Water Analysis

Organic and Inorganic Micropollutants

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Agilent Technologies

New Developments in GC and GC/MS for the analysis of trace and ultratrace contaminants in water samples

State-of-the-art HPLC and LC/MS technologies for water analysis

Micropollutants ?

- ***Those listed in official methods***
  - ***VOCs***
  - ***Semi-VOCs***
  - ***PAHs***
  - ***…***
- ***Endocrine disrupting chemicals***
  - ***Detergents***
  - ***Organotin compounds***
  - ***…***
- ***Drug residues***
  - ***Pharmaca***
  - ***Contraceptiva***
  - ***…***
- ***Odour compounds***

Flow diagram analysis of micropollutants

- ***Sampling***
  - *Collection*
  - *Storage*
- ***Sample preparation***
  - *Extraction*
  - *Fractionation/clean-up*
  - *Concentration*
  - *Derivatization*
- ***Chromatographic analysis***
  - *Separation*
- ***Data handling***
  - *Identification*
  - *Quantification*
- ***Reporting***

What chromatographic technique to select ?

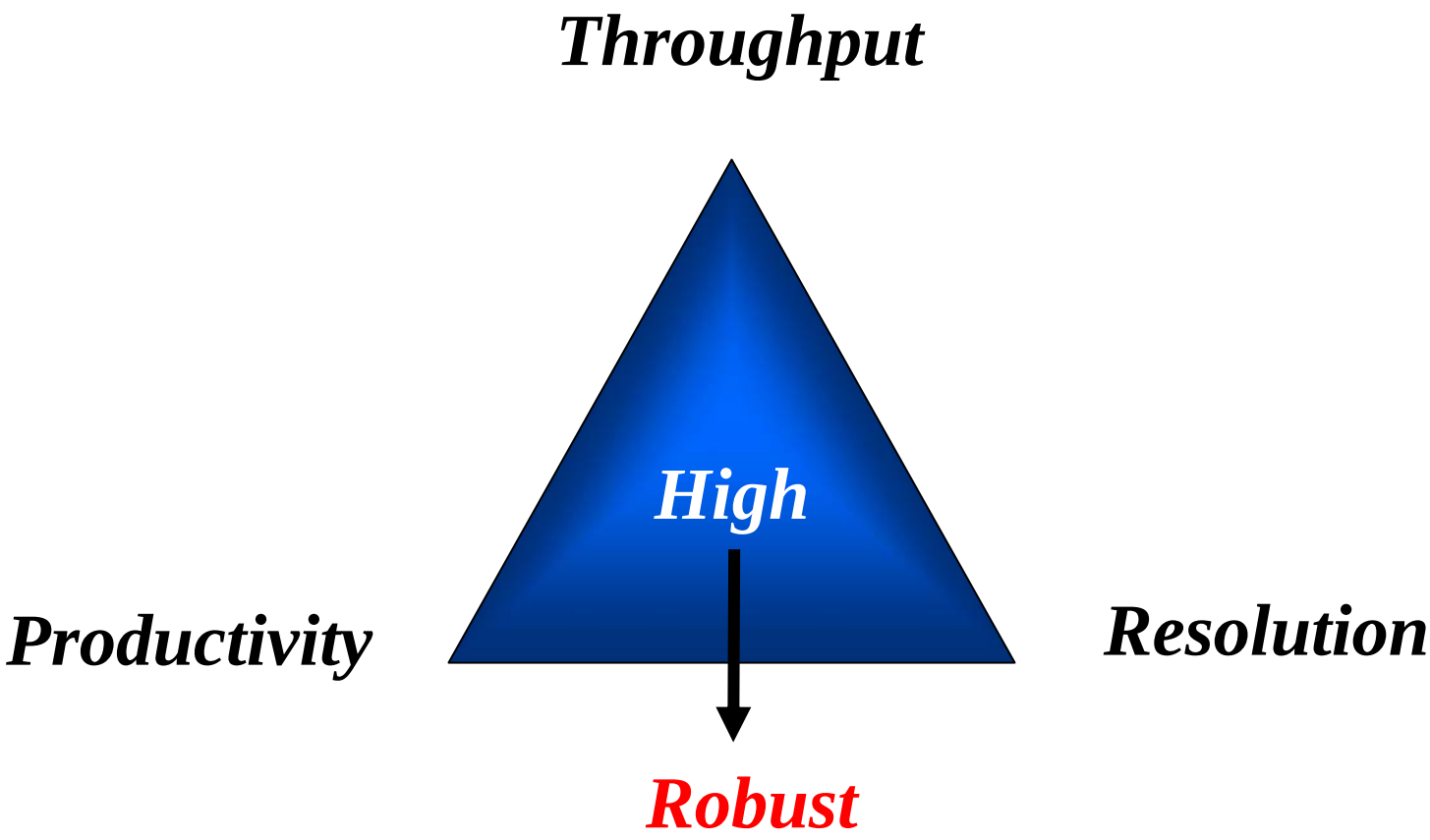
- ***For target compound analysis***

  If capillary GC can be applied, this should always be the technique of choice !

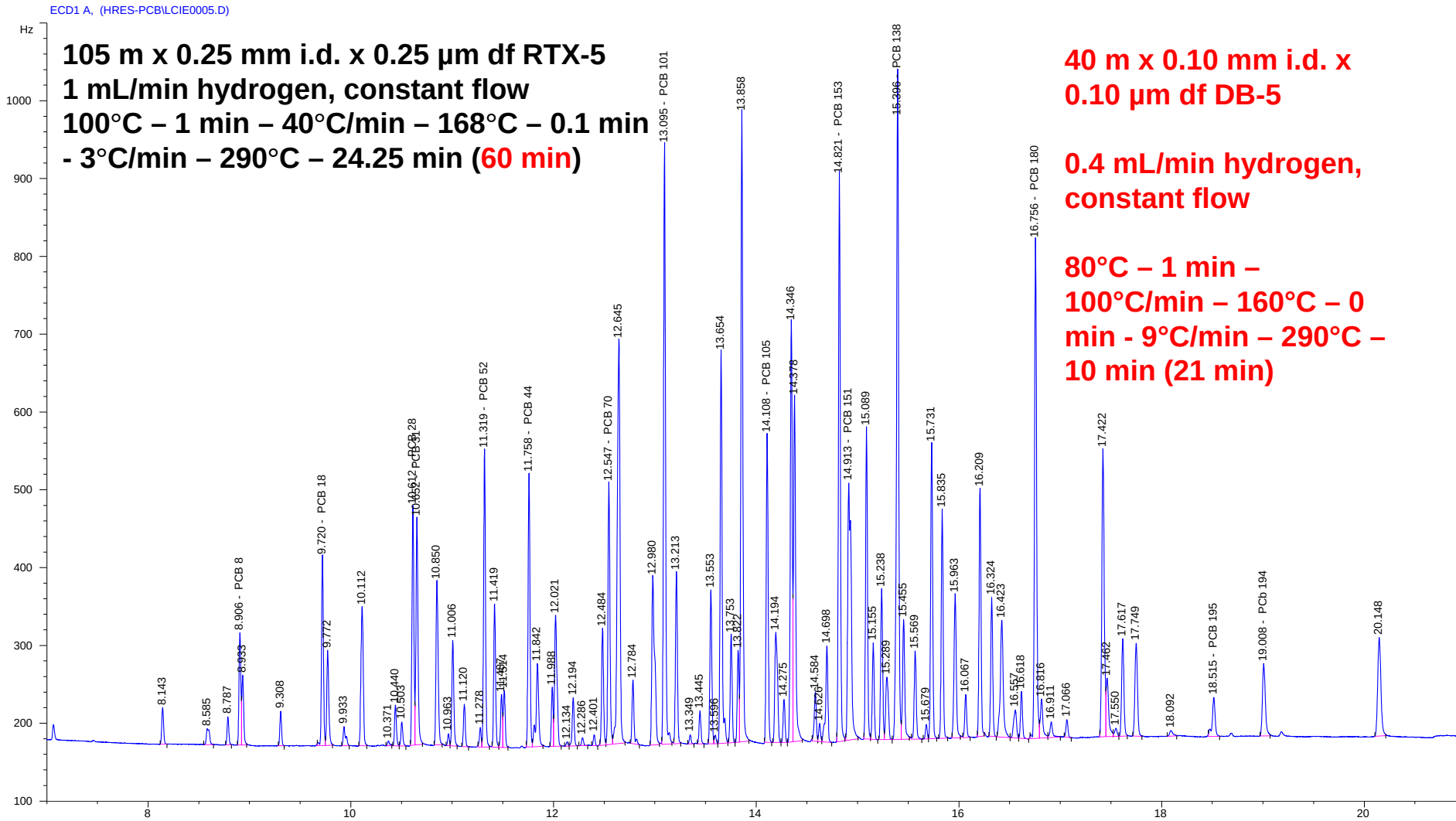
- ***For multi-residue analysis***

  The application of both GC and LC is mandatory !
  GC preferably on a PDMS type column
  LC preferably on a ODS type column

The "21st century" triangle ?



High Resolution GC PCB analysis



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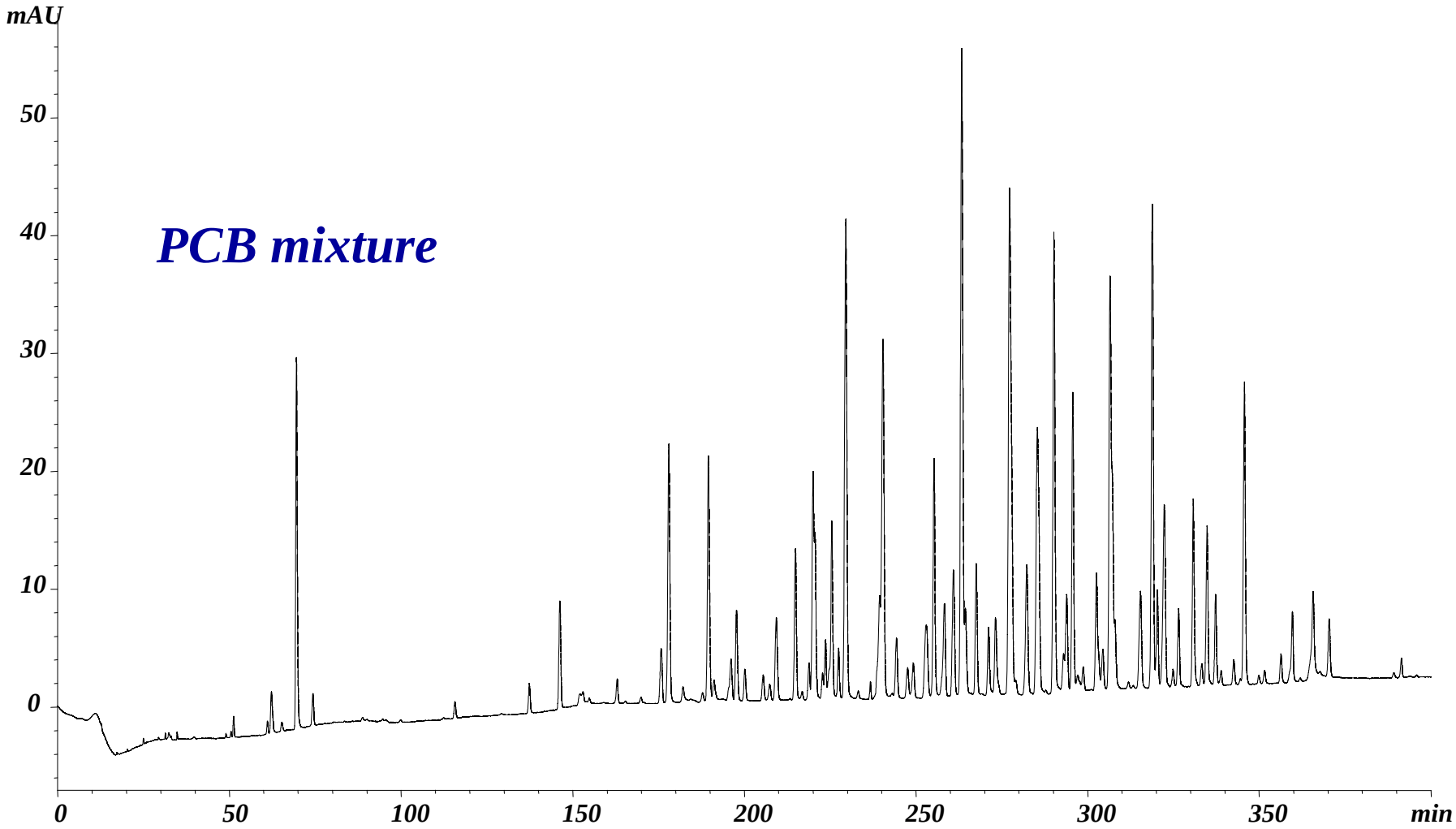
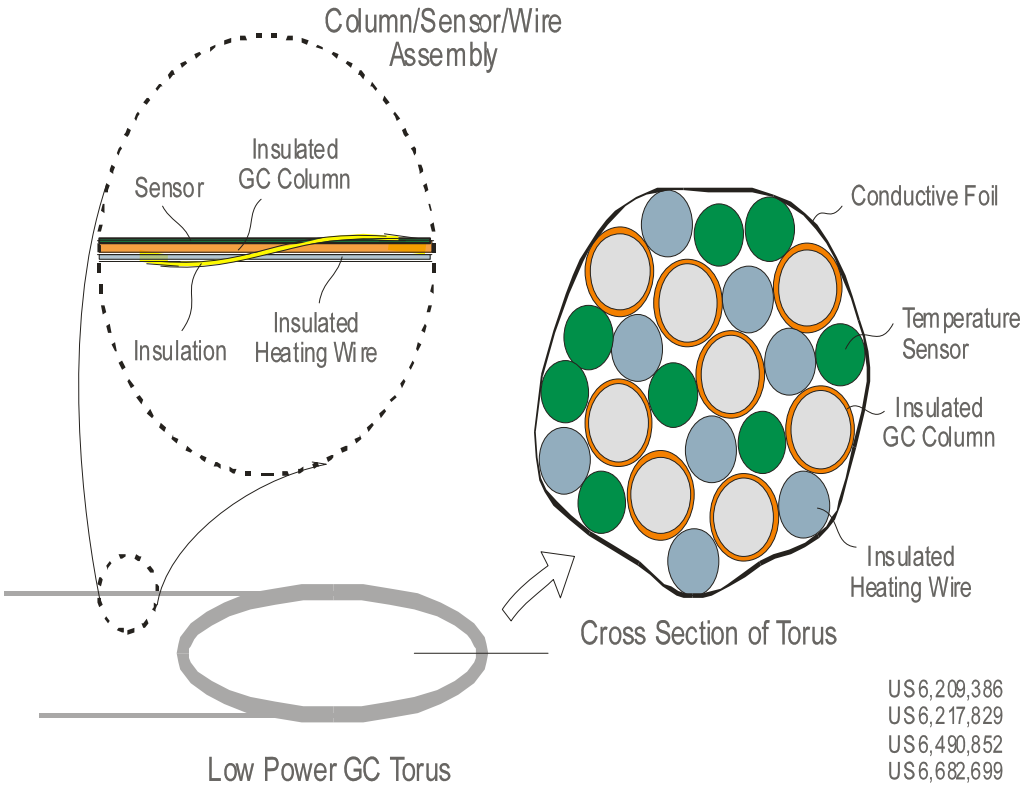
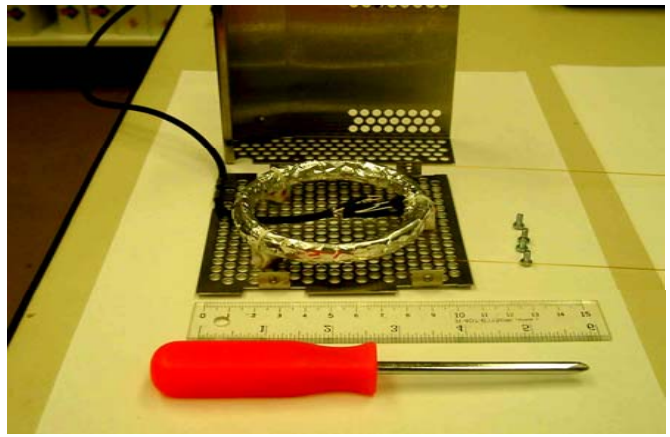
High Resolution LC PCB analysis

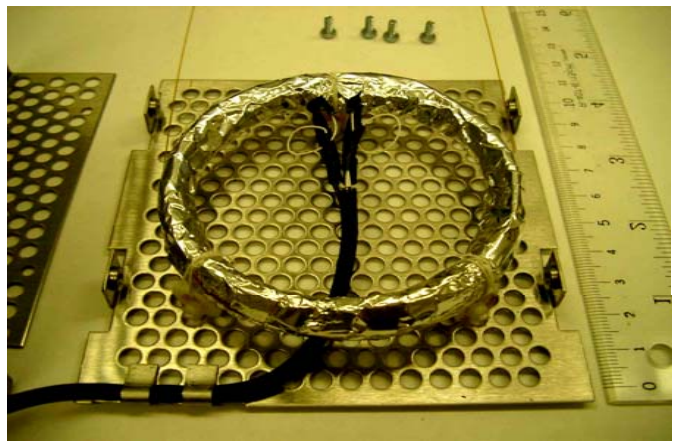


Modular Accelerated Column Heater (MACH™)

Low Thermal Mass GC Technology







Heating rates: up to 1200°C/min !!

Gerstel MACH™ Twin Module

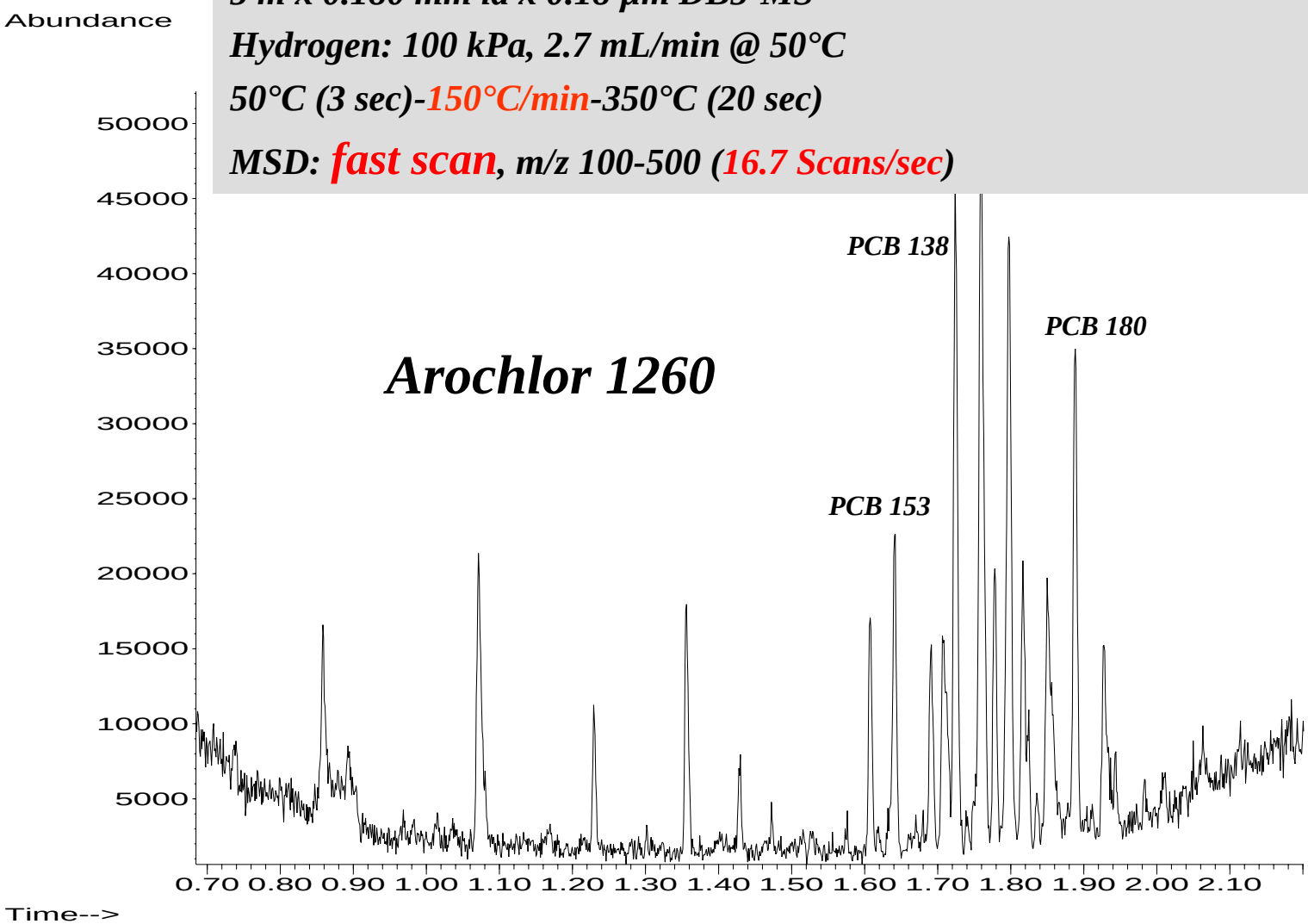
Polychlorinated Biphenyls

5 m x 0.180 mm id x 0.18 µm DB5-MS

Hydrogen: 100 kPa, 2.7 mL/min @ 50°C

50°C (3 sec)-150°C/min-350°C (20 sec)

MSD: fast scan, m/z 100-500 (16.7 Scans/sec)



Recent developments – state-of-the art !

- *In capillary GC and GC-MS*
- *In HPLC and LC/MS*
- *In sample preparation*

Recent developments – state-of-the art !

- ***In capillary GC and GC-MS***
  - ***The concept of retention time locking***
  - ***Deconvolution reporting software***
  - ***Method translation software***
  - ***Microfluidics***
  - ***SCAN/SIM mode***
  - ***Electron impact ionization***
  - ***Positive and negative chemical ionization***

Recent developments – state-of-the art !

- ***In HPLC and LC/MS***
  - ***Sub 2 µm particles***
  - ***High pressure***
  - ***High temperature***
  - ***Modes of ionization***
    - ***ESI-APCI-APPI***
  - ***Mass Analyzer***
    - ***Single quadrupole***
    - ***Triple quadrupole***
    - ***Ion trap***
    - ***Time-of-flight***

Recent developments – state-of-the art !

- *In sample preparation*

Recent developments – state-of-the art !

- ***In sample preparation***

  In the era of green chemistry … environmental analysis should be "environmentally" friendly !

  The time is over that 1 L water is extracted with 250 mL dichloromethane !

- ***Important***

  - ***miniaturization or even solventless !***
  - ***from trace to ultratrace … contamination !***
  - ***the problem of "adsorption" on the walls***

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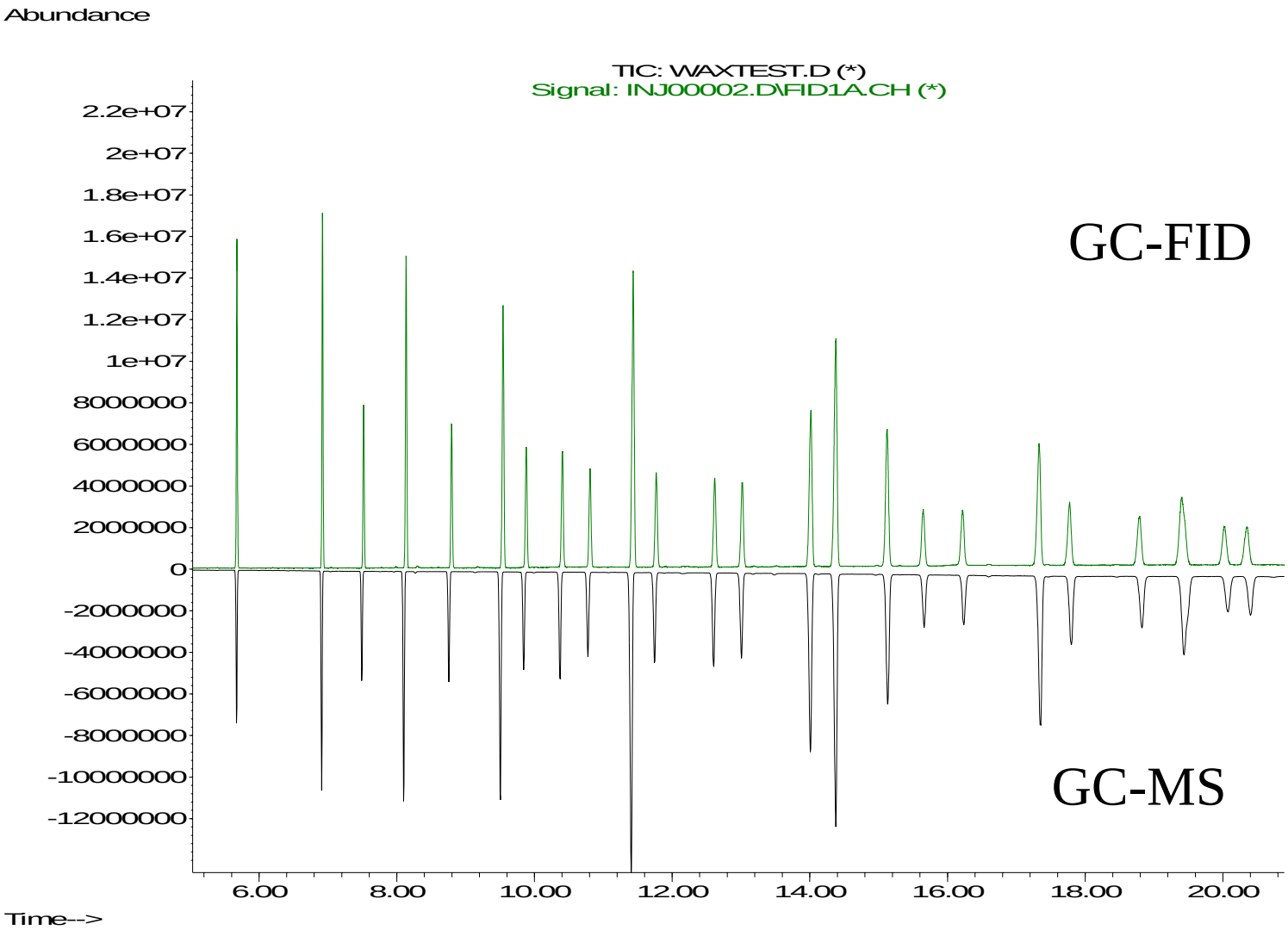
1995: Agilent 6890 GC Retention Time Locking.

