nm, 258nm, 833nm, 685nm, USB4000 Integration time 100, Avg 0
IMS	500 mL/min air, 115°C, scanning Vc -15 to +5V, RF 600V
$\mu$ ECD	250°C, 60 mL/min N2



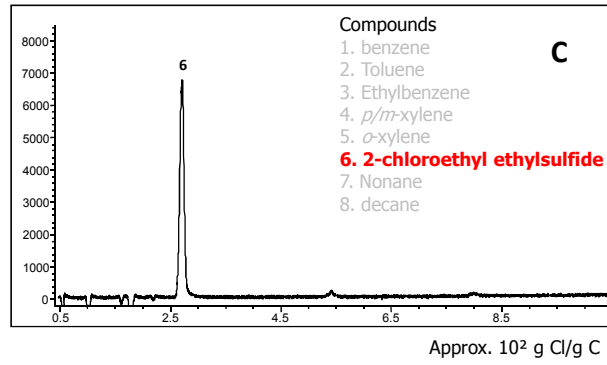
## $\mu$ CAD-PED Standard mixture in air (C2 @ 558 nm)



## $\mu$ CAD-PED Standard mixture in air (C1 @ 858 nm)

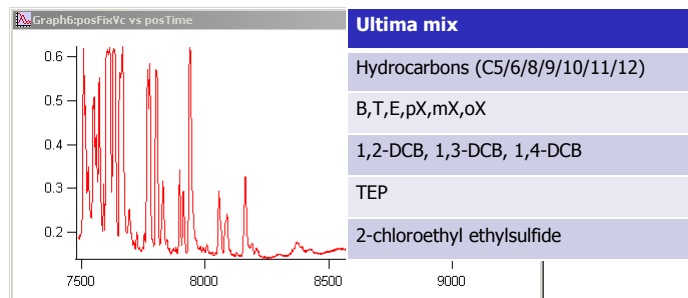


## μCAD-PED Standard mixture in air (corrected CI)

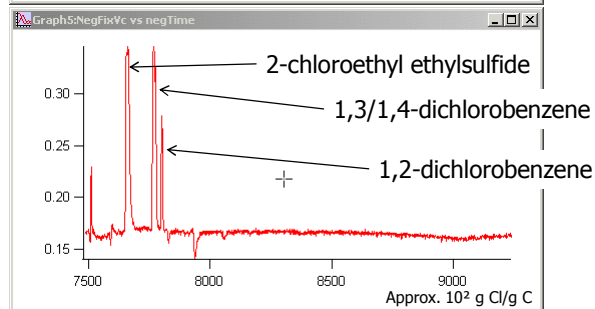


## μCAD-IMS

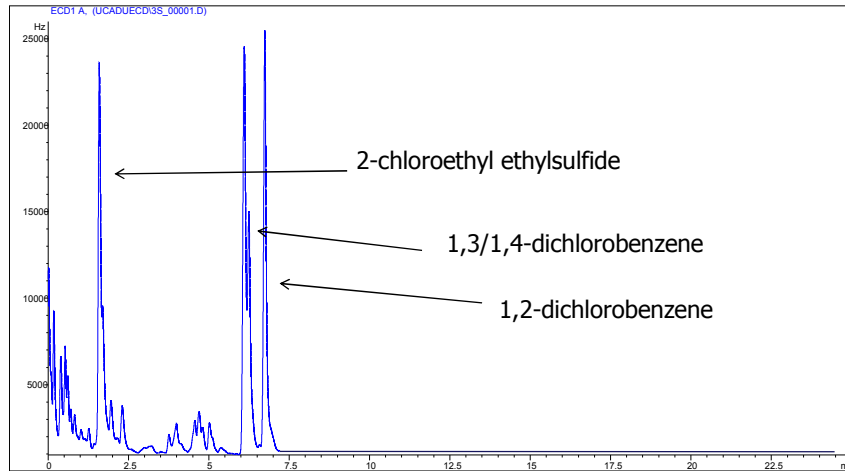
**POS MODE**  
**V<sub>c</sub> = -0.82V**



**NEG MODE**  
**V<sub>c</sub> = -7.26V**



## $\mu$ CAD- $\mu$ ECD

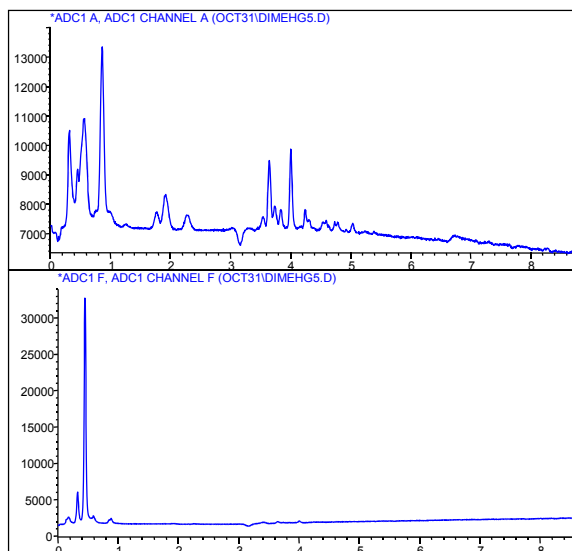


## Application 6

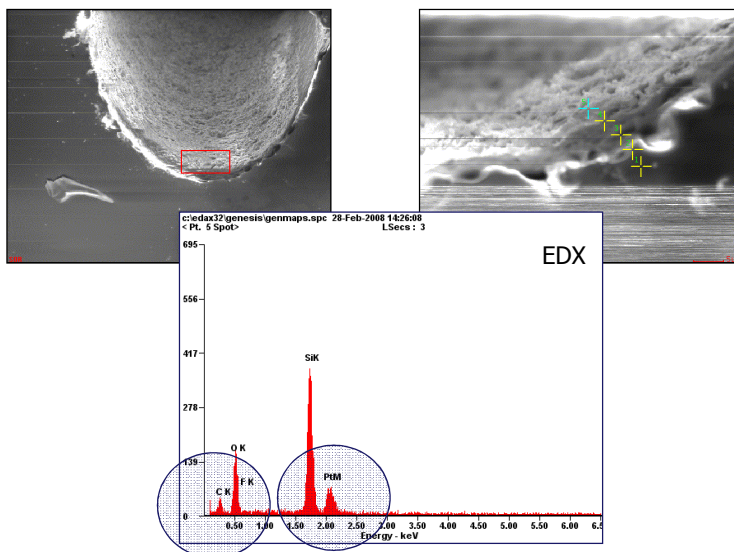
### Organomercury in air



## Di-methyl mercury in air



## Fouling: carbon – Pt sputtering



## Conclusion

- Novel GC column heating technology : allows temperature programming
- Fully integrated air sampling and enrichment trap
- Detectors customized to application