The ability to exactly match chromatographic retention times in one GC system to those in another GC system, using the same nominal column.

Identical Retention Times from Column to Column, Instrument to Instrument, Lab to Lab, Country to Country


Abundance
TIC: WAXTEST.D (*)
Signal: INJ00002.D\FID1A.CH (*)
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
-2000000
-4000000
-6000000
-8000000
-10000000
-12000000
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Time-->
GC-FID
GC-MS

Introducing the Agilent 7890 GC
The Evolution of Excellence

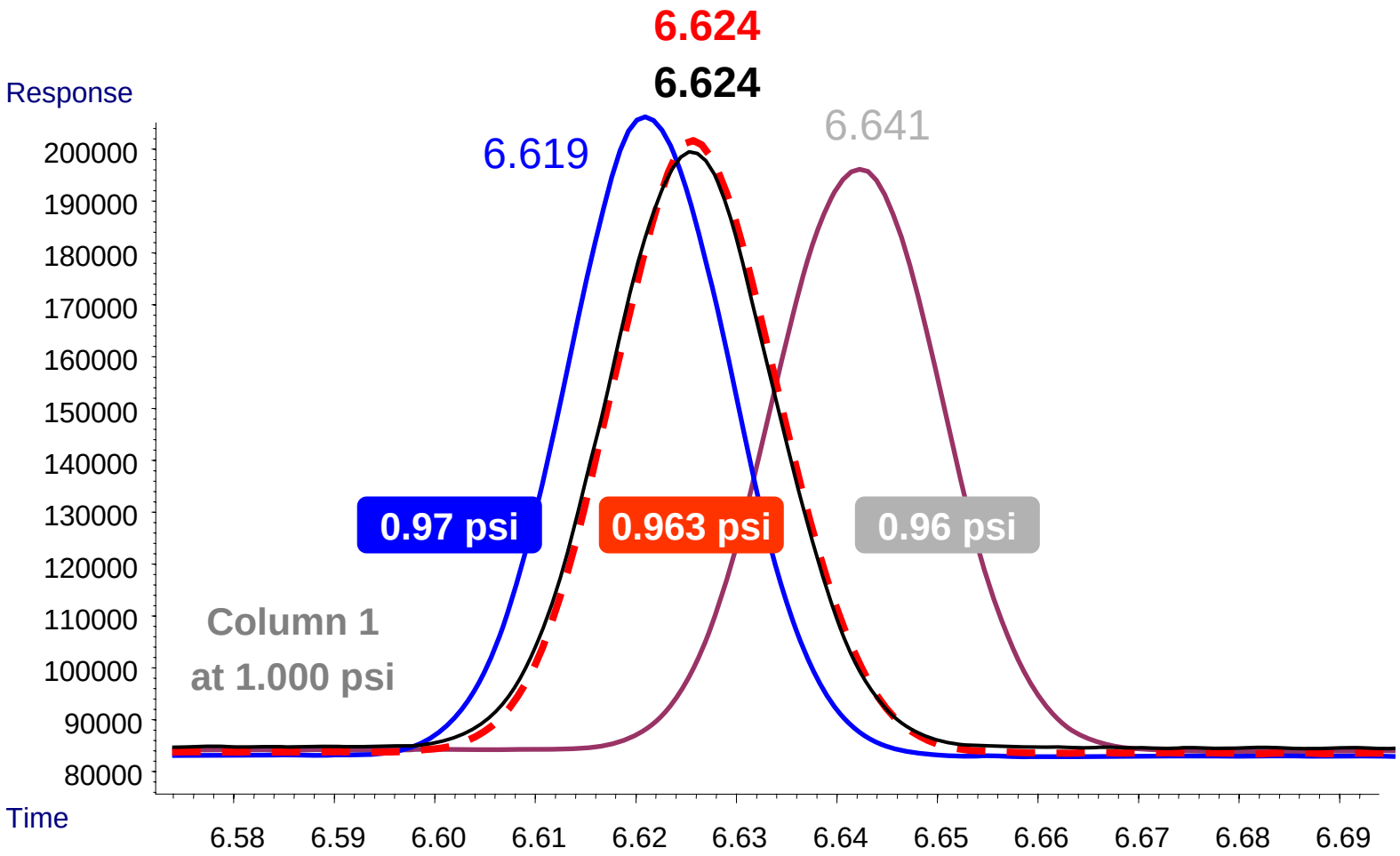
R.I.C.

Agilent Technologies

RTL

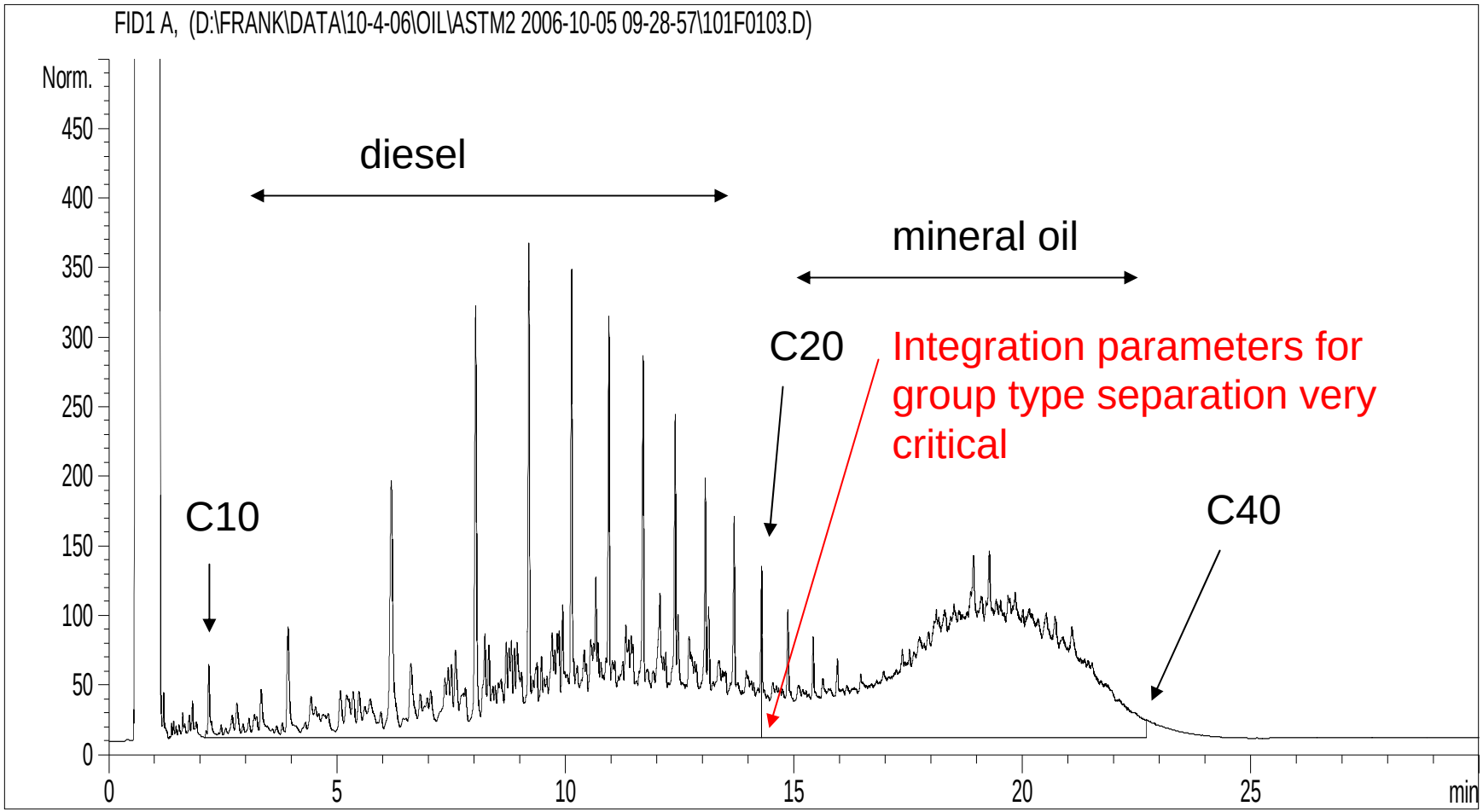
- Column 1: 5 runs
  - Nominal @ 1.000 psi – C20 @ 6.624 min
- Column 2:
  - Scout (1.000 psi): C20 @ 6.565 min
  - Calculate from RTL calibration: 0.963 psi for relocking
  - Set 0.960 psi: C20 @ 6.640 min
  - Set 0.970 psi: C20 @ 6.619 min
  - Set 0.963 psi: C20 @ 6.624 min

Why 1/1000 psi Matters!
Key to even better Retention Time Locking (RTL)



Determination of Hydrocarbon Oil Index

15 m x 530 µm x 0.15 µm HP-1 (SIMDIST)



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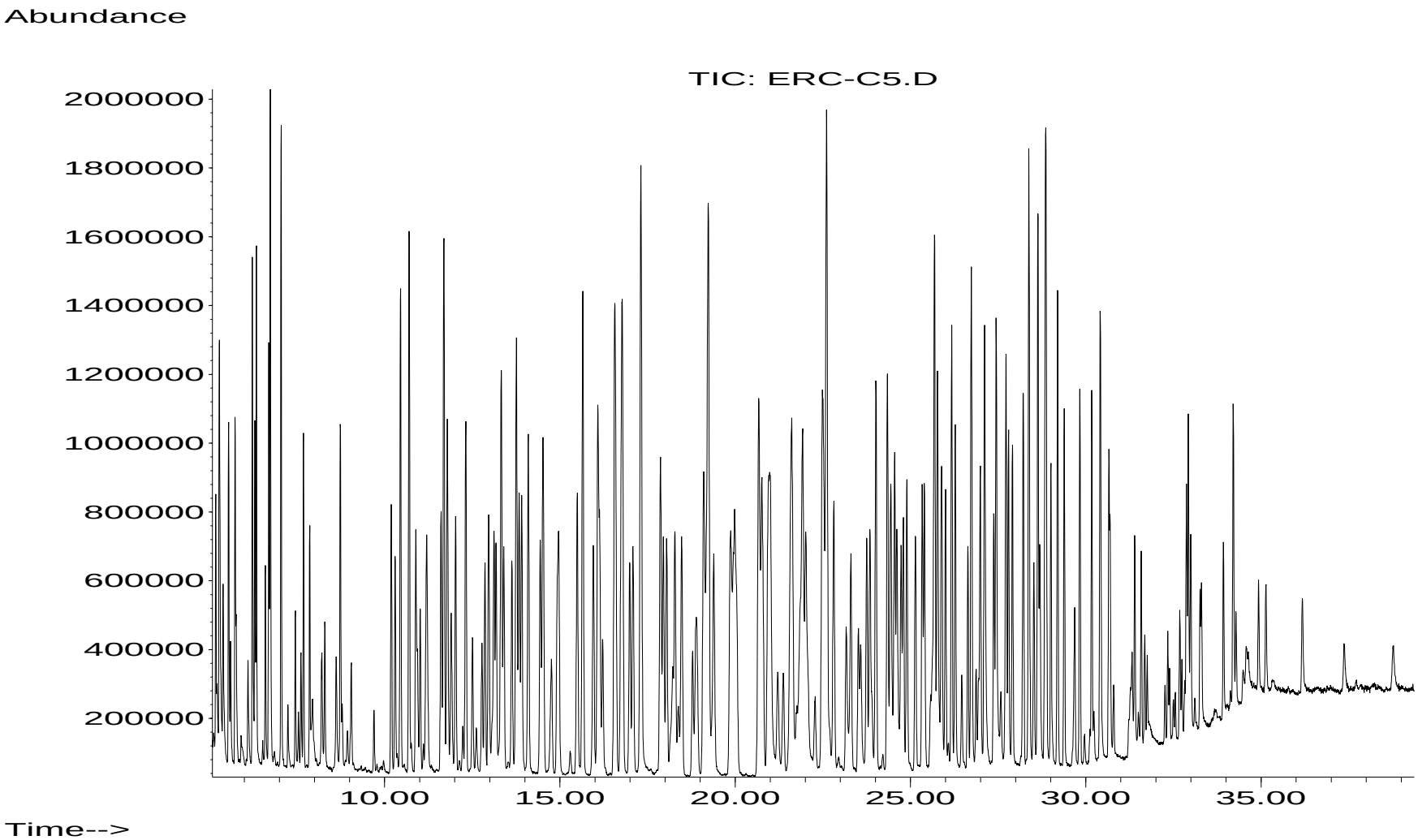
CGC-MS of pesticide (n=200) mixture



Contact Us

Pesticide Screening

- Library
- Technical Support
- Online Store
- Education
- Events
- News Releases
- Alliances
- Registration

Stay current with e-notes

Finding the needle in the haystack. It's time.

Over 700 pesticides are regulated worldwide to ensure safer foods. Typical pesticide screening programs search for 100 or fewer. Usually, samples are run on two or more gas chromatographs with element-selective detectors to tentatively identify compounds, then on a GC/mass spectrometer system for confirmation. Unfortunately, retention times may vary from GC to GC, even when using the same method. And there is even more variation between GC and GC/MS retention times. In all, pesticide identification can be difficult and time-consuming.

In contrast, pesticide identification is fast, easy, and certain with Agilent's 6890N gas chromatograph system equipped with our 5973N GC/MSD or sensitive element-specific detectors, retention time locking (RTL) software, and pesticide library software. This system can narrow the possible identity of unknown pesticides to three or fewer. Or in many cases, to one. And when you run your sample on an Agilent GC/MS system for confirmation, RTL will ensure that the unknowns appear at the same retention time, increasing your confidence in results.

Features

Key Information

Library Information

- Applications
- Brochure (2.4 Mbytes)
- More...

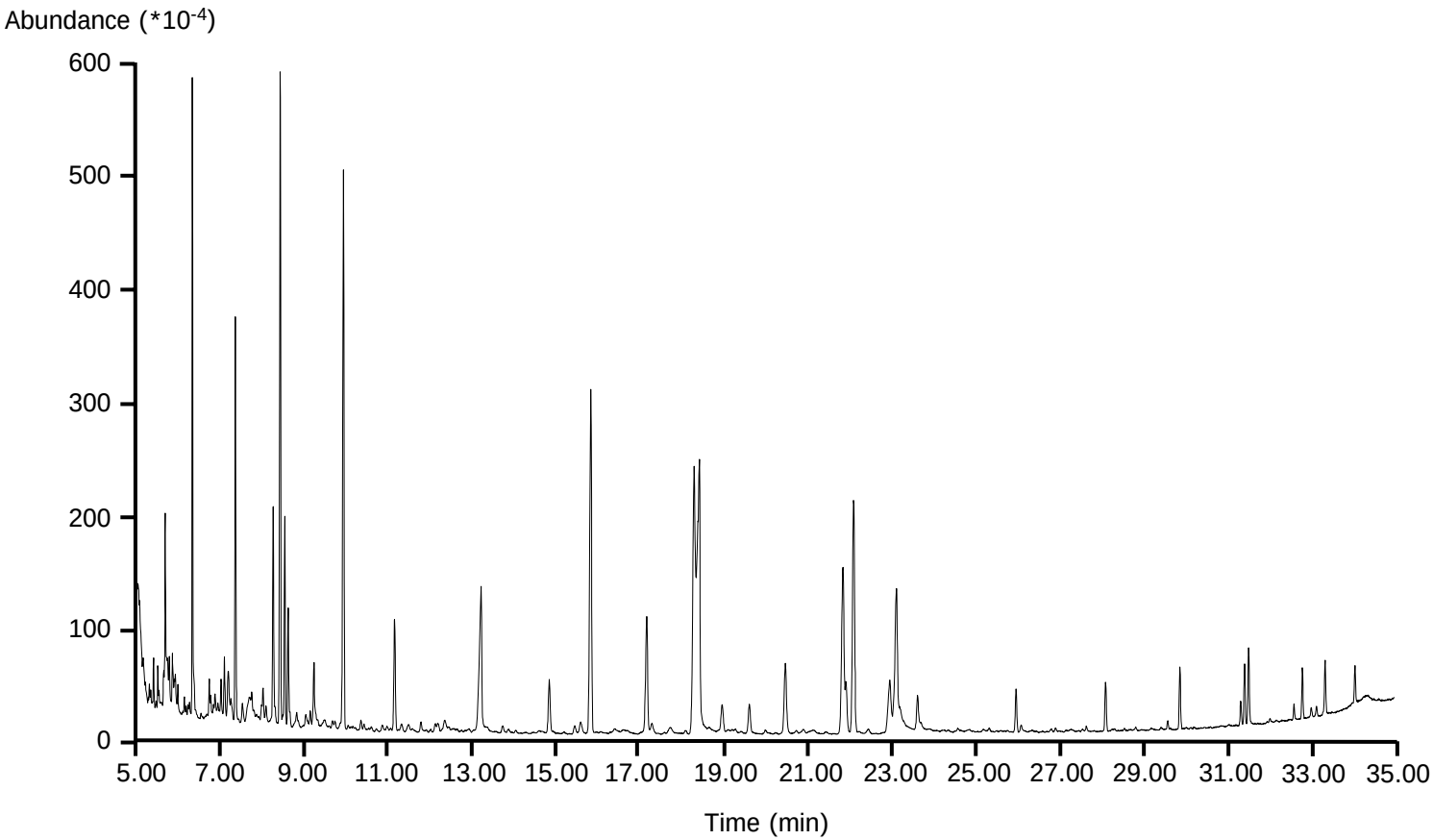
Technical Support

- User-contributed RTL Macros

Ordering Information

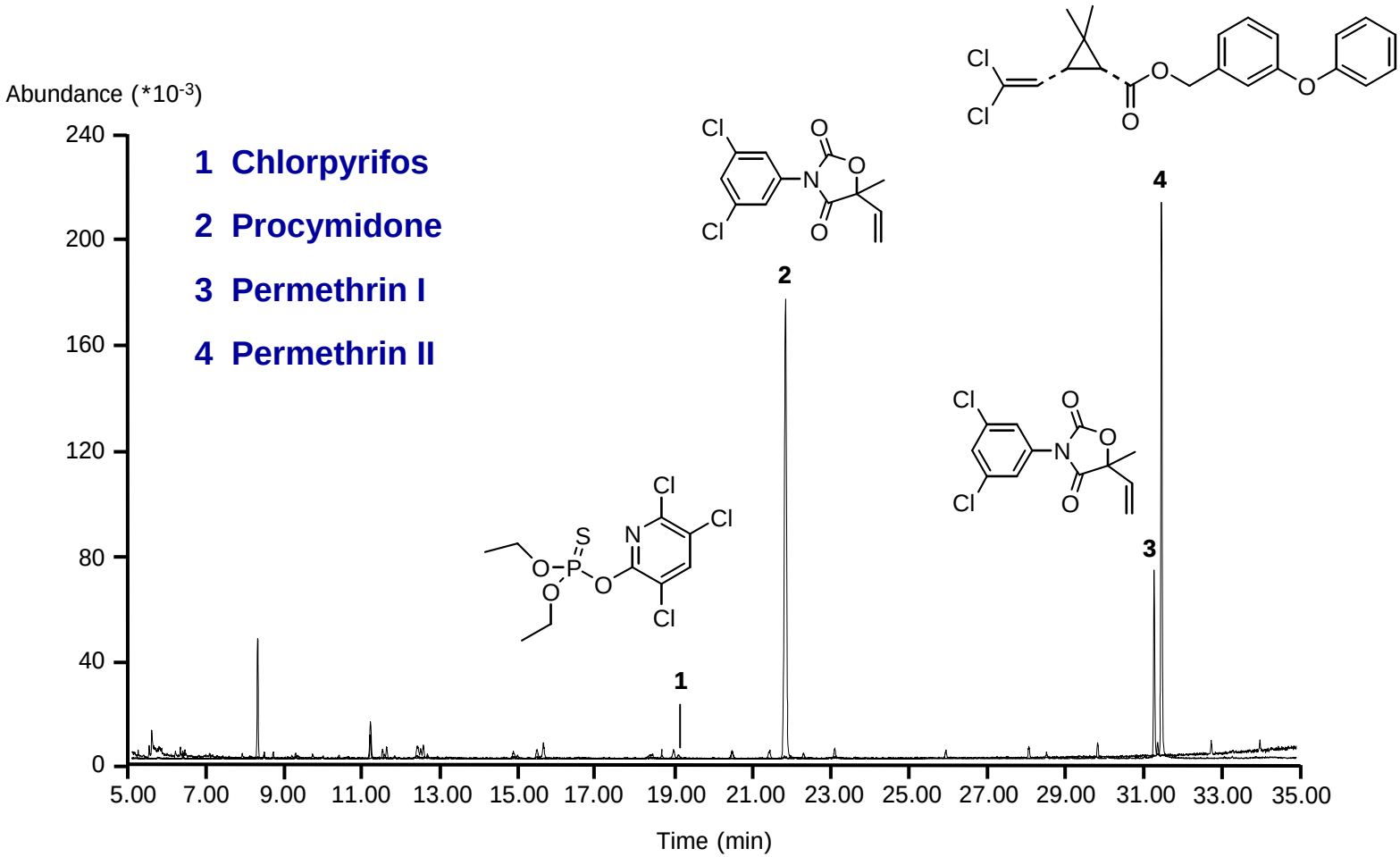
- Ordering Details
- Request a Quote
- Where to Buy

Illustration



Total ion chromatogram (TIC)

DRS result



EIC: m/z 183, 197, 283

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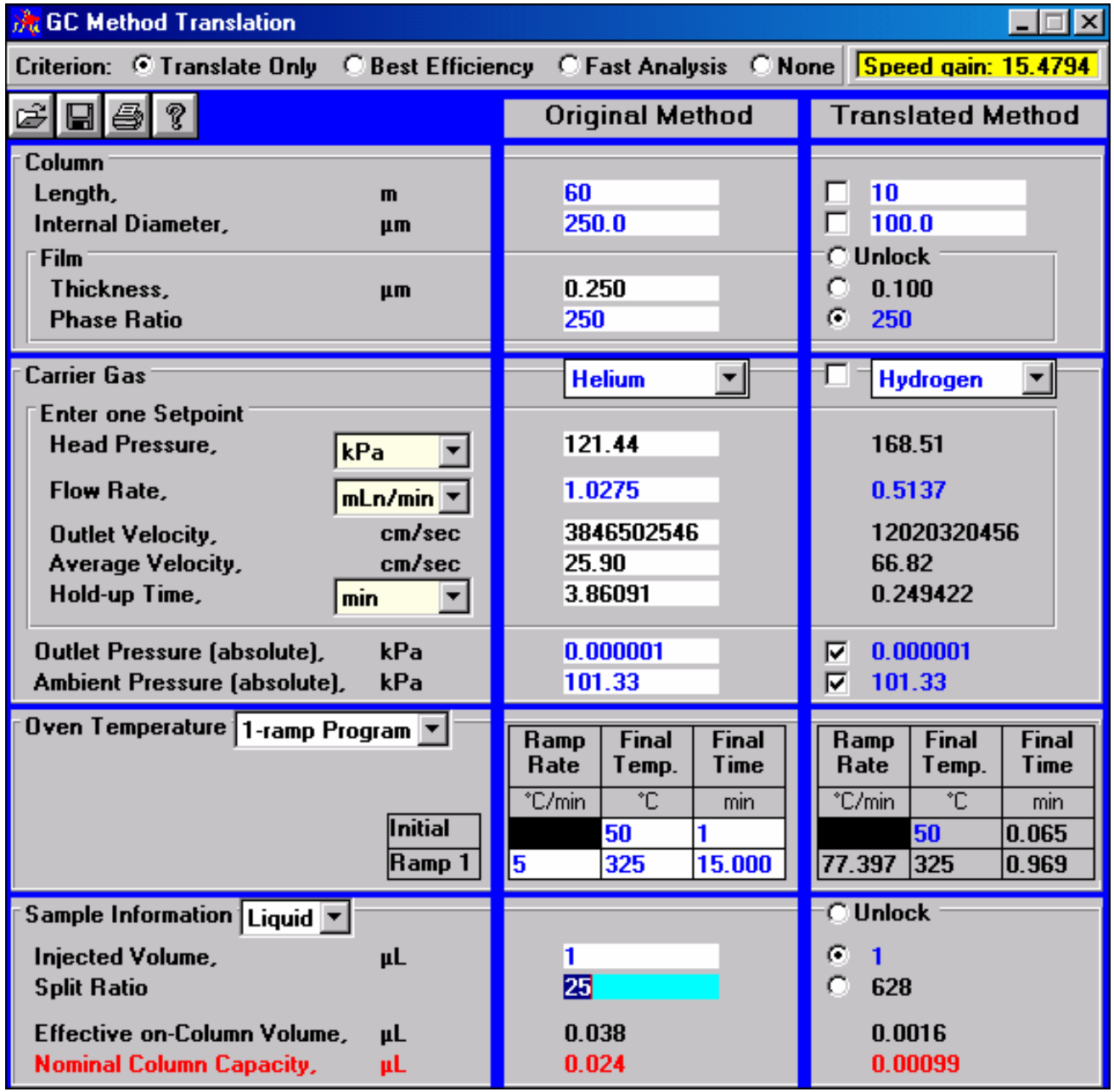
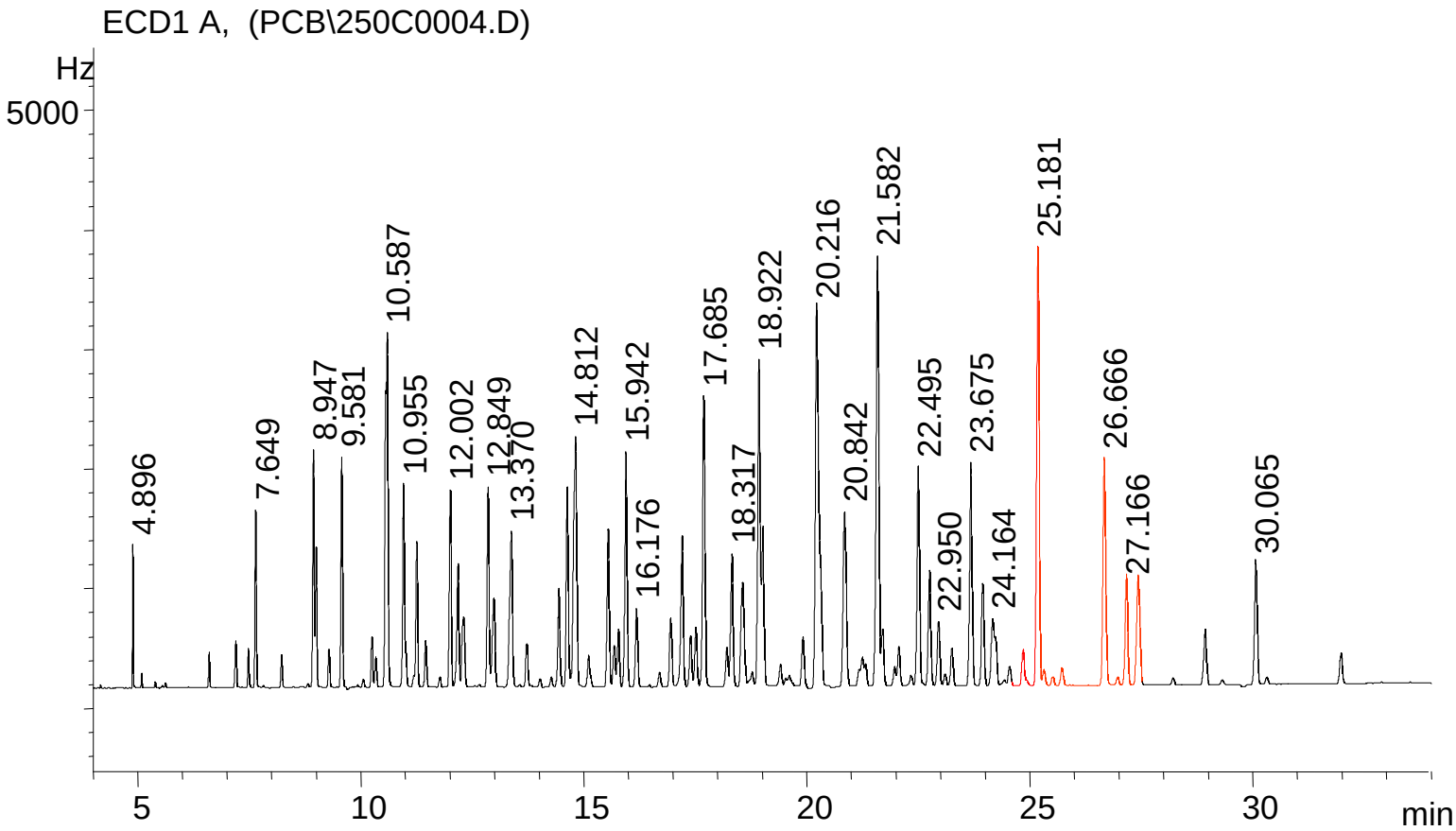

GC Method Translation
Criterion: Translate Only Best Efficiency Fast Analysis None
Speed gain: 15.4794
Original Method
Translated Method
Column
Length, m
60
10
Internal Diameter, µm
250.0
100.0
Film
Thickness, µm
0.250
Unlock
0.100
Phase Ratio
250
250
Carrier Gas
Helium
Hydrogen
Enter one Setpoint
Head Pressure, kPa
121.44
168.51
Flow Rate, mLn/min
1.0275
0.5137
Outlet Velocity, cm/sec
3846502546
12020320456
Average Velocity, cm/sec
25.90
66.82
Hold-up Time, min
3.86091
0.249422
Outlet Pressure (absolute), kPa
0.000001
0.000001
Ambient Pressure (absolute), kPa
101.33
101.33
Oven Temperature
1-ramp Program
Ramp Rate °C/min
Final Temp. °C
Final Time min
Initial
50
1
50
0.065
Ramp 1
5
325
15.000
77.397
325
0.969
Sample Information
Liquid
Unlock
Injected Volume, µL
1
1
Split Ratio
25
628
Effective on-Column Volume, µL
0.038
0.0016
Nominal Column Capacity, µL
0.024
0.00099

High Resolution Separation of PCB congeners



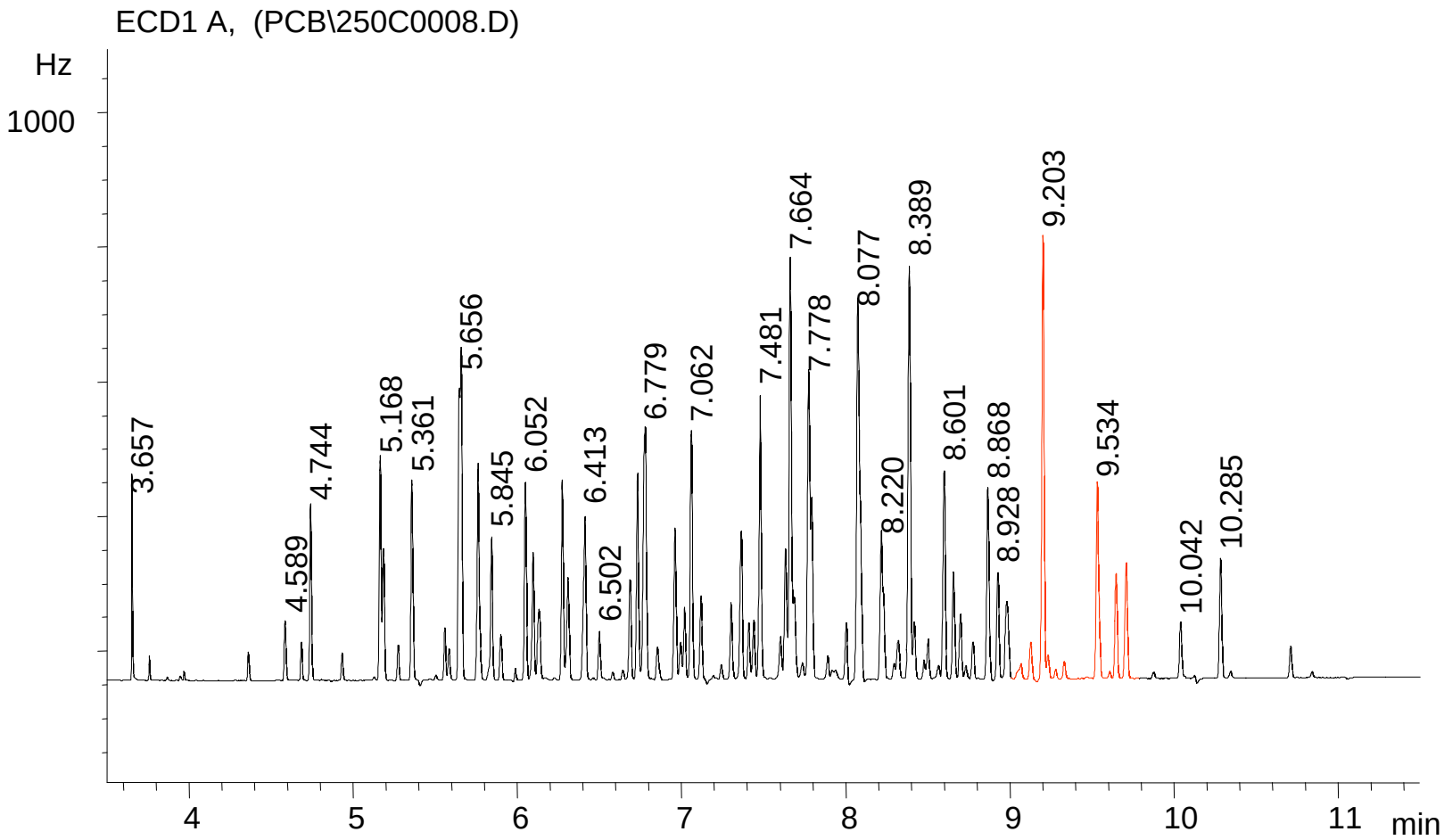
Fast RTL GC-µECD

- *30 m x 250 µm i.d. x 0.25 µm HP-5MS*
- *71 kPa hydrogen.*
- *70°C - 2 min - 25°C/min - 150°C - 3°C/min - 200°C - 8°C/min - 300°C*

- *10 m x 100 µm i.d. x 0.10 µm HP-5MS*
- *233 kPa hydrogen.*
- *70°C - 0.45 min - 110°C/min - 150°C - 13.2°C/min - 200°C - 35.2°C/min - 300°C*

Both splitless injection !

Short Narrow Bore column
= equal resolution + shorter analysis time



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QuickSwap for MS no-vent and Backflush

Aux EPC In

5 psi during run

90 psi during backflush

25+ psi during run

S/SL Inlet

1 psi during backflush

Carrier/Aux flow

Column flow

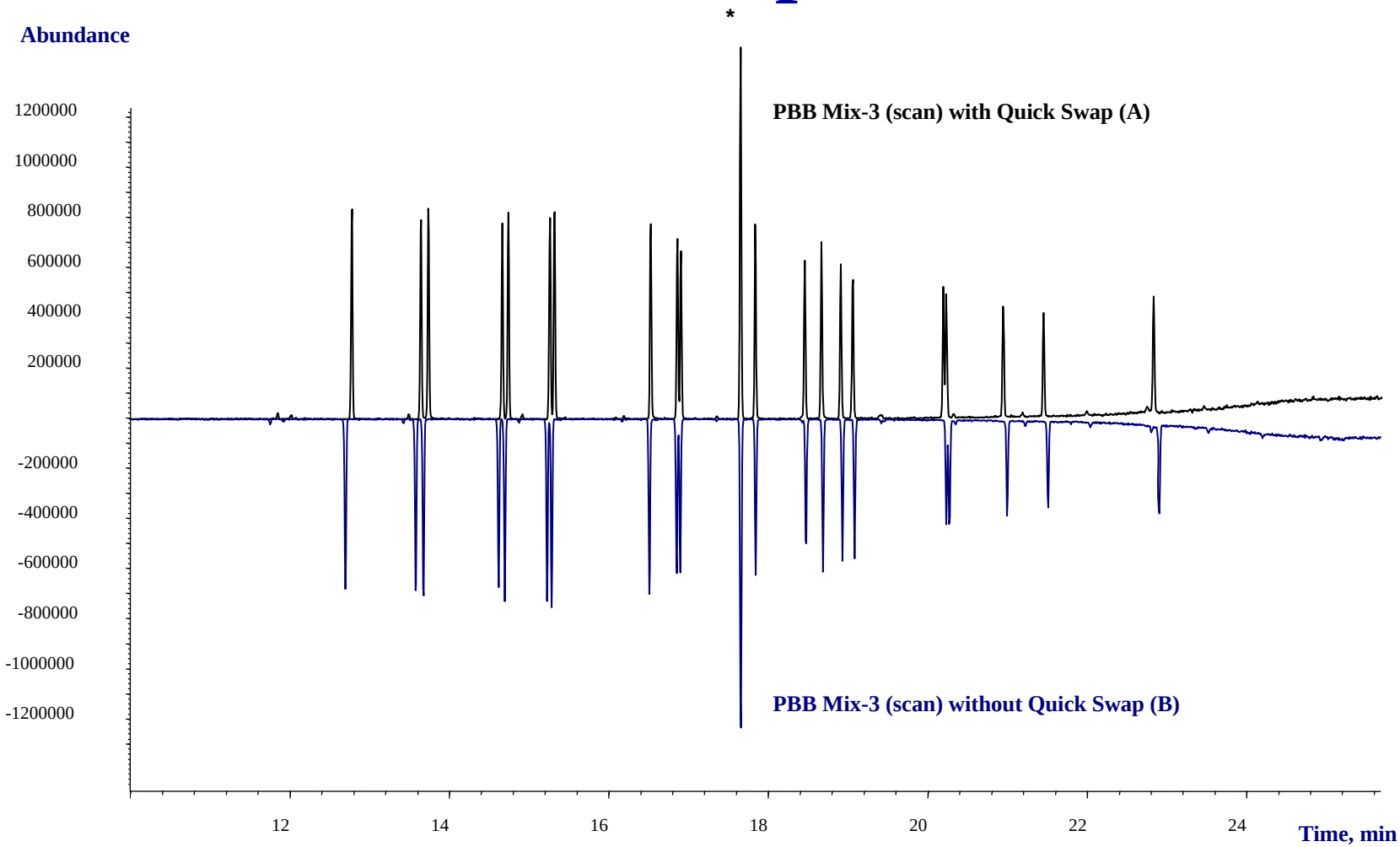
MSD Transfer line

During run

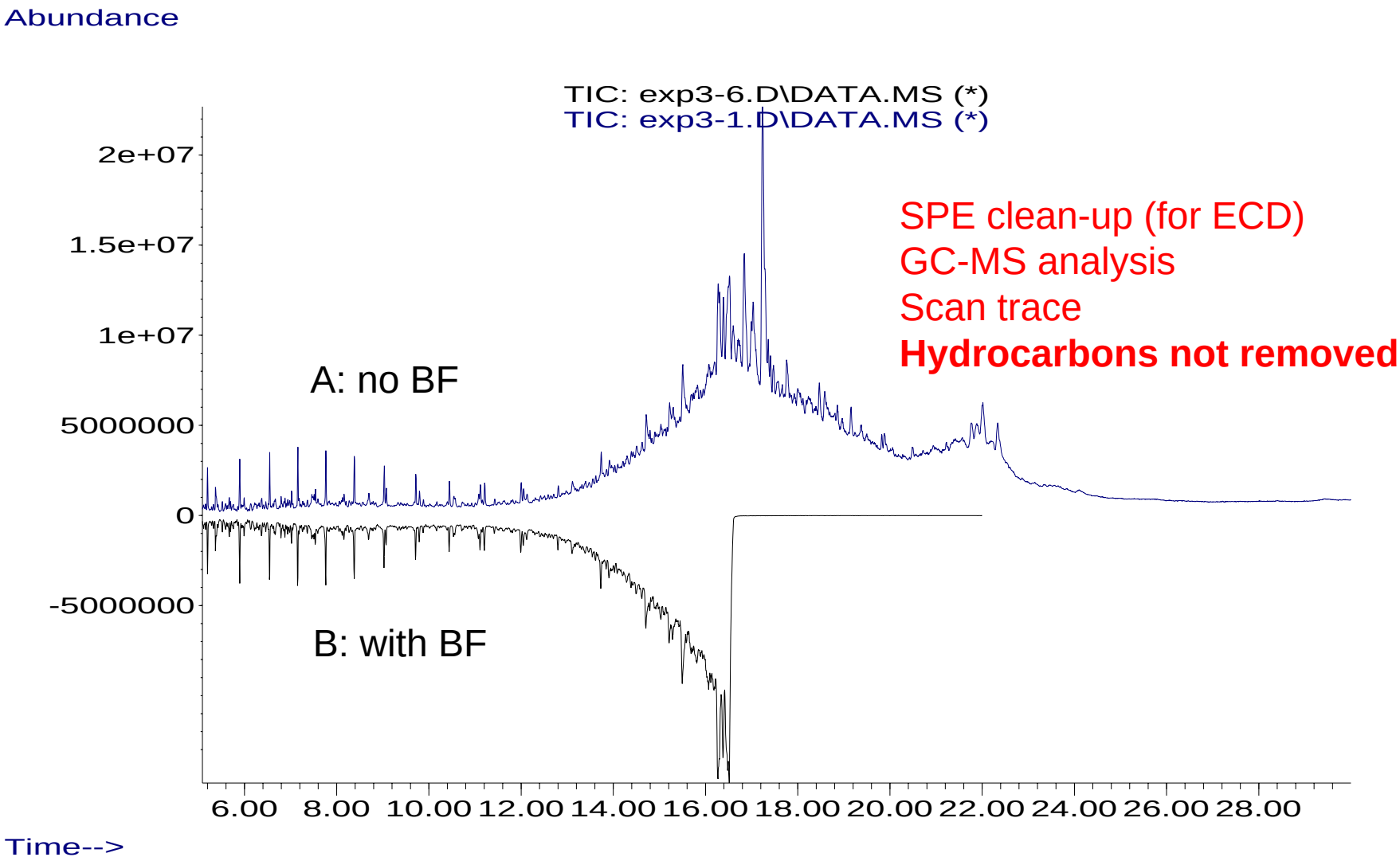
During backflush

Quick Swap restrictor

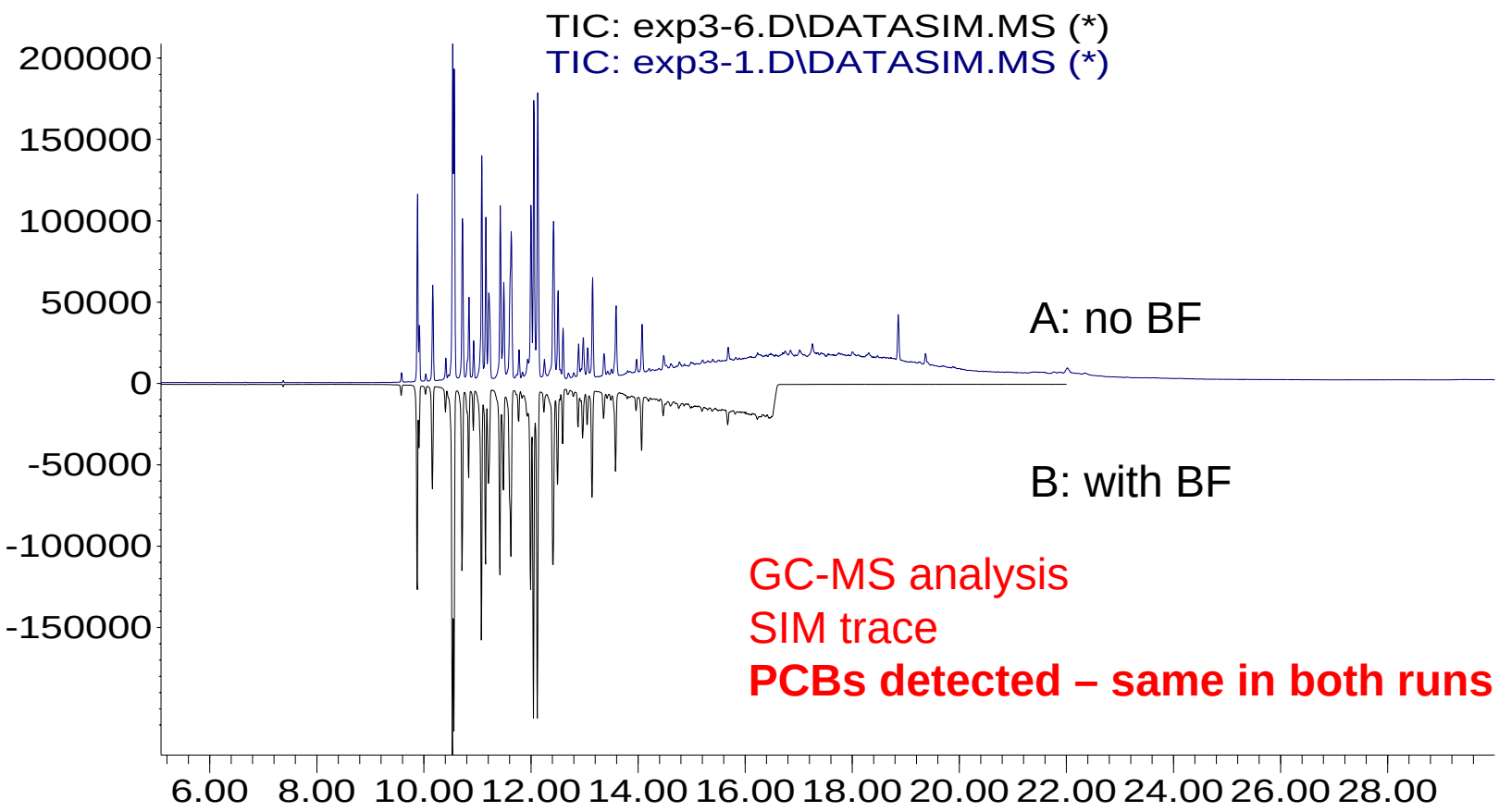
Analysis of Polybrominated biphenyls: no cold spot



Determination of PCBs in waste water extract



SPE clean-up (for ECD)
GC-MS analysis
Scan trace
Hydrocarbons not removed


Abundance
TIC: exp3-6.D\DATASIM.MS (*)
TIC: exp3-1.D\DATASIM.MS (*)
200000
150000
100000
50000
0
-50000
-100000
-150000
A: no BF
B: with BF
GC-MS analysis
SIM trace
PCBs detected – same in both runs
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00
Time-->

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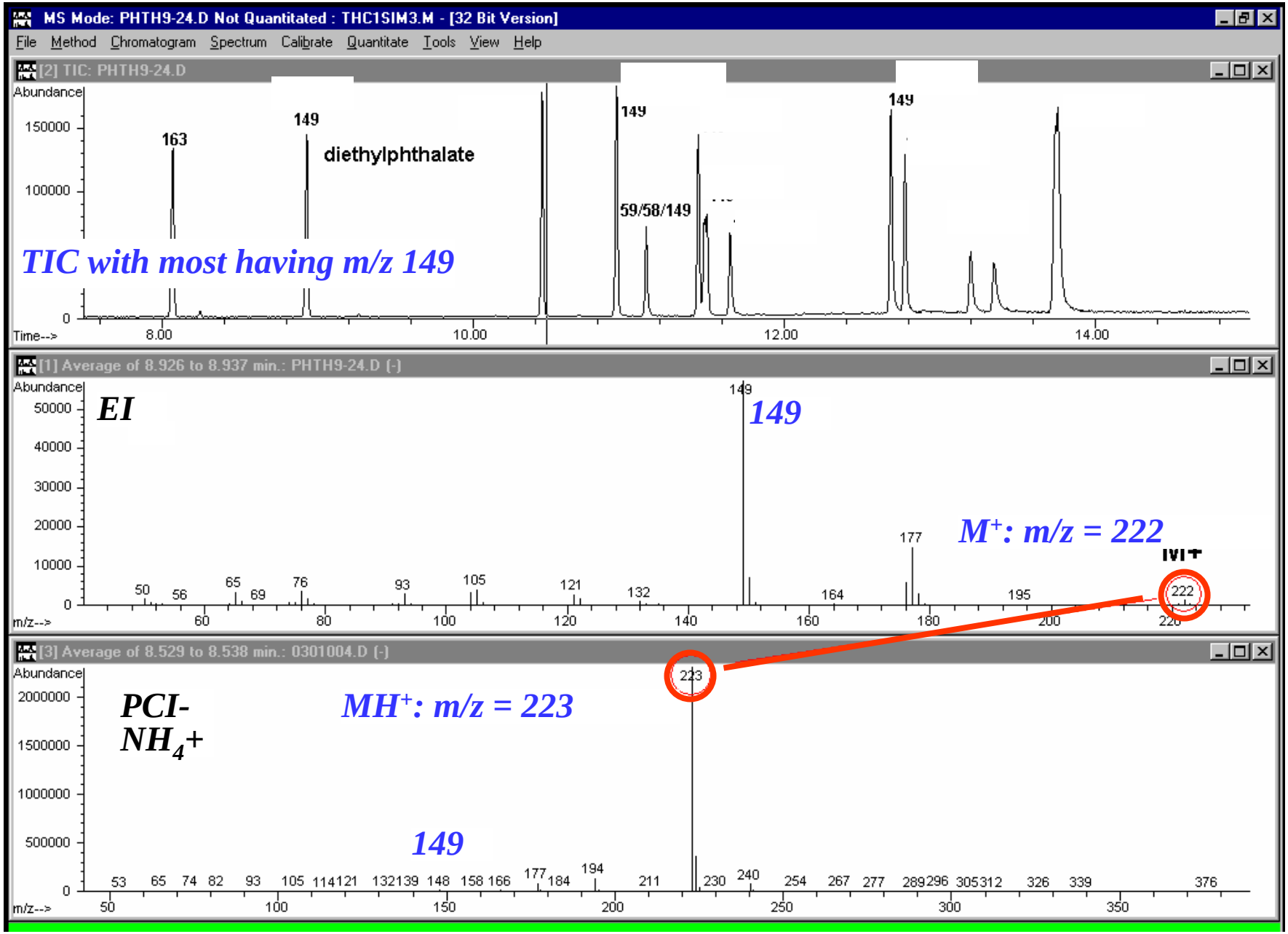
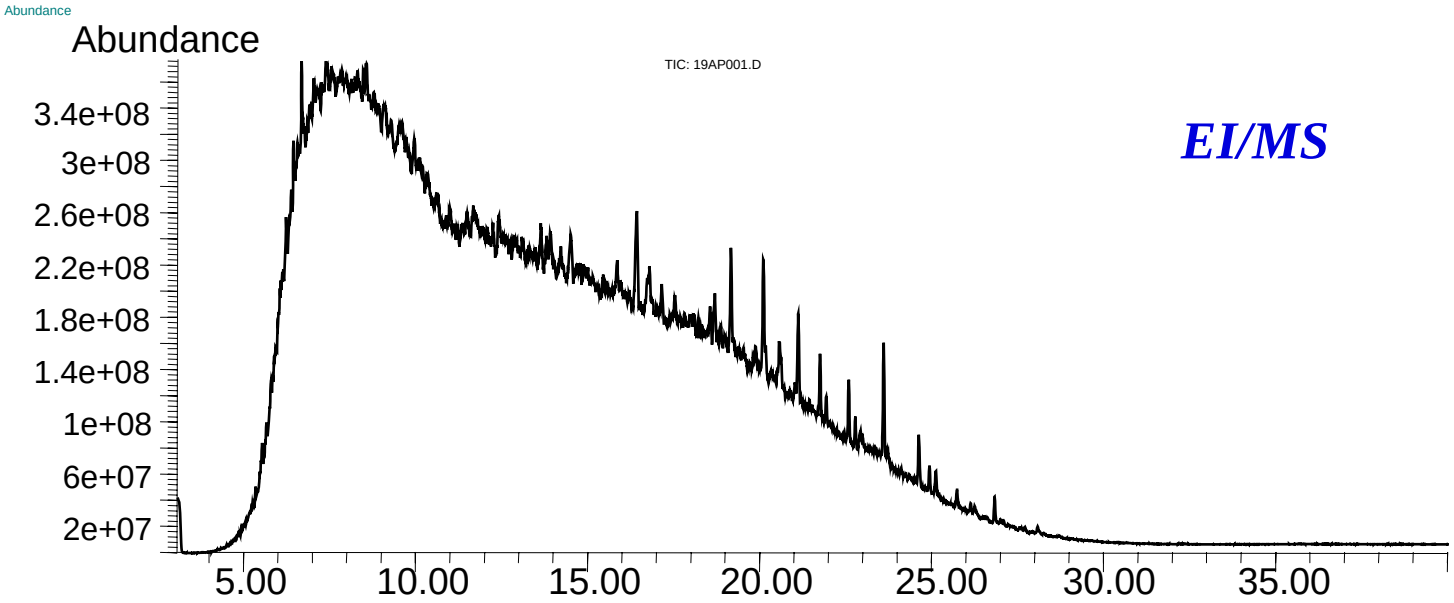
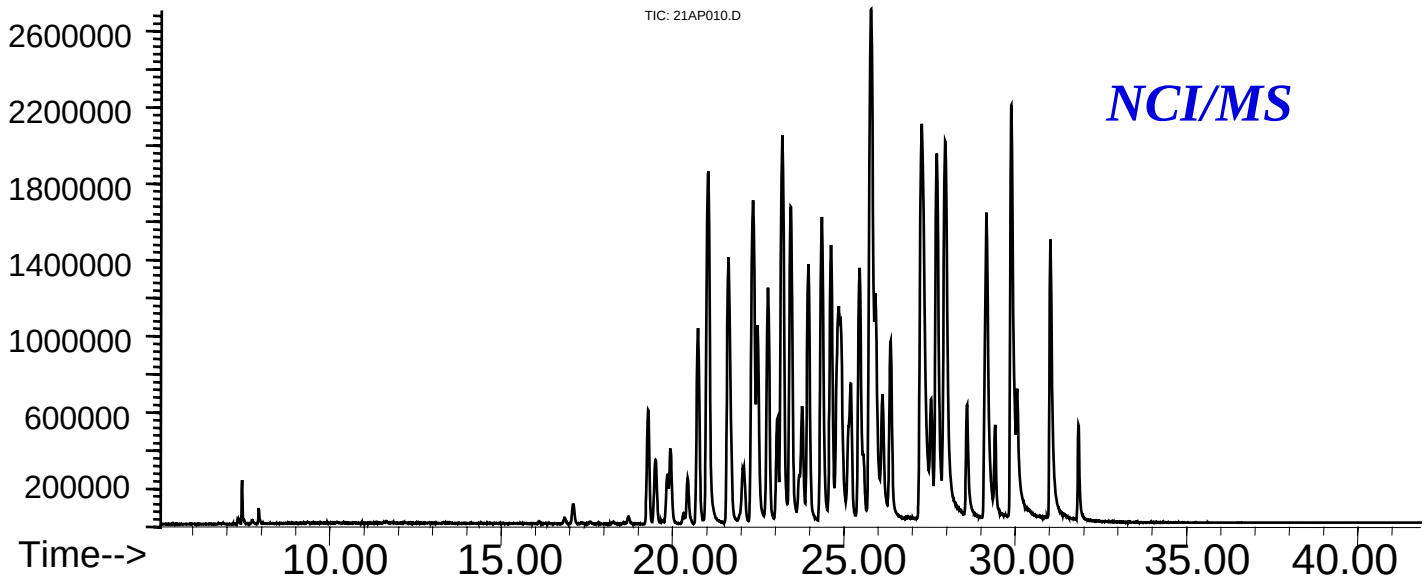

MS Mode: PHTH9-24.D Not Quantitated : THC1SIM3.M - [32 Bit Version]
File Method Chromatogram Spectrum Calibrate Quantitate Tools View Help
[2] TIC: PHTH9-24.D
Abundance
163
149
diethylphthalate
149
59/58/149
149
TIC with most having m/z 149
Time-->
[1] Average of 8.926 to 8.937 min.: PHTH9-24.D (-)
EI
149
149
M+: m/z = 222
177
222
[3] Average of 8.529 to 8.538 min.: 0301004.D (-)
PCI-
NH4+
MH+: m/z = 223
223
149
m/z-->


Abundance
TIC: 19AP001.D
3.4e+08
3e+08
2.6e+08
2.2e+08
1.8e+08
1.4e+08
1e+08
6e+07
2e+07
5.00
10.00
15.00
20.00
25.00
30.00
35.00
EI/MS


TIC: 21AP010.D
2600000
2200000
1800000
1400000
1000000
600000
200000
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
40.00
NCI/MS

Recent developments – state-of-the art !

- ***In HPLC and LC/MS***
  - ***Sub 2 µm particles***
  - ***High pressure***
  - ***High temperature***
  - ***Modes of ionization***
    - ***ESI-APCI-APPI***
  - ***Mass Analyzer***
    - ***Single quadrupole***
    - ***Triple quadrupole***
    - ***Ion trap***
    - ***Time-of-flight***

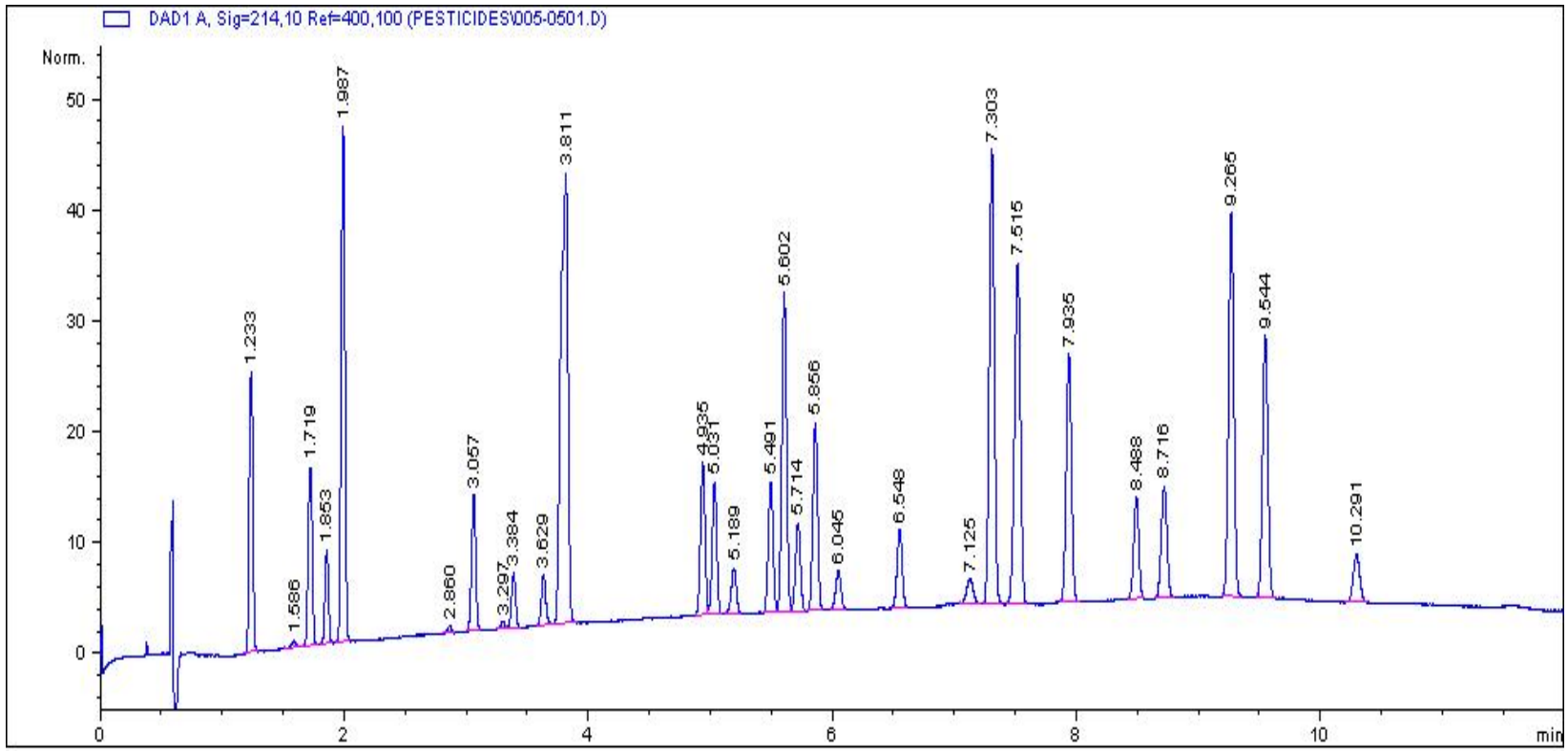
High Productivity – High Throughput

Using

- ***smaller particle sizes (sub-2 micron)***
- ***short columns***
- ***high pressure***
- ***high temperature***

fast analysis with no loss in efficiency

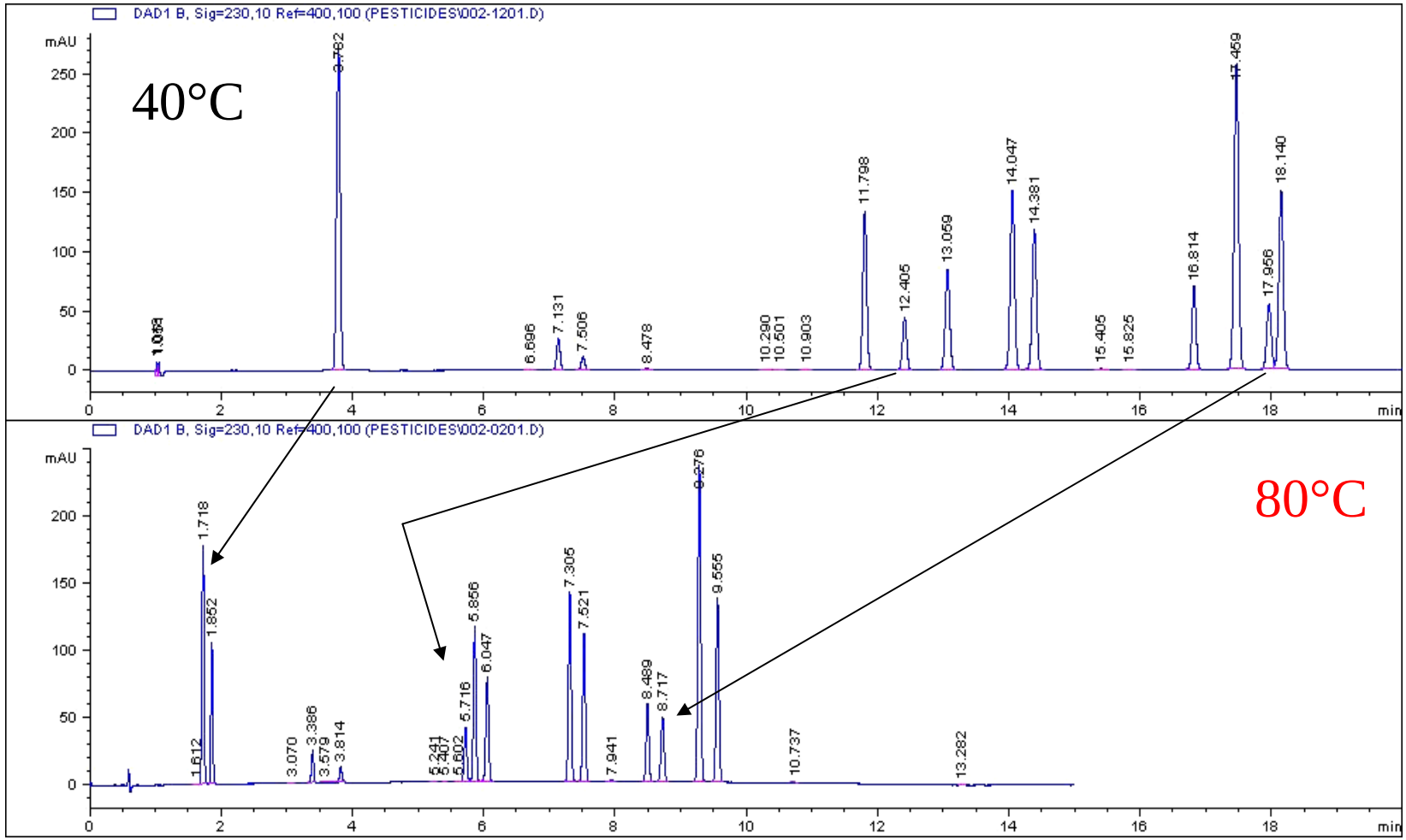
Pesticides in water (DIN 38 407 F12) (triazines, phenylurea)



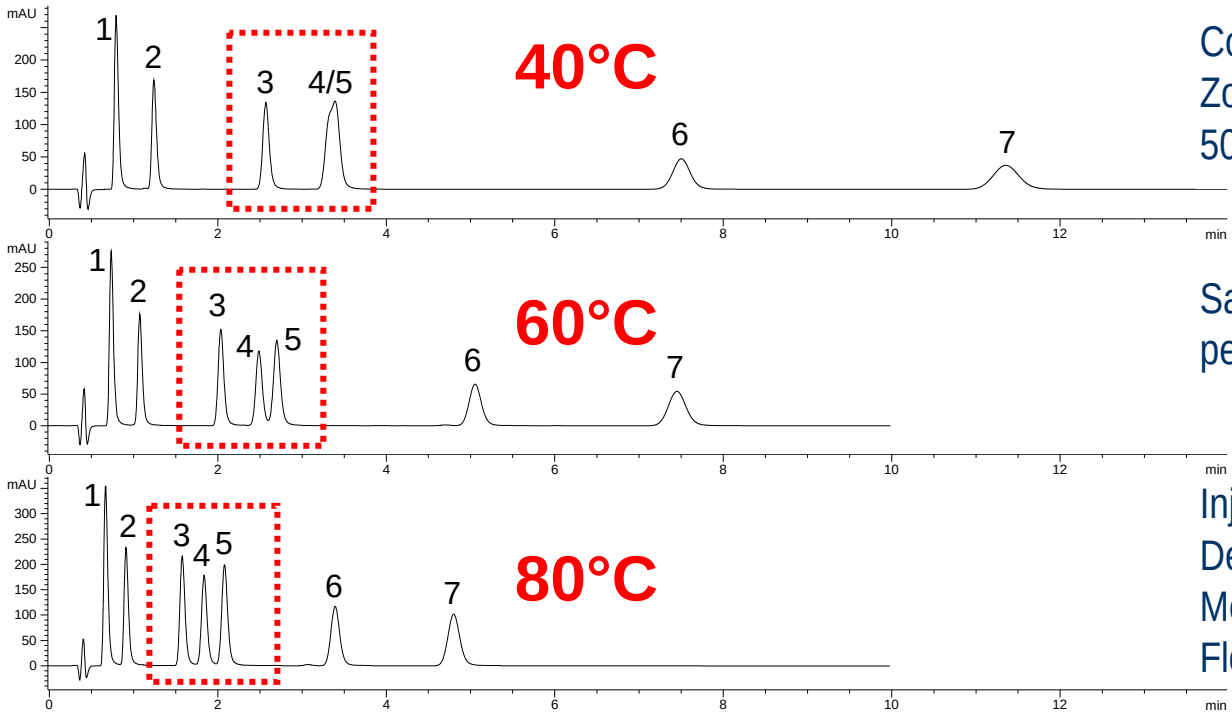
Classical method >60 min – 1200 method: 15 min with maintained R

Selectivity changes at increased temperature

Phenylurea pesticides – 15 cm x 4.6 mm i.d. x 1.8 µm



Phenylurea pesticides – Speed/Selectivity



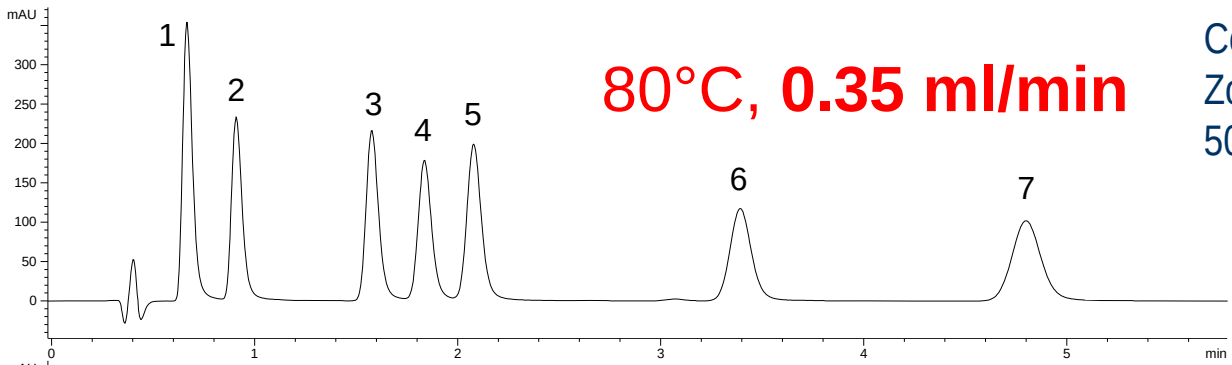
Column:
Zorbax StableBond C18,
50 mm L x 2.1 mm ID x 1.8 µm particles

Sample: Standard solution Phenylurea pesticides (100 ppm each)

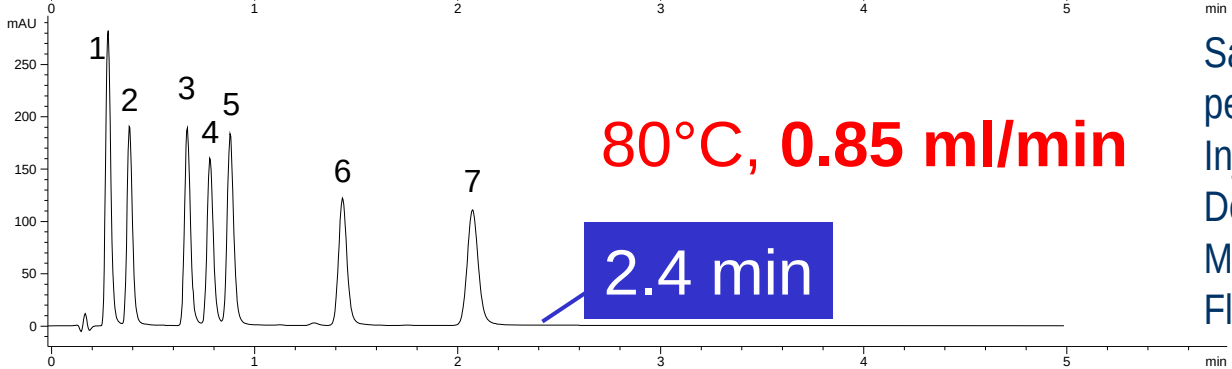
Injection: 1 µl
Detection: UV, 245 nm
Mobile phase: ACN/Water 30/70
Flow-rate: 0.35 ml/min

1. Fenuron, 2. Metoxuron, 3. Chlortoluron, 4. Diuron,
5. Isoproturon, 6. Linuron, 7. Chloroxuron

Phenylurea pesticides - Speed



80°C, **0.35 ml/min**



80°C, **0.85 ml/min**

Column:
Zorbax StableBond C18,
50 mm L x 2.1 mm ID x 1.8 µm particles

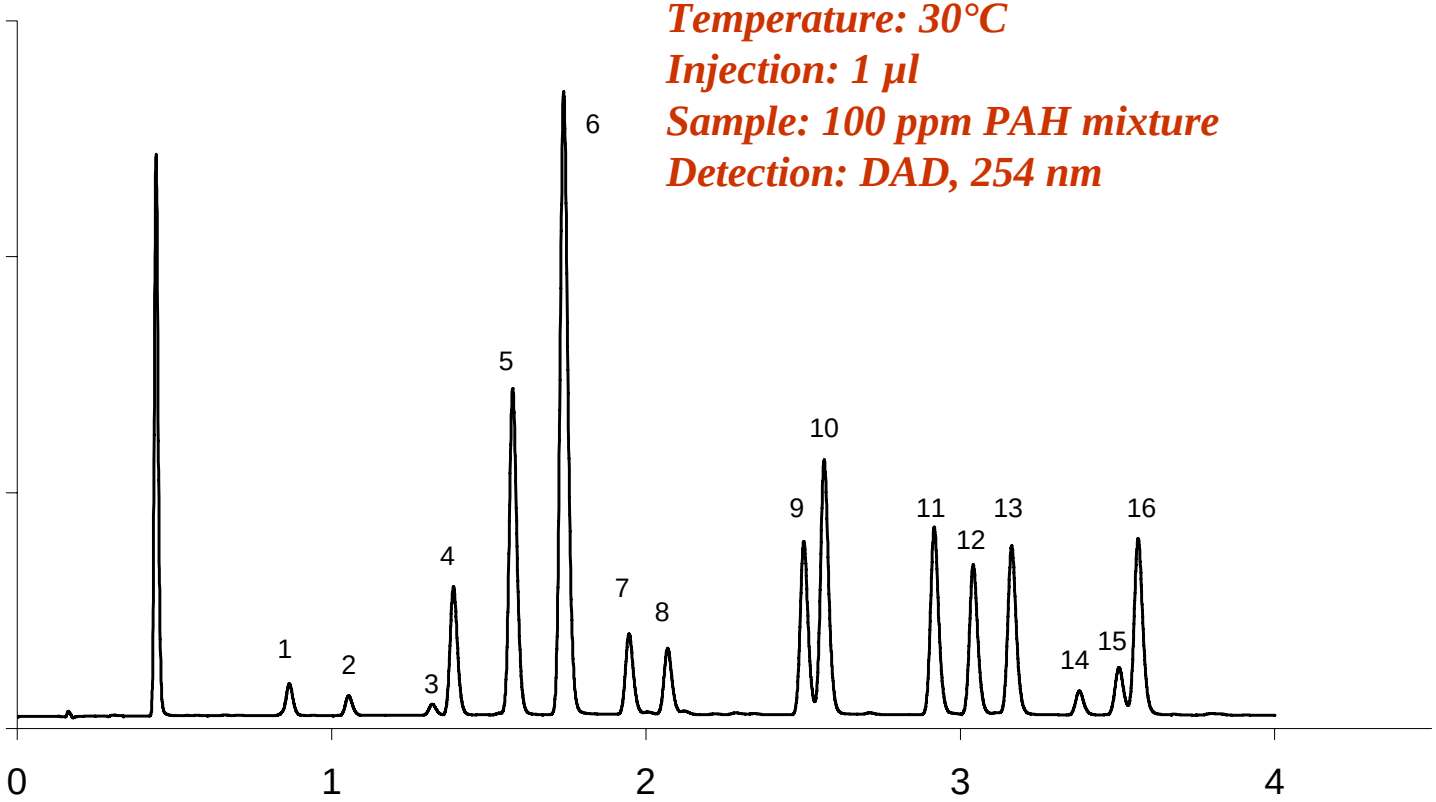
Sample: Standard solution Phenylurea pesticides (100 ppm each)
Injection: 1 µl
Detection: UV, 245 nm
Mobile phase: ACN/Water 30/70
Flow-rate: 0.35 or 0.85 ml/min

1. Fenuron, 2. Metoxuron, 3. Chlortoluron, 4. Diuoron,
5. Isoproturon, 6. Linuron, 7. Chloroxuron

16 PAHs in < 4 min

1.6 mL/min
560 bar

Column: ChromSphere 3 PAH, 100 mm x 2 mm, 3 µm
Mobile phase: water/acetonitrile, gradient 50 to 100% B
Temperature: 30°C
Injection: 1 µl
Sample: 100 ppm PAH mixture
Detection: DAD, 254 nm

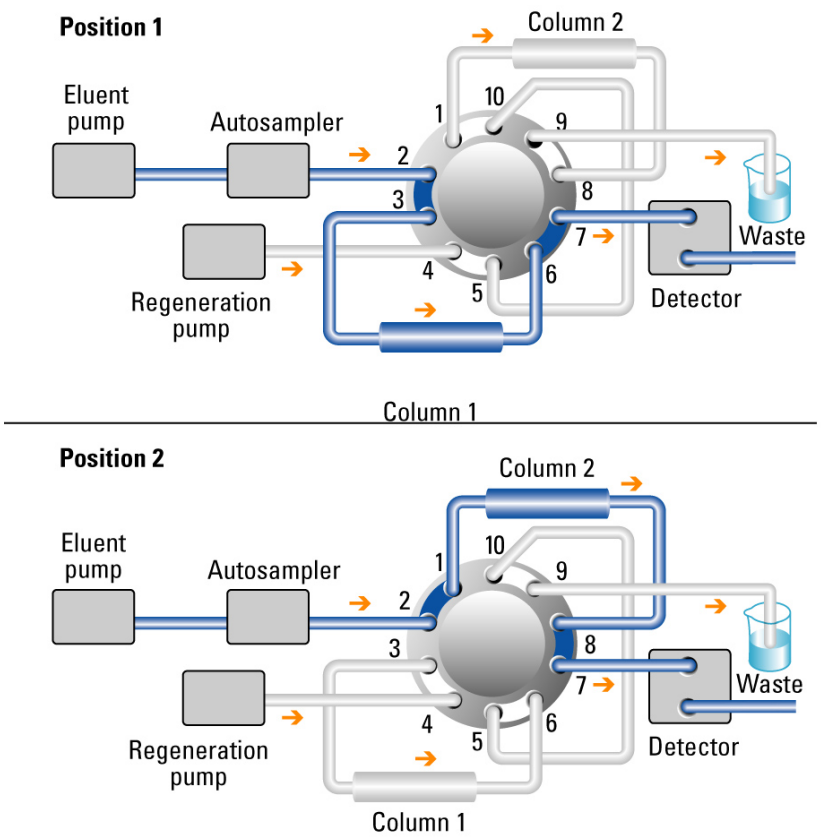


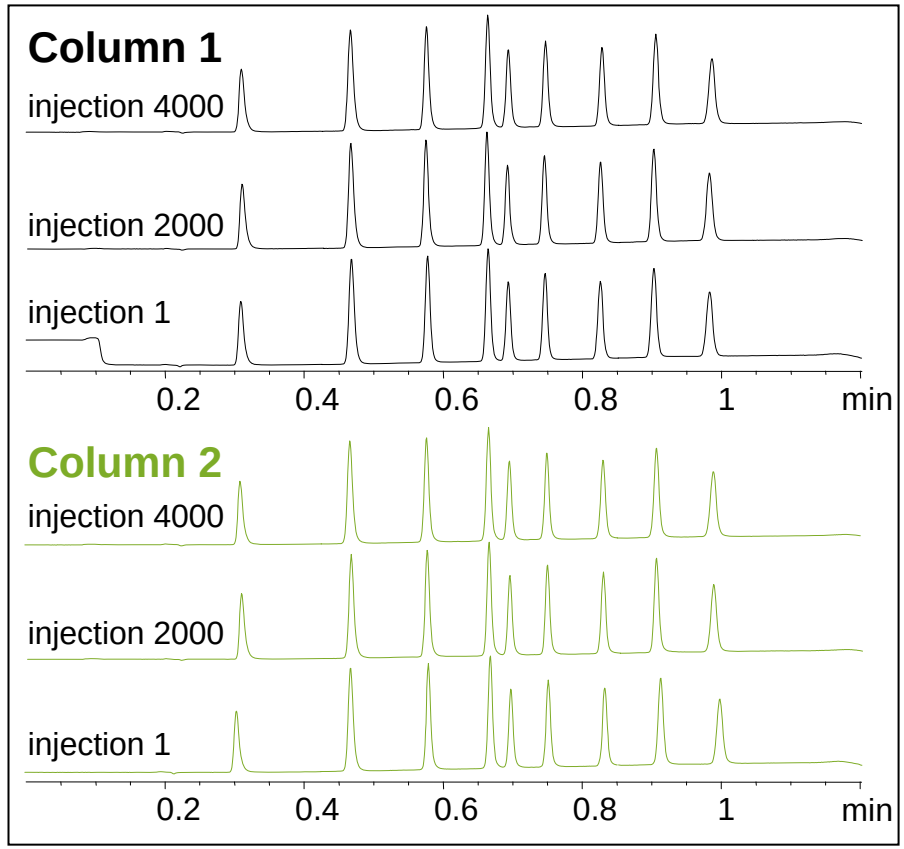
High Throughput

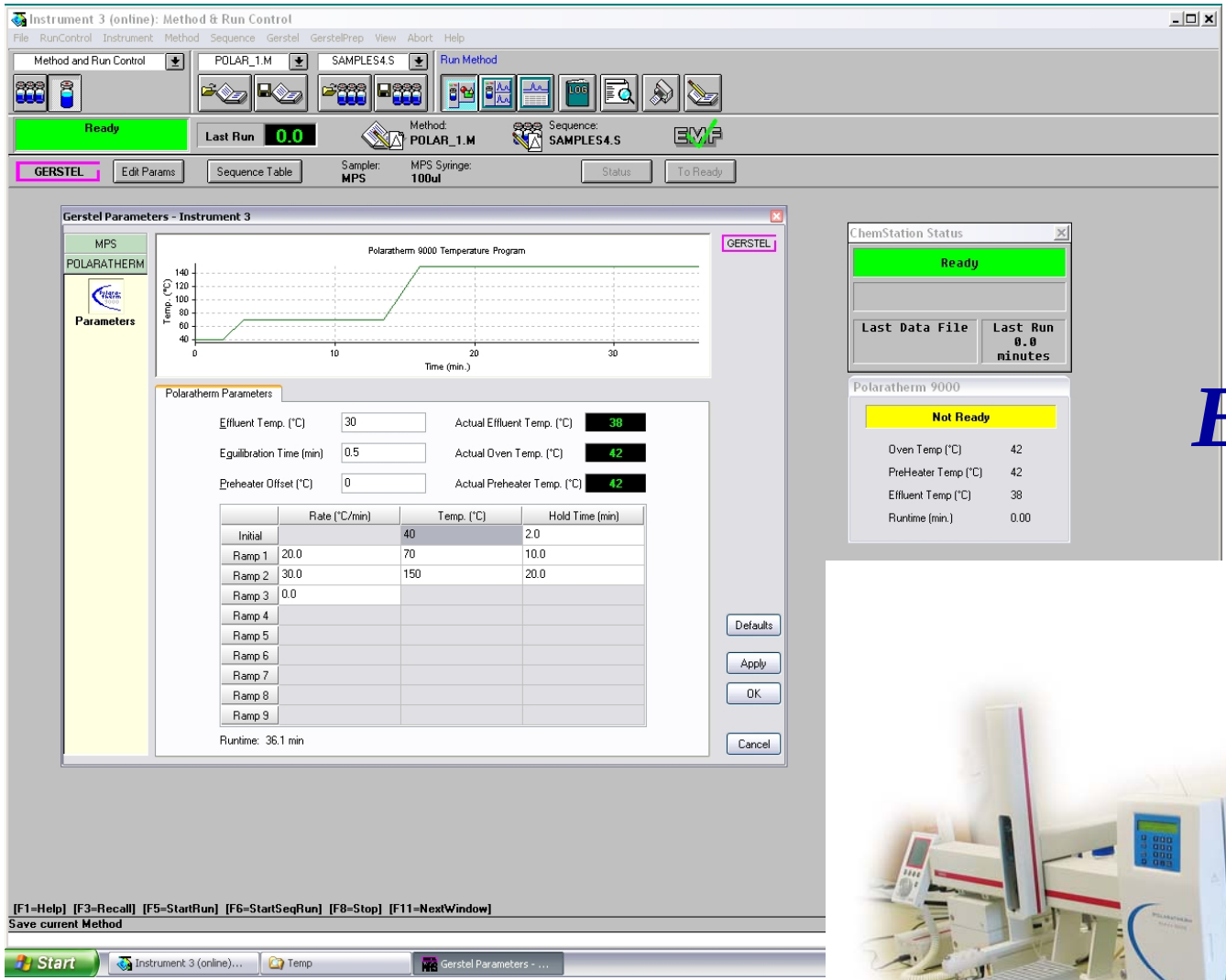
Agilent 1200 HT system equipped with 10 port switching valve:

allows elimination of rinsing and regeneration time

2-Position/10-Port Valve for Automated Alternating Column Regeneration



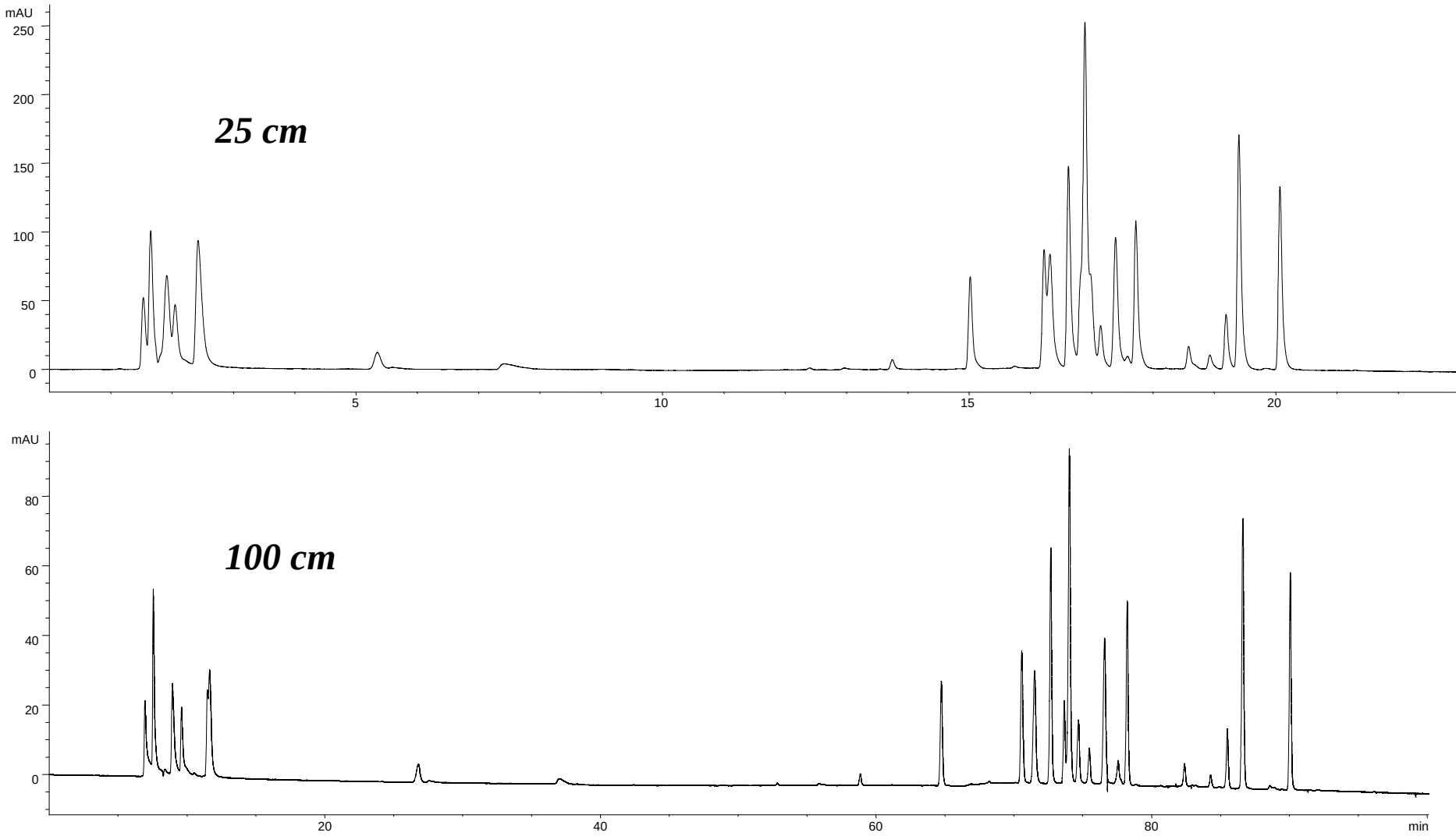




High Efficiency

1 to 3 m column length !

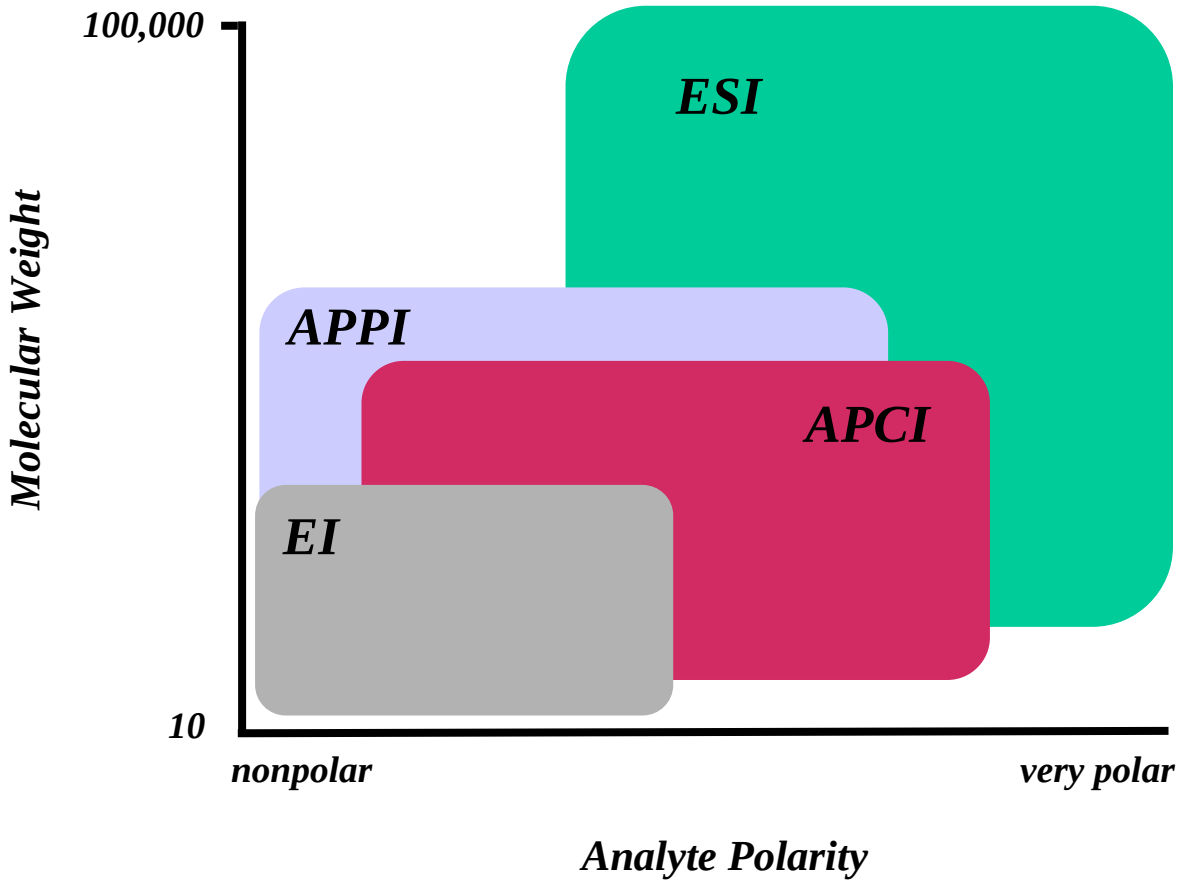
Agilent Technologies


mAU
250
200
150
100
50
0
25 cm
5
10
15
20
mAU
80
60
40
20
0
100 cm
20
40
60
80
min

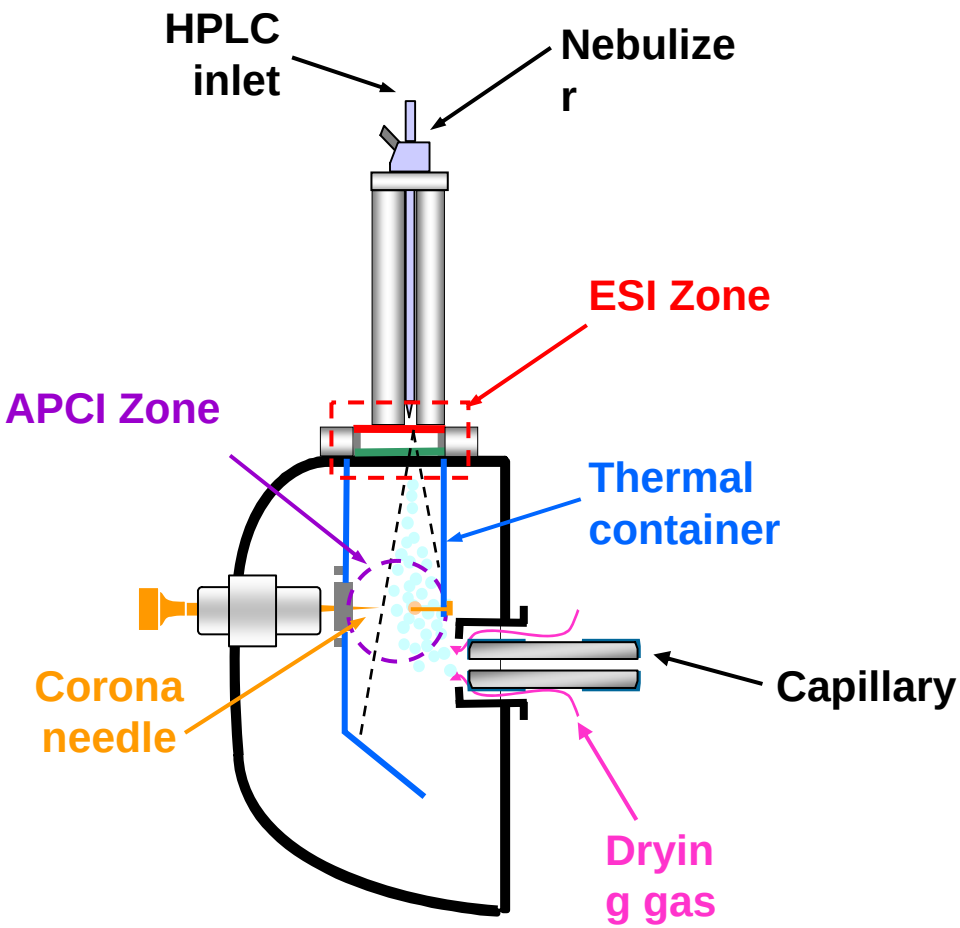
Recent developments – state-of-the art !

- ***In HPLC and LC/MS***
  - *Sub 2 µm particles*
  - *High pressure*
  - *High temperature*
  - ***Modes of ionization***
    - ***ESI-APCI-APPI***
  - *Mass Analyzer*
    - *Single quadrupole*
    - *Triple quadrupole*
    - *Ion trap*
    - *Time-of-flight*

Relative Applicability of Ionization Techniques



Agilent G1978A Multimode Source



- *Liquid enters the grounded nebulizer*
- *A charged aerosol is made in the ESI Zone*
- *The aerosol is dried by IR lamps*
- *Neutral analytes and ESI charged analytes pass through the APCI Zone*
- *ESI and APCI ions enter the capillary*

Propazine

Atrazine

Simazine

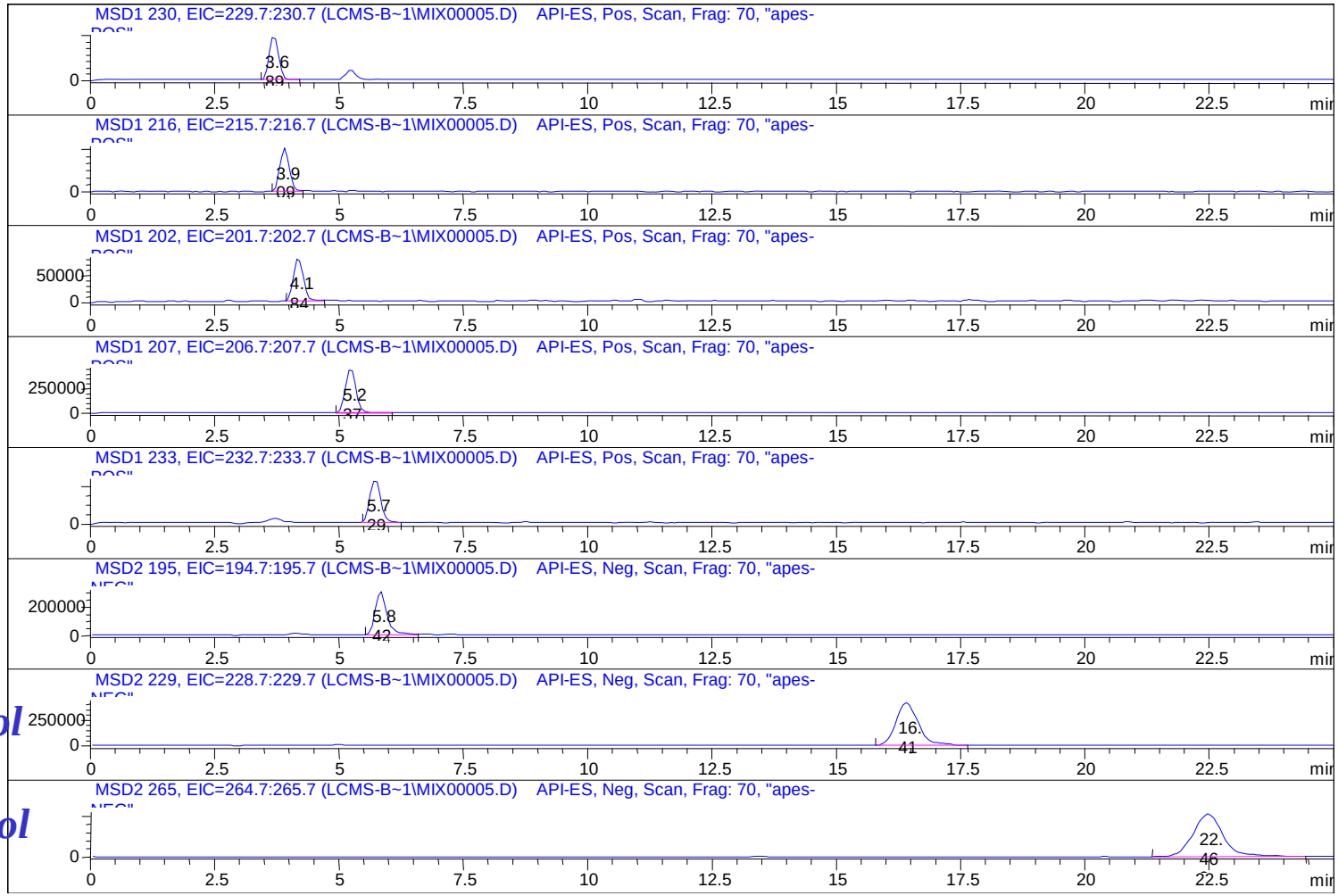
Isoproturon

Diuron

Tri-Cl-phenol

Tetra-Cl-phenol

Penta-Cl-phenol



Analysis of some pesticides by NPLC-APESI-MS in the alternating positive and negative mode … NH_4OAc !!!

Adapting an LC Method for LC/MS

AP ESI

Replace non-volatile buffer with volatile buffer

e.g. NH_4^+ $^-$OAc, NH_4^+ $^-$OOCH

Volatile buffer concentration should be < 10 mM

AP CI

Must use volatile buffer

Volatile buffer concentration should be < 60 mM

Buffers for APESI and APCI

Positive Ion (use pH <7.0; 5 preferred)

- ***Acetic acid, CH_3COOH***
- ***Formic acid, HCOOH***

Negative Ion (pH > 7.0; 9 preferred)

Ammonium hydroxide

Triethylamine

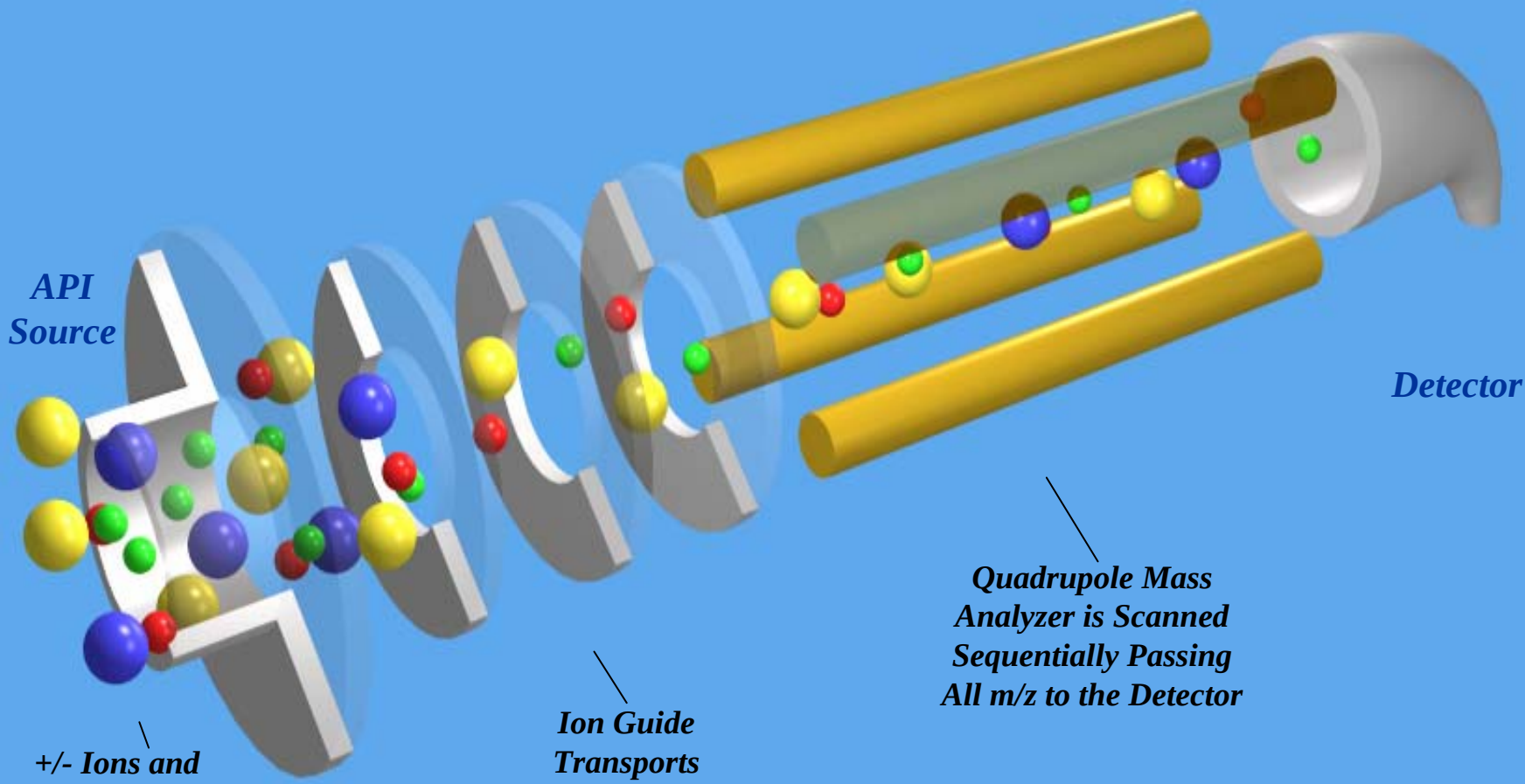
Post-column addition of acid or base may be used to adjust the pH if the chromatography won't work at the desired pH

LC/MS Portfolio

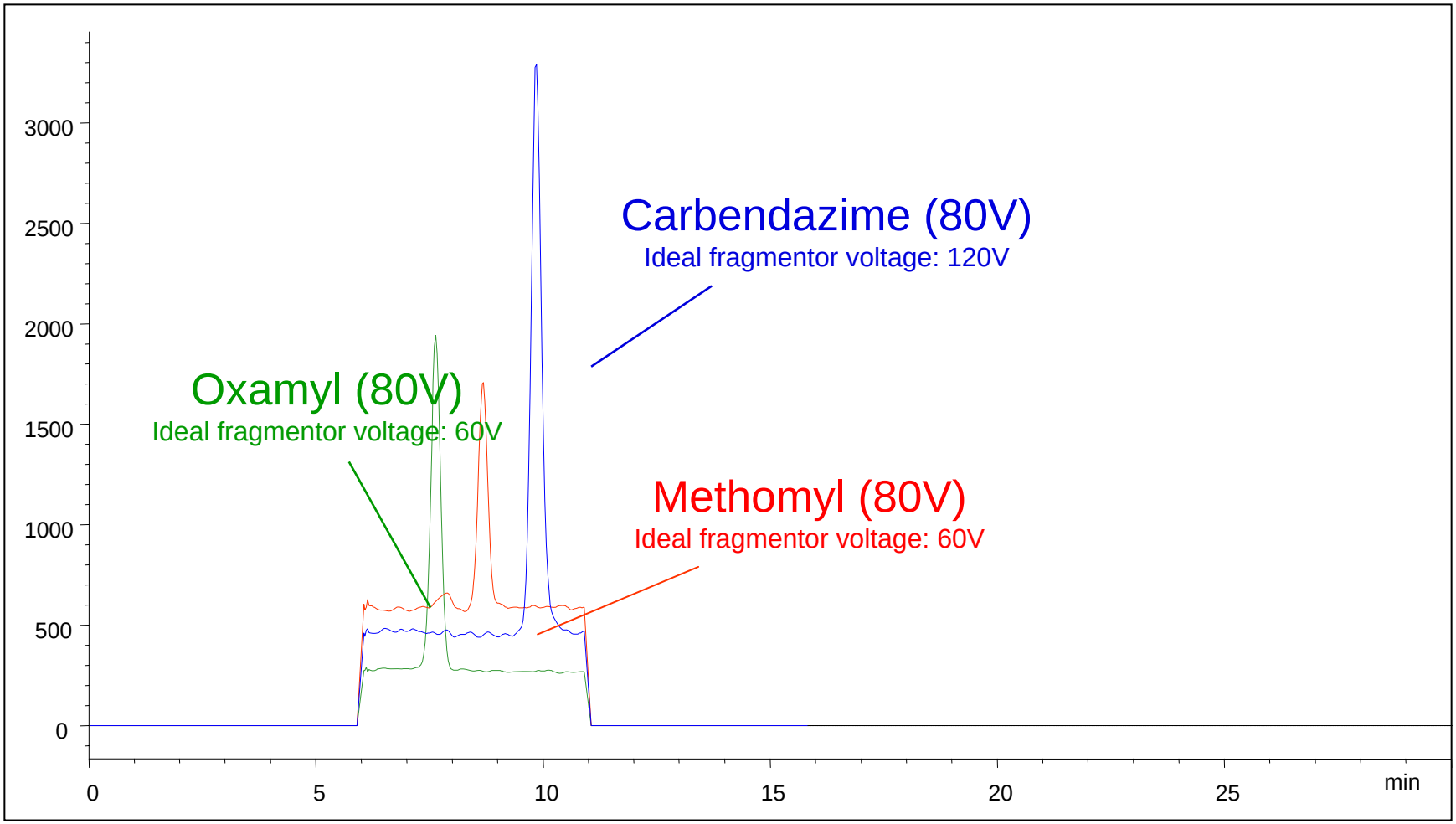
Recent developments – state-of-the art !

- ***In HPLC and LC/MS***
  - *Sub 2 µm particles*
  - *High pressure*
  - *High temperature*
  - *Modes of ionization*
    - *ESI-APCI-APPI*
  - ***Mass Analyzer***
    - ***Single quadrupole***
    - ***Triple quadrupole***
    - ***Ion trap***
    - ***Time-of-flight***

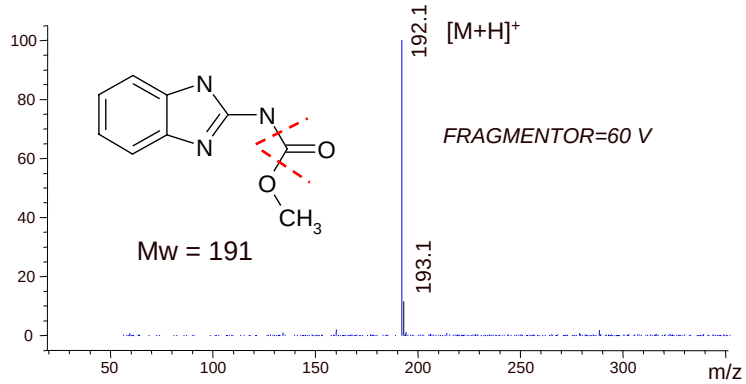
(Single) Quadrupole - CID

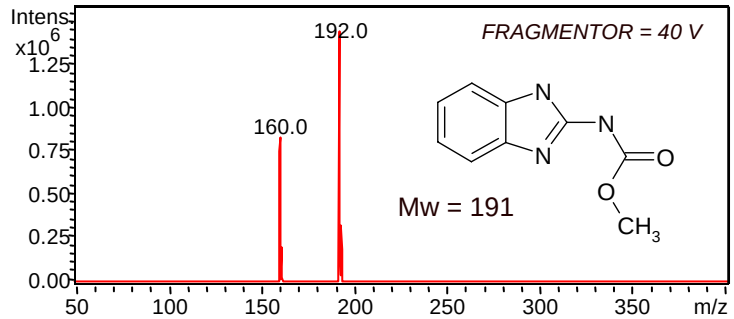


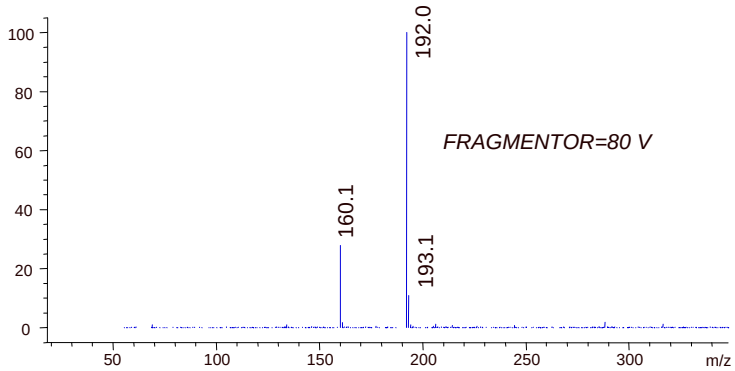
LC-Q-MS

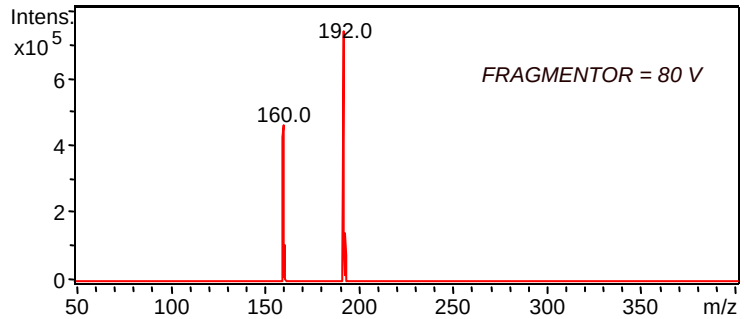

Carbendazime (80V)
Ideal fragmentor voltage: 120V
Oxamyl (80V)
Ideal fragmentor voltage: 60V
Methomyl (80V)
Ideal fragmentor voltage: 60V
3000
2500
2000
1500
1000
500
0
0
5
10
15
20
25
min

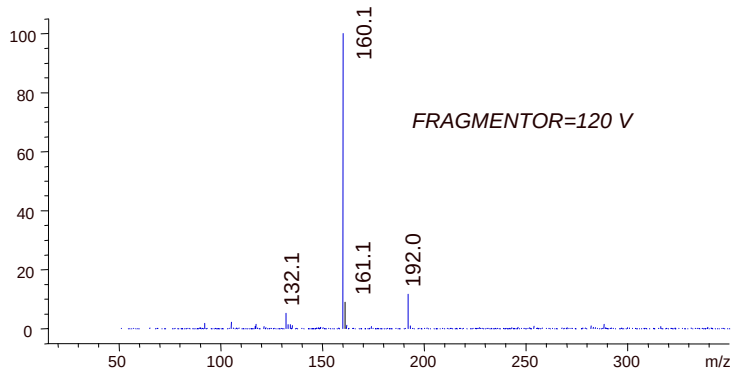
CARBENDAZIME - ACN/H_2O (50:50) - Formate 50 mM

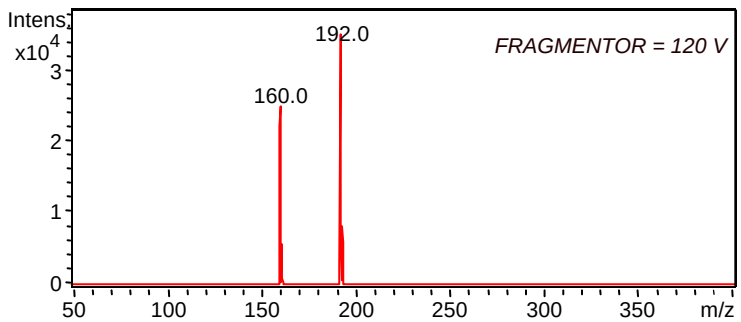




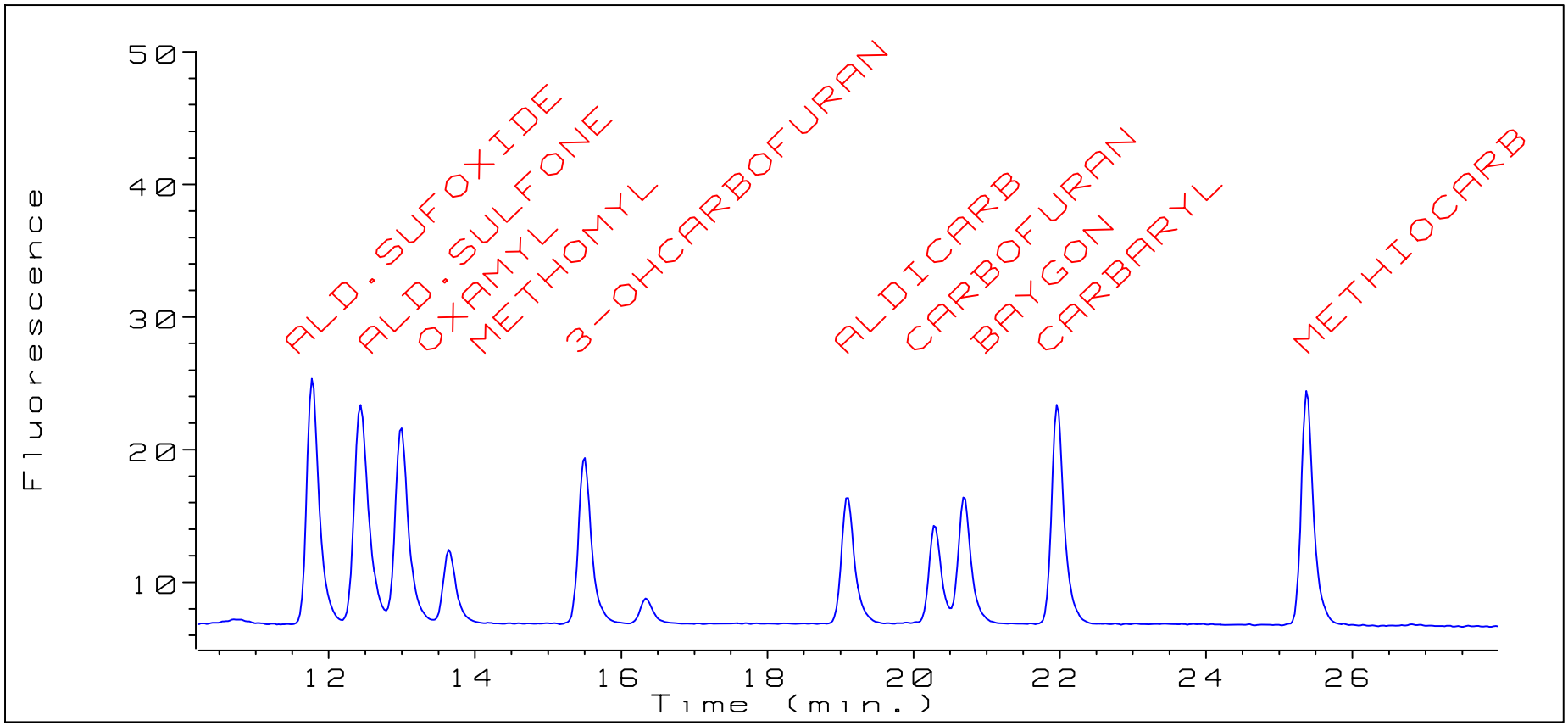






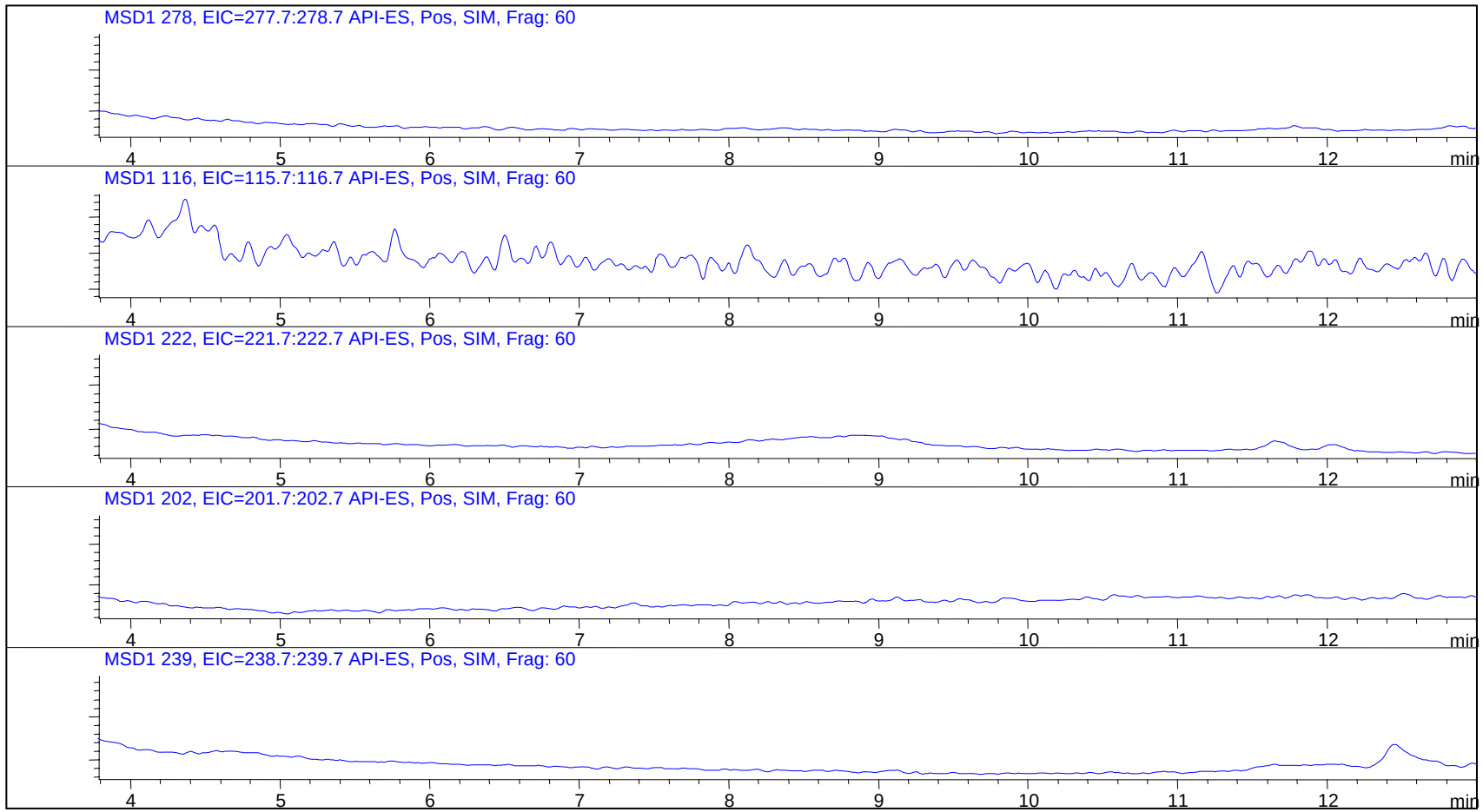


CARBAMATES IN DRINKING WATER
EPA METHOD 531

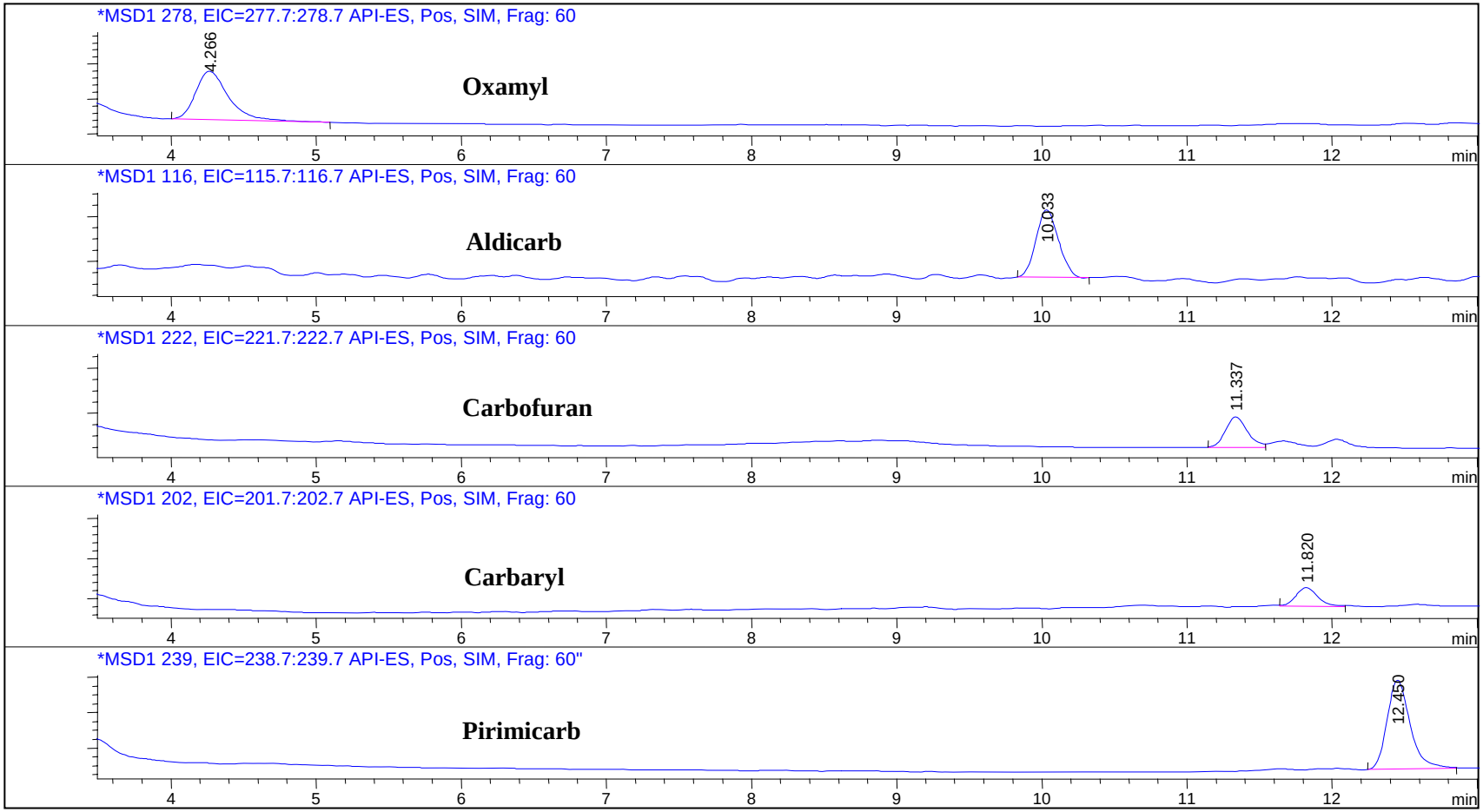


1. Column	*Hypersil ODS (100 mm, 2.1 mm, 5 µm)*
2. Mobile phase	*A: 90% 10mM NH_4^+OAc - 10% MeOH* *B: 10% 10mM NH_4^+OAc - 90% MeOH* *90%A → 10%A in 10 min*
3. Oven temperature	*25°C*
4. Flow rate	*0.25 ml/min*
5. Ionization mode	*Electrospray (ESI) - +*
6. Fragmentor voltage	*60 V*
7. Capillary voltage	*4000V*
8. Drying gas	*12 l/min 350°C*
9. Nebulizer gas	*35 psi*

Direct injection – water sample – 100 µL injection



Direct injection – 0.3 ppb spiked water sample – 100 µL injection



SPE Conditions

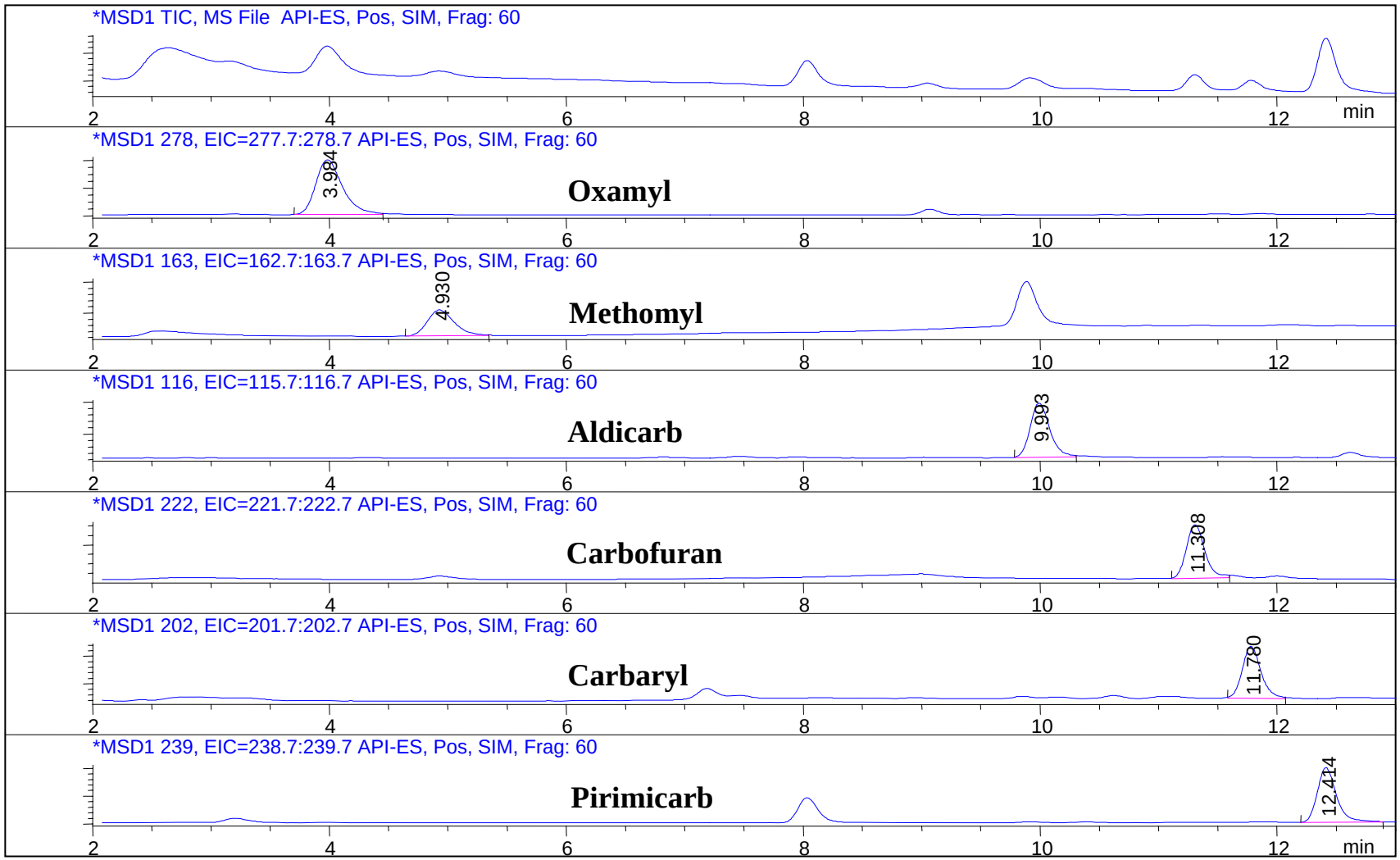
1. SPE Cartridge	*C18 – Agilent - Supelco - Varian*
2. Conditioning	*2 x 3 mL MeCN-MeOH 50%-50%* *1 x 3 mL MeOH* *2 x 3 mL H2O*
3. Loading	*50 mL Sample*
4. Washing	*2 x 3 mL H2O*

5. Drying the cartridge under vacuum for 10 minutes

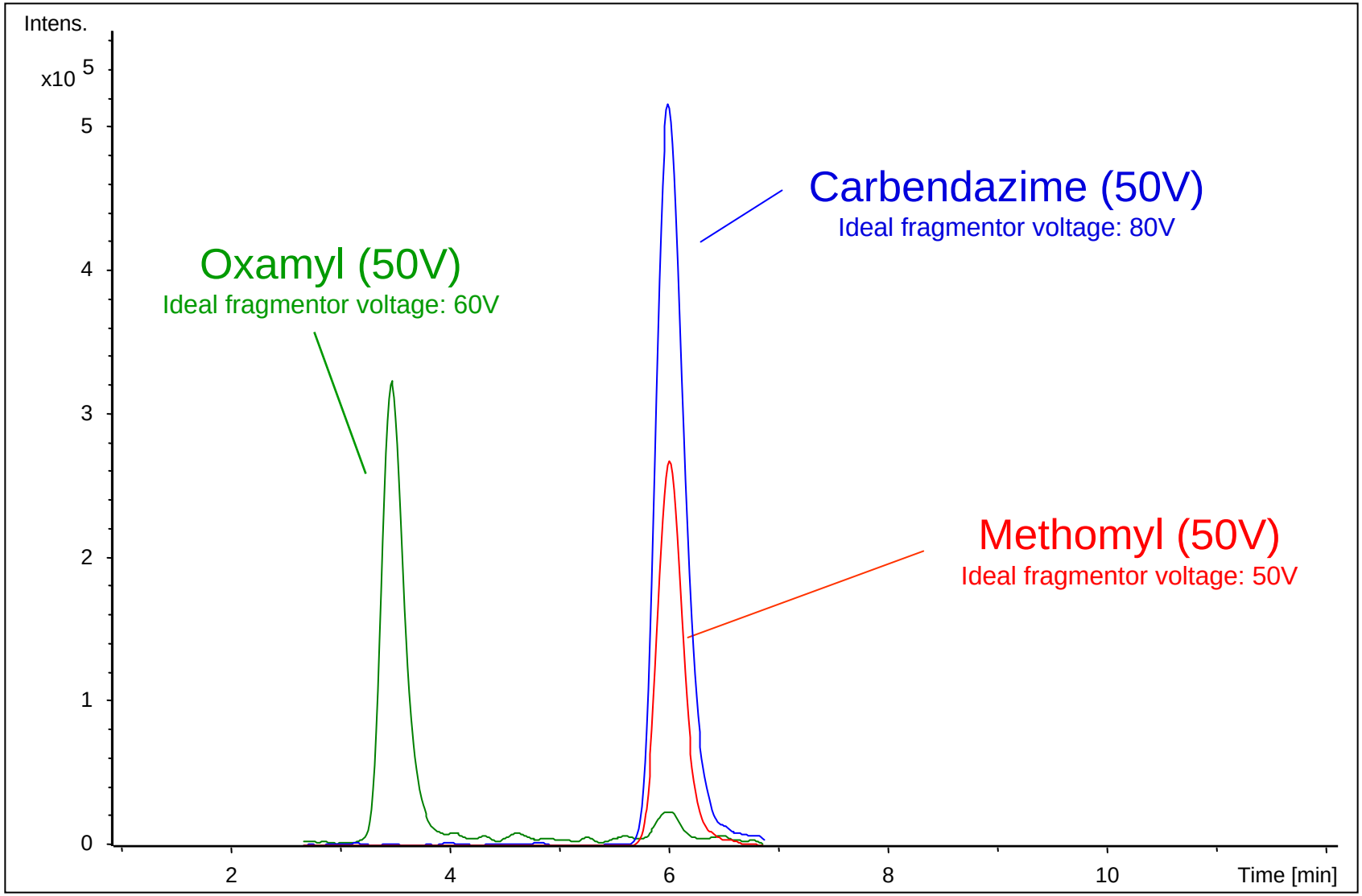
6. Elution	*3 x 1 mL MeCN-MeOH 50%-50%*

7. Evaporate to dryness and redissolve in 200 µL H2O -> LCMS

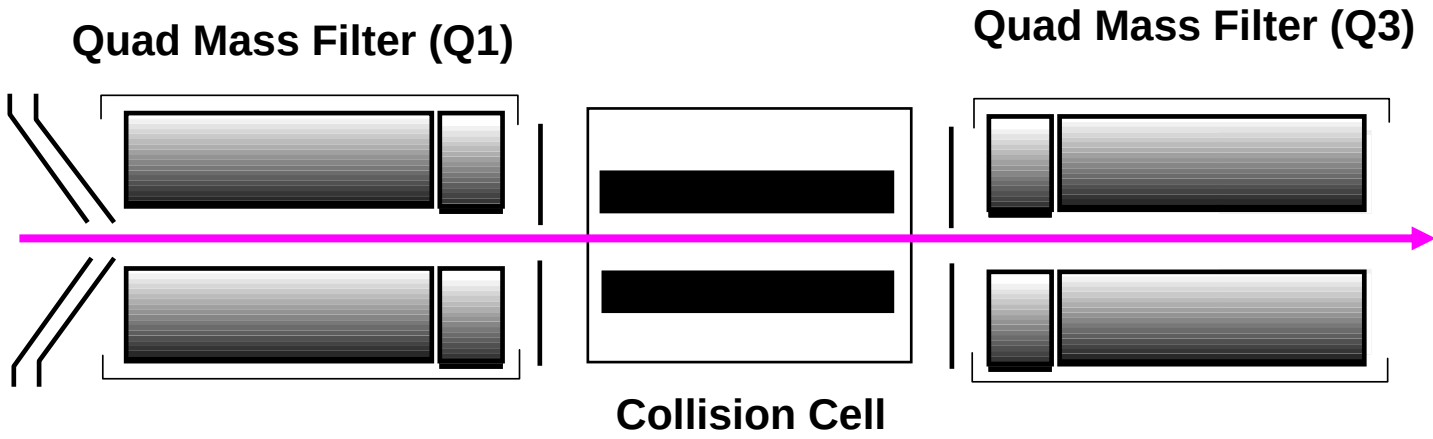
SPE – 0.05 ppb – LC/MS Analysis



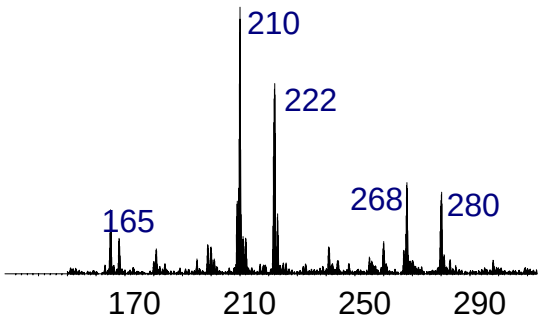
LC-MS-MS


Intens.
x10 5
5
4
3
2
1
0
2
4
6
8
10
Time [min]
Carbendazime (50V)
Ideal fragmentor voltage: 80V
Oxamyl (50V)
Ideal fragmentor voltage: 60V
Methomyl (50V)
Ideal fragmentor voltage: 50V

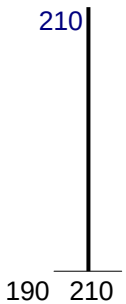
MRM (Multiple Reaction Monitoring)



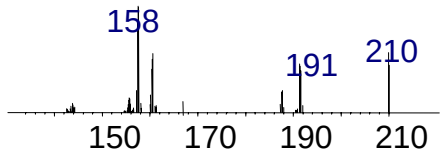
Spectrum with <u>background ions</u> (from ESI)



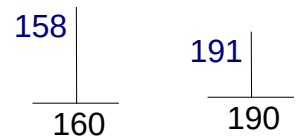
Q1 lets **only** target ion 210 pass through



Collision cell breaks ion 210 apart



Q3 monitors **only** characteristic fragments 158 and 191 from ion 210 for quant and qual.



no chemical background

Pharmaceuticals in waste water

Filter water samples in the field or in the laboratory using 0.7-µm glass fiber filters.

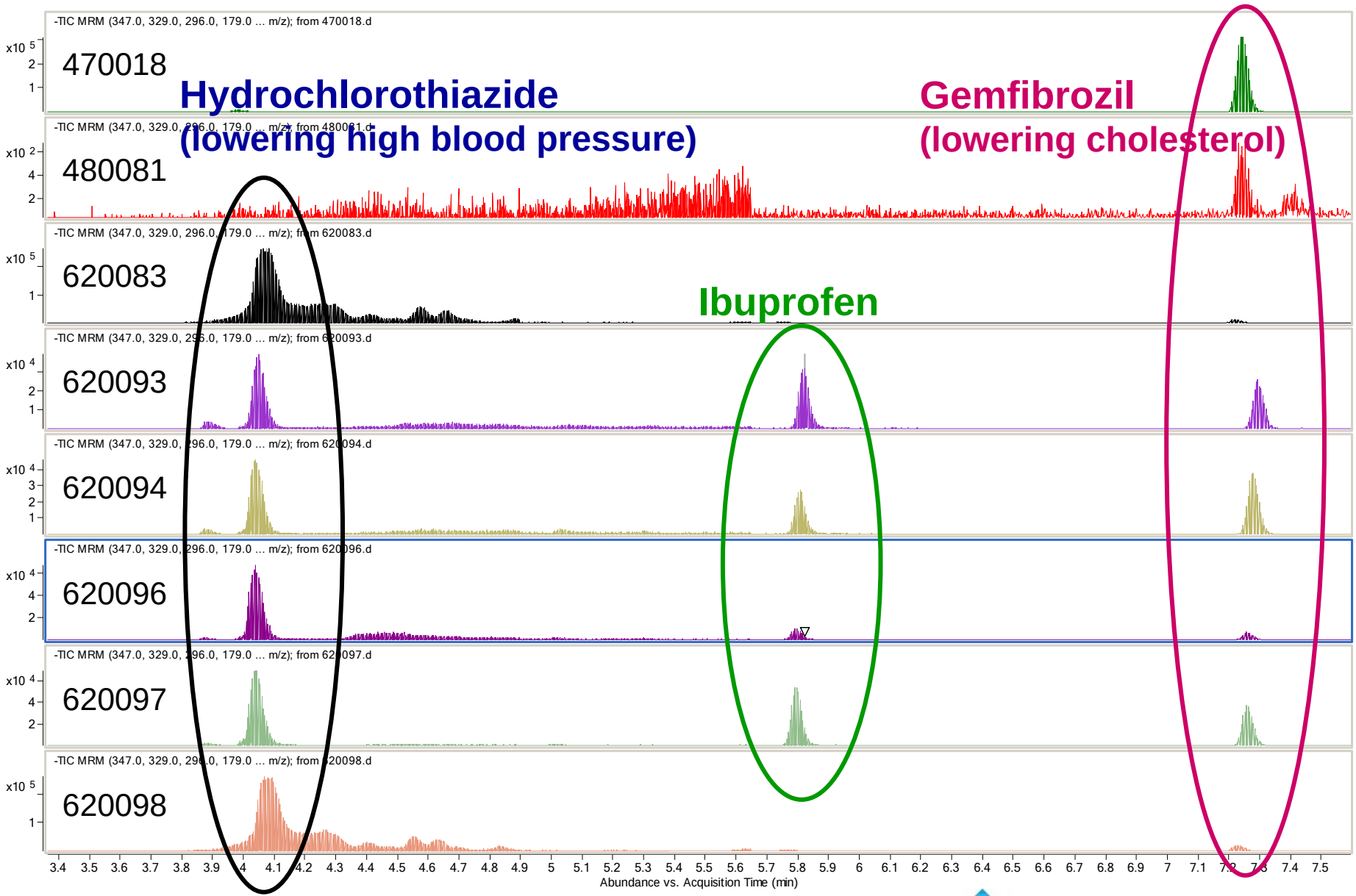
Pump 1-L of the filtered water sample, at a flow rate of 10 mL/min, through an Oasis HLB (SPE) cartridge containing 0.5 g of sorbent.

Elute the HLB column with 6 mL of methanol followed by 4 mL of 0.1% TFA in methanol.

The resulting solvent extract is then concentrated to approximately 100 µL.

Add internal standard (ISTD). The extract is reconstituted to 1 mL.

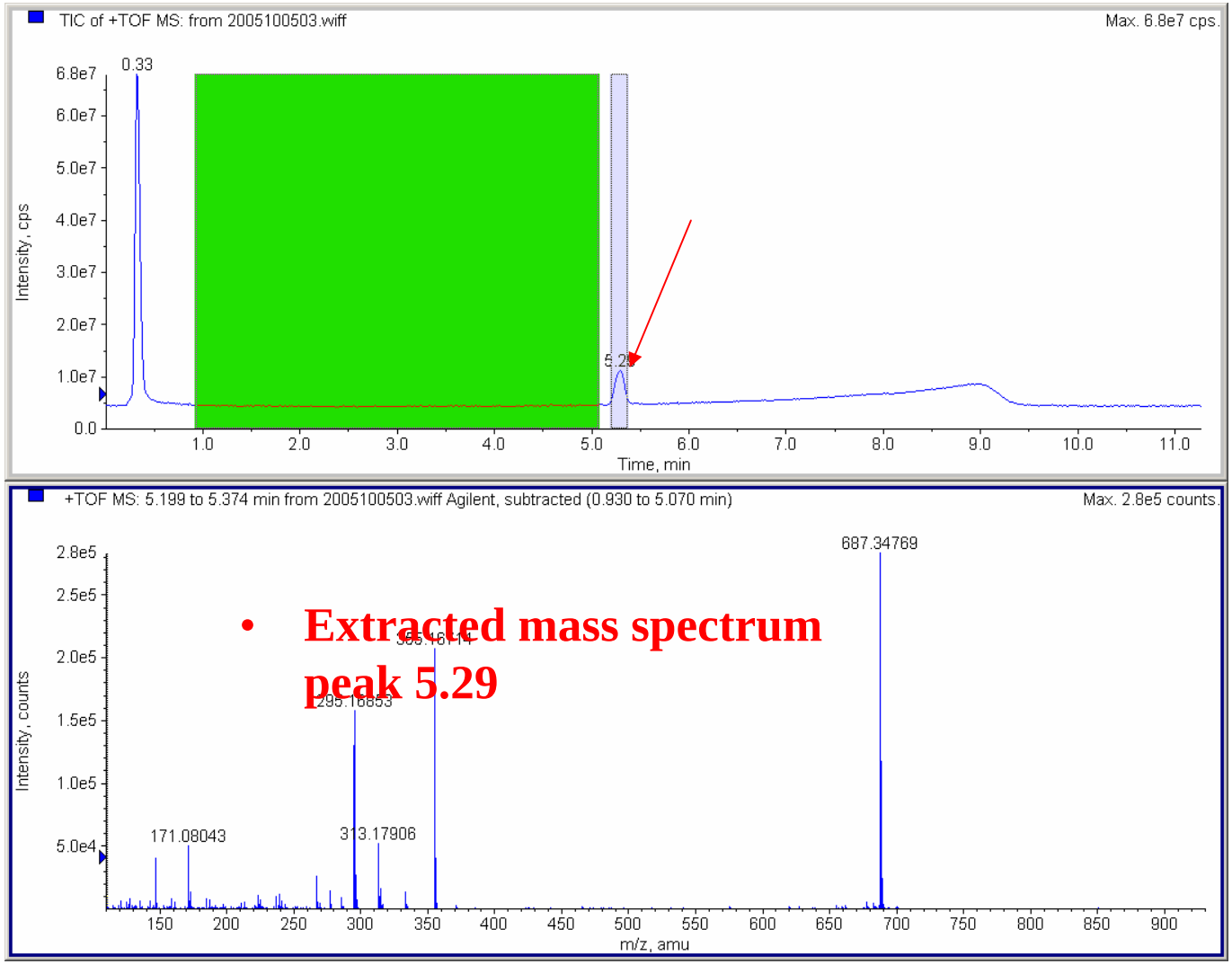
1 L ➡ final volume of 1 mL.


-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 470018.d
470018
Hydrochlorothiazide
(lowering high blood pressure)
Gemfibrozil
(lowering cholesterol)
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 480081.d
480081
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620083.d
620083
Ibuprofen
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620093.d
620093
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620094.d
620094
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620096.d
620096
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620097.d
620097
-TIC MRM (347.0, 329.0, 296.0, 179.0 ... m/z); from 620098.d
620098
Abundance vs. Acquisition Time (min)

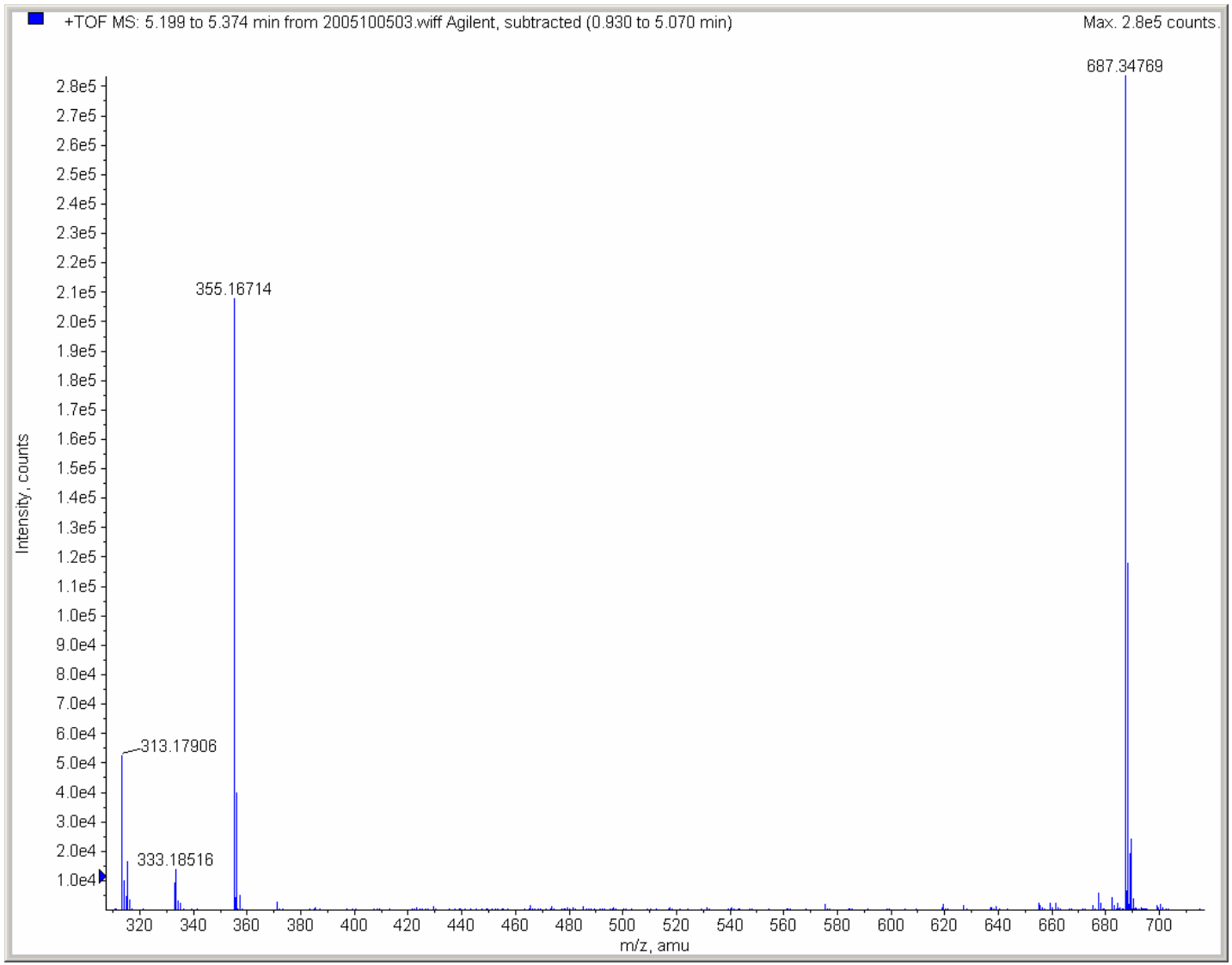
TOF- Identification of Unknowns with Accurate Mass Measurement

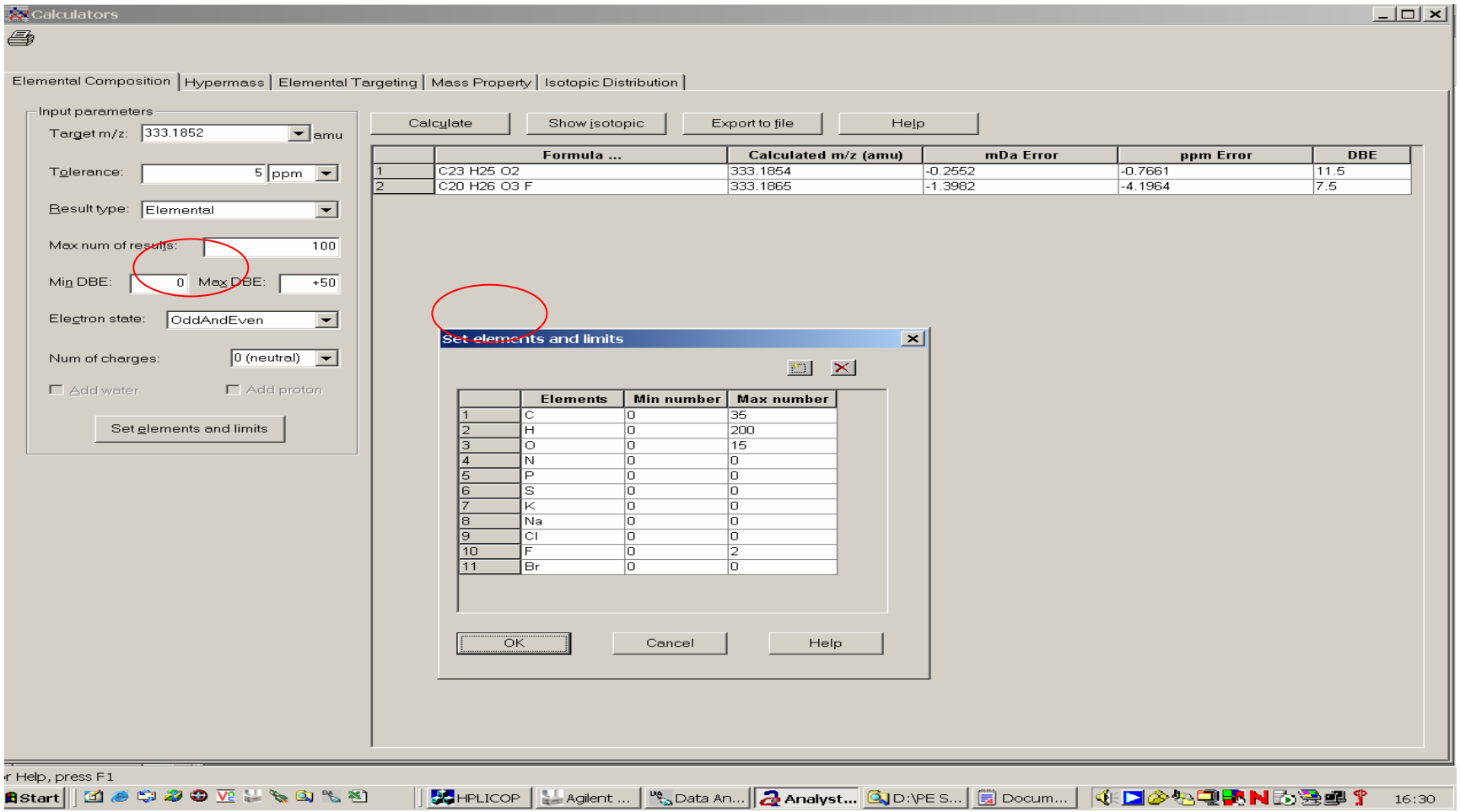
- *Use of databases for compound id from empirical formula*
- *Use of in-source accurate-mass fragmentation for confirmation*

Analysis of a unknown compound and identification



- **Extracted mass spectrum peak 5.29**


+TOF MS: 5.199 to 5.374 min from 2005100503.wiff Agilent, subtracted (0.930 to 5.070 min)
Max. 2.8e5 counts.
687.34769
355.16714
313.17906
333.18516
Intensity, counts
m/z, amu

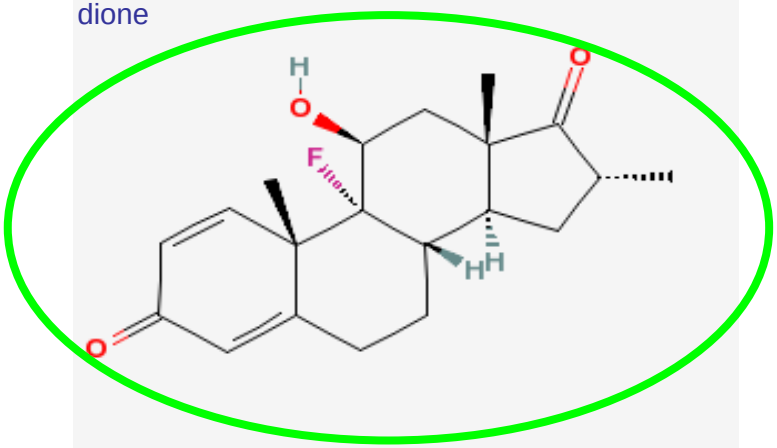

Calculators
Elemental Composition
Hypermass
Elemental Targeting
Mass Property
Isotopic Distribution
Input parameters
Target m/z: 333.1852 amu
Tolerance: 5 ppm
Result type: Elemental
Max num of results: 100
Min DBE: 0
Max DBE: +50
Electron state: OddAndEven
Num of charges: 0 (neutral)
Add water
Add proton
Set elements and limits
Calculate
Show isotopic
Export to file
Help
Formula ... | Calculated m/z (amu) | mDa Error | ppm Error | DBE
1 C23 H25 O2 | 333.1854 | -0.2552 | -0.7661 | 11.5
2 C20 H26 O3 F | 333.1865 | -1.3982 | -4.1964 | 7.5
Set elements and limits
Elements | Min number | Max number
1 C | 0 | 35
2 H | 0 | 200
3 O | 0 | 15
4 N | 0 | 0
5 P | 0 | 0
6 S | 0 | 0
7 K | 0 | 0
8 Na | 0 | 0
9 Cl | 0 | 0
10 F | 0 | 2
11 Br | 0 | 0
OK
Cancel
Help
r Help, press F1
Start
HPLICOP
Agilent ...
Data An...
Analyst...
D:\PE S...
Docum...
16:30

Analysis of a unknown compound and identification

PubChem

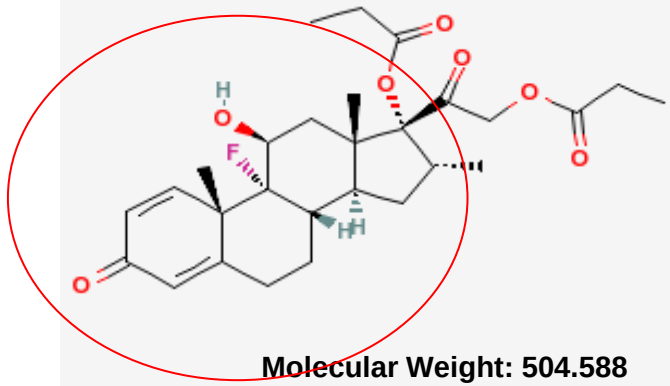
National Library of Medicine NLM

IUPAC Name: 9-fluoro-11-hydroxy-10,13,16-trimethyl-7,8,9,10,11,12,13,14,15,16-decahydro-6H-cyclopenta[a]phenanthrene-3,17-dione



Molecular Weight: 332.409 g/mol
Molecular Formula: C20H25FO3

Dexamethason Dipropionate



Molecular Weight: 504.588 g/mol
Molecular Formula: C28H37FO7

Conclusion compound is of the group steroids: 17 oxo-dexamethason

Recent developments – state-of-the art !

- *In sample preparation*

EPA Method 524 Compounds

1. *Dichlorodifluoromethane*
2. *Chloromethane*
3. *Vinyl chloride*
4. *Bromomethane*
5. *Chloroethane*
6. *Trichlorofluoromethane*
7. *1,1-Dichloroethene*
8. *Methylene chloride*
9. *trans-1,2-Dichloroethene*
10. *1,1-Dichloroethane*
11. *cis-1,2-Dichloroethene*
12. *2,2-Dichloropropane*
13. *Bromochloromethane*
14. *Chloroform*
15. *1,1,1-Trichloroethane*
16. *Carbon tetrachloride*
17. *1,1-Dichloropropene*
18. *Benzene*
19. *1,2-Dichloroethane*
20. *Trichloroethene*
21. *1,2-Dichloropropane*
22. *Dibromomethane*
23. *Bromodichloromethane*
24. *cis-1,3-Dichloropropene*
25. *Toluene*
26. *trans-1,3-Dichloropropene*
27. *1,1,2-Trichloroethane*
28. *Tetrachloroethene*
29. *1,3-Dichloropropane*
30. *Dibromochloromethane*
31. *1,2-Dibromomethane*
32. *Chlorobenzene*
33. *1,1,1,2-Tetrachloroethane*
34. *Ethylebenzene*
35. *m-Xylene*
36. *p-Xylene*
37. *o-Xylene*
38. *Styrene*
39. *Bromoform*
40. *Isopropylbenzene*
41. *1,1,2,2-Tetrachloroethane*
42. *Brombenzene*
43. *1,2,3-Trichloropropane*
44. *n-Propylbenzene*
45. *2-Chlorotoluene*
46. *1,3,5-Trimethylbenzene*
47. *4-Chlorotoluene*
48. *tert-Butylbenzene*
49. *1,2,4-Trimethylbenzene*
50. *sec-Butylbenzene*
51. *1,3-Dichlorobenzene*
52. *p-Isopropyltoluene*
53. *1,4-Dichlorobenzene*
54. *n-Butylbenzene*
55. *1,2-Dichlorobenzene*
56. *1,2-Dibromo-3-chloropropane*
57. *1,2,4-Trichlorobenzene*
58. *Hexachlorobutadiene*
59. *Naphthalene*
60. *1,2,3-Trichlorobenzene*

Analytes Added to Method 524.2

61. Acetone

62. Diethyl ether

63. Methyl iodide

64. Acrylonitrile

65. Allyl Chloride

66. Carbon disulfide

67. Methyl-tert-butyl ether

68. Propionitrile

69. 2-Butanone

70. Methacrylonitrile

71. Methyl acrylate

72. Tetrahydrofuran

73. 1-Chlorbutane

74. Chloroacetonitrile

75. 2-Nitropropane

76. Methylmethacrylate

77. 1,1-Dichloro-2-propanone

78. 4-Methyl-2-pentanone (MIBK)

79. Ethylmethacrylate

80. 2-Hexanone

81. trans-1,4-Dichloropropanone

82. Pentachloroethane

83. Hexachloroethane

84. Nitrobenzene

Volatile Organic Compounds (VOCs)

- *Purge and Trap (P&T)*
- *Static Headspace (SHS)*
- *Solid Phase Microextraction (SPME)*
- *Headspace Sorptive Extraction (HSSE)*

EPA Method 524.2

Volatile Organic Compounds (VOCs) … the Purgeables

Column: 60m x 0.25mm x 1.4 µm, DB-VRX

Agilent Technologies

Semivolatile Organic Compounds (SVOCs)

- *Liquid-liquid Extraction (LLE)*
- *Solid Phase Extraction (SPE)*
- *Solid Phase Microextraction (SPME)*
- *Stir Bar Sorptive Extraction (SBSE-Twister)*

EPA Method 525.2

1	Isophorone
2	1,3-Dimethyl-2-nitrobenzene (SS)
3	Dichlorovos
4	Hexchlorocyclopentadiene
5	EPTC
6	Mevinphos
7	Vernolate
9	Dimethyl phthalate
10	Terrazole (aka Etridazole)
11	2,6-Dinitrotoluene
12	Tillam (aka Pebulate)
13	Acenaphthylene
14	Acenaphthene-d10 (IS#1)
15	Chlorneb
16	2-Chlorobiphenyl
17	Tebuthiuron
18	2,4-Dinitrotolune
19	Molinate
20	Diethyl phthalate
21	Fluorene
22	Propachlor
23	Ethoprop
24	Cycloate
25	Chlorpropham
26	Trifluralin
27	a-BHC
28	2,3-Dichlorobiphenyl
29	Hexachlorobenzene
30	Gesatamine (aka Atraton)
31	Prometon
32	Atrazine
33	Simazine
34	b-BHC
35	Pentachlorophenol
36	Propazine
37	g-BHC
38	Terbufos
39	Pronamide
40	Diazinon
41	Phenanthrene-d10 (IS#2)

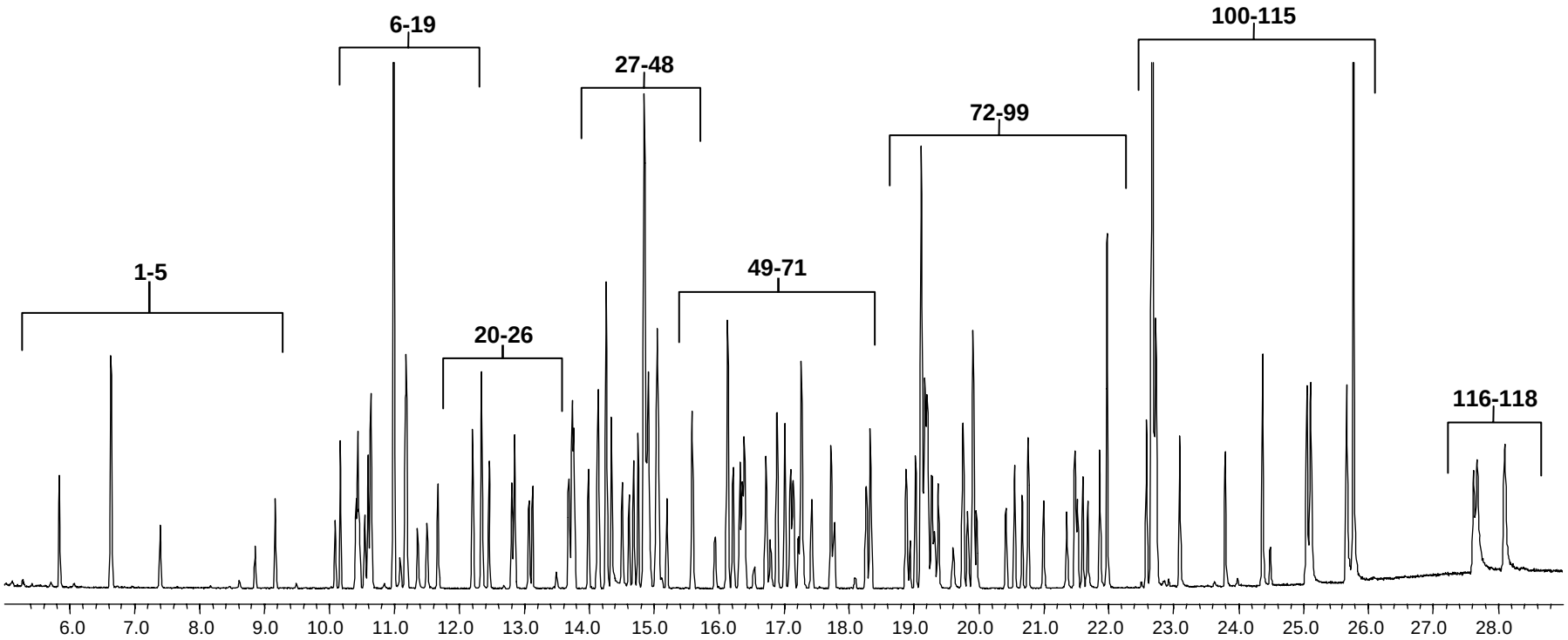
42	*Chlorothalonil*	*62*	*Cyanazine*
43	*Phenanthrene*	*63*	*Dacthal (aka DCPA methyl ester)*
44	*Terbacil*	*64*	*Aldrin*
45	*Methyl paraoxon*	*65*	*Triadimefon*
46	*Disulfoton*	*66*	*Dephenimid*
47	*Anthracene*	*67*	*MGK-264 (isomer A)*
48	*d-BHC*	*68*	*MGK-264 (isomer B)*
49	*2,4,5-Trichlorobiphenyl*	*69*	*Heptachlor epoxide*
50	*Metribuzin*	*70*	*2,2´,3´,4,6-Pentachlorobiphenyl*
51	*Alachlor*	*71*	*Merphos*
52	*Simetryn*	*72*	*g-Chlordane*
53	*Ametryn*	*73*	*Tetrachlorvinphos (aka Stirifos)*
54	*Heptachlor*	*74*	*Butachlor*
55	*Prometryne*	*75*	*Pyrene-d10 (SS)*
56	*Prebane (aka Terbutryne)*	*76*	*Pyrene*
57	*Bromacil*	*77*	*a-Chlordane*
58	*Di-n-butyl phthalate*	*78*	*Endosulfan I*
59	*2,2´,4,4´-Tetrachlorobiphenyl*	*79*	*trans-Nonachlor*
60	*Metolachlor*	*80*	*Fenamiphos*
61	*Dursban (aka Chlorpyrifos)*	*81*	*Napropamide*

82	Tricyclazole
83	p,p´-DDE
84	DEF
85	2,2´,4,4´,5,6´-Hexachlorobiphenyl
86	Dieldrin
87	Carboxin
88	Endrin
89	Chlorobenzilate
90	Endosulfan II
91	p,p´-DDD
92	Endrin aldehyde
93	Norflurazon
94	Benzyl butyl phthalate
95	Endosulfan sulfate
96	p,p´-DDT
97	Hexazinone
98	bis(2-Ethylexyl) adipate
99	Triphenylphosphate (SS)

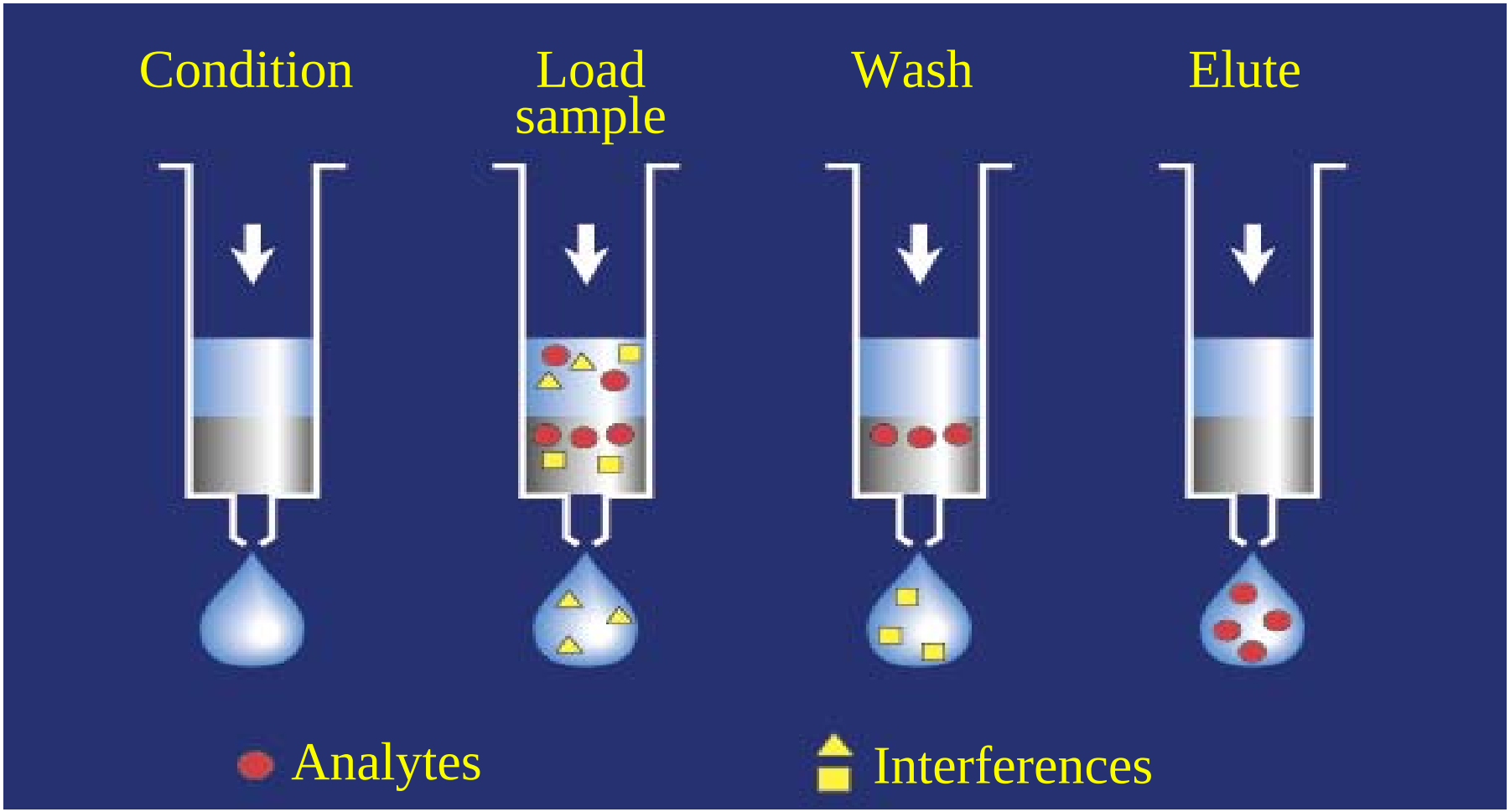
100	Endrin ketone
101	2,2´,3,3´,4,5´,6,6´-Octachlorobiphenyl
102	Benz[a]anthracene
103	Chrysene-d12 (IS#3)
104	2,2´,3,3´,4,5´,6,6´-Octachlorobiphenyl
105	Methoxychlor
106	Chrysene
107	bis(2-Ethylhexyl)phthalate
108	Fenarimol
109	cis-Permethrin
110	trans-Permethrin
111	Benzo[b]fluoranthene
112	Benzo[k]fluoranthene
113	Fluridone
114	Benzo[a]pyrene
115	Pereylene-d12 (SS)
116	Ideno[1,2,3-cd]pyrene
117	Dibenz[a,h]anthracene
118	Benzo[g,h]perylene

The Semivolatile Organic Compounds (VOCs)

Column: 30 m x 0.25 mm x 0.25 µm, DB-5MS




Solid Phase
Extraction



All modes of LC available

<u>Reversed Phase</u> - Normal Phase - Ion Exchange, RAM, MIP, etc.

NOT Size Exclusion

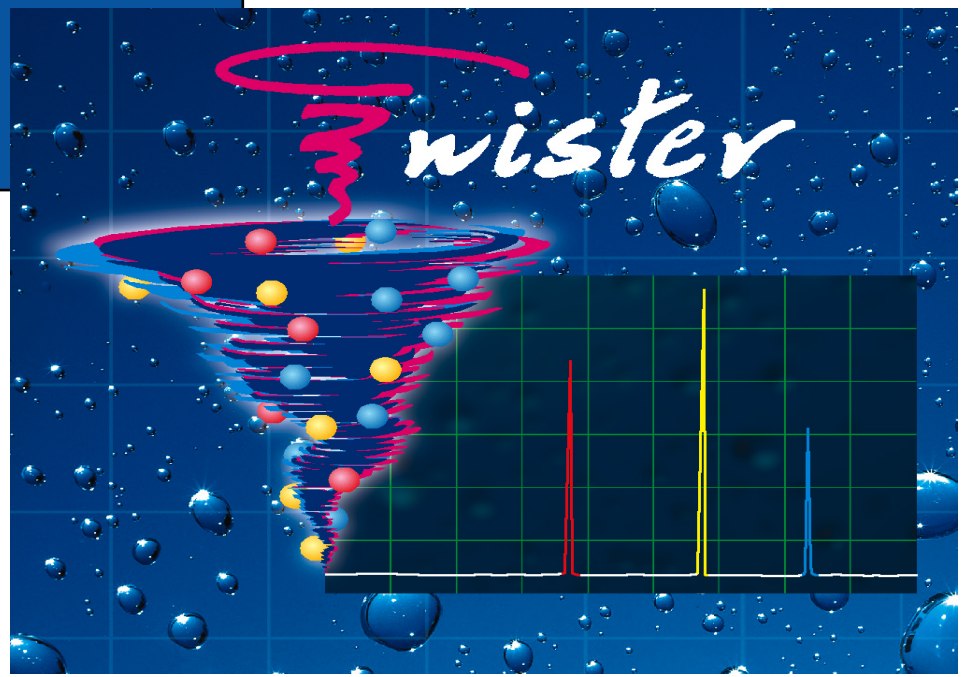

Sorptive
Extraction

Multipurpose Sampler for Automated Sample Prep/Injection

Agilent Technologies

Automated – Miniaturized – Solvent Free

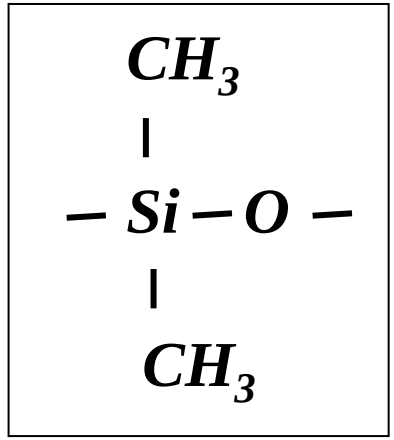
- *Static Headspace (SHS)*
- *In-tube Extraction (ITEX)*
- *Dynamic Headspace (DHS)*
- *Solid Phase Micro-Extraction (SPME)*
- *Stir Bar Sorptive Extraction (SBSE)(Twister™)*
- *Headspace Sorptive Extraction (HSSE)*
  - *passive sampling (PSSE) - PATCH*
- *Automatic Liner Exchange (ALEX™)*
- *LC-GC (on-line clean-up/fractionation)*
- *Solid Phase Extraction (not on line yet)*



Gerstel GmbH
Mulheim a/d Ruhr
Germany

Channel partner Agilent

Best Sorptive Extraction Medium
PDMS

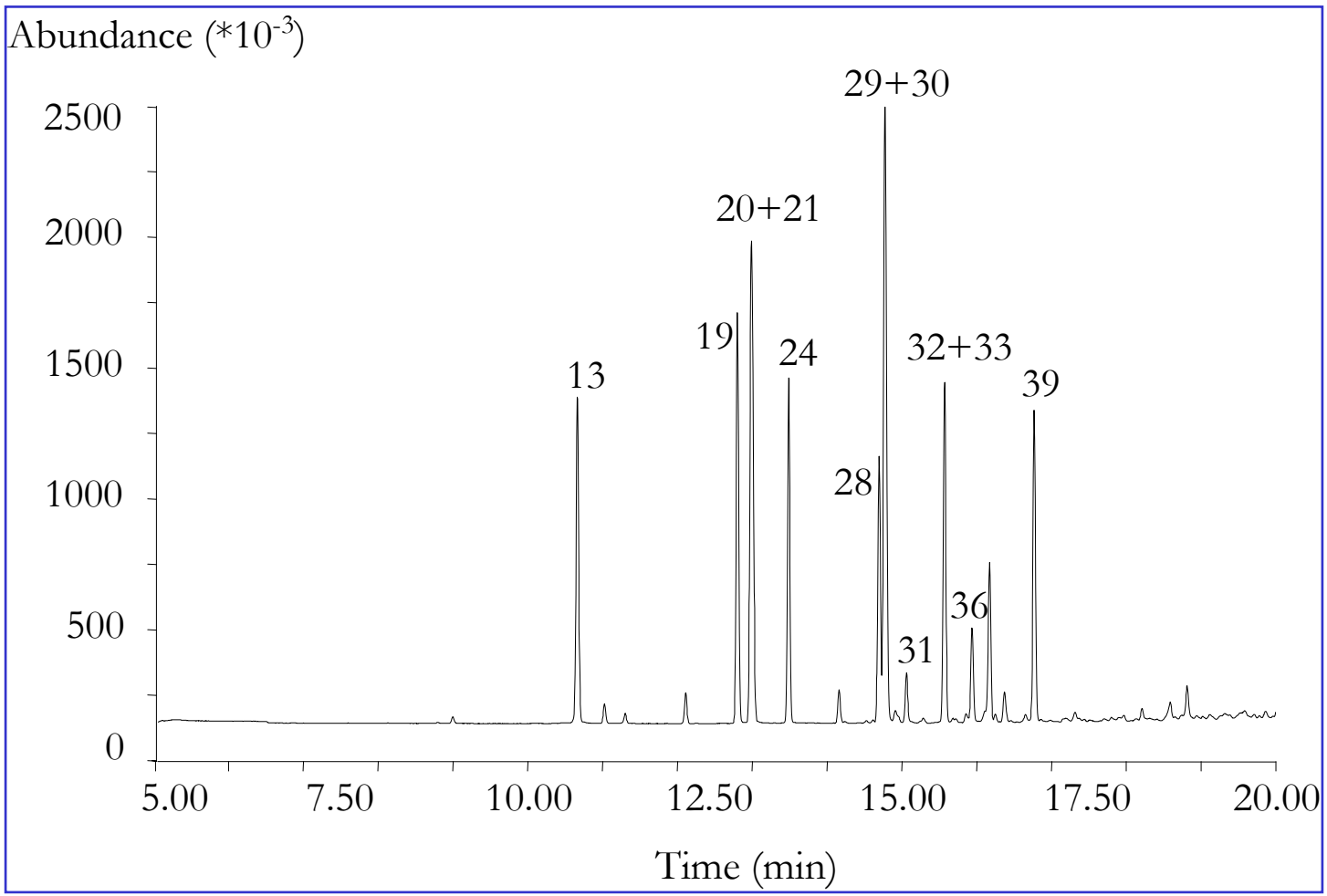


- Best GC stationary phase (apolar)
- Decomposition products very specific and not related with solutes of interest
- Retention indices available for a wide number of compounds
- PDMS/water distribution ~ Octanol/water distribution, $K_{o/w}$ values can be applied

  (if not available log P can be calculated using KOWWIN)


GERSTEL
Twister
MPS2
F1
F2
F3
F4
Esc
Stop
GERSTEL
MultiPurposeSampler
MPS
GERSTEL
TDU
TWISTER Desorption Unit

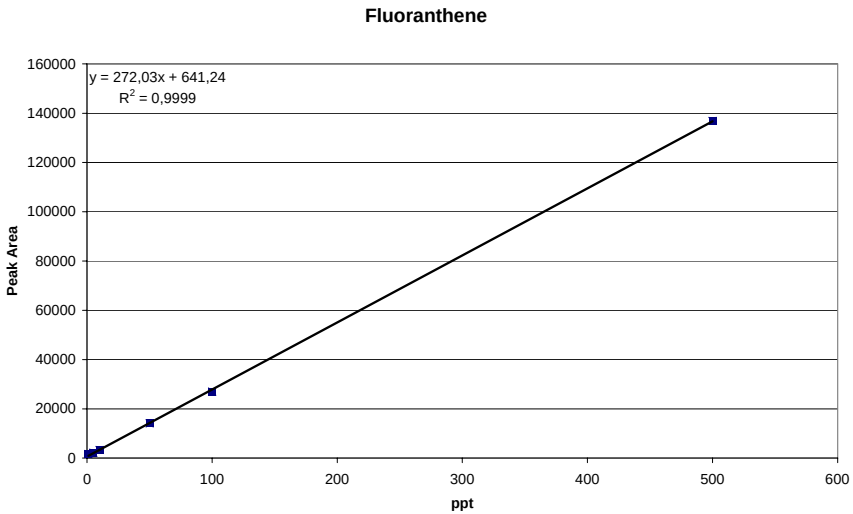
SBSE - Volatiles - 200 mL
5 ppt level - ion monitoring - Aromatics

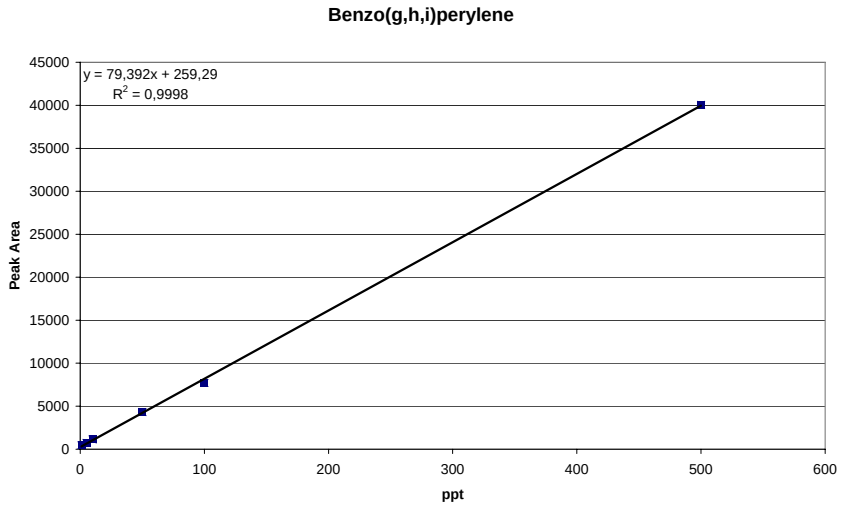


PAH Analyser - Conditions

- ***Twister (10 mm x 0.5 mm)***
  - ***Sample volume: 10 mL***
  - ***Extraction: 3 hours, 500 rpm and at room temperature***
- ***Desorption***
  - ***TDS, splitless, 20°C, 60°C/min, 300°C (10 min)***
  - ***Transfer line: 320°C***
- ***Cryo-focussing***
  - ***CIS, glass wool, split: 10:1, -150°C, 12°C/s, 300°C (5 min)***

Linearity

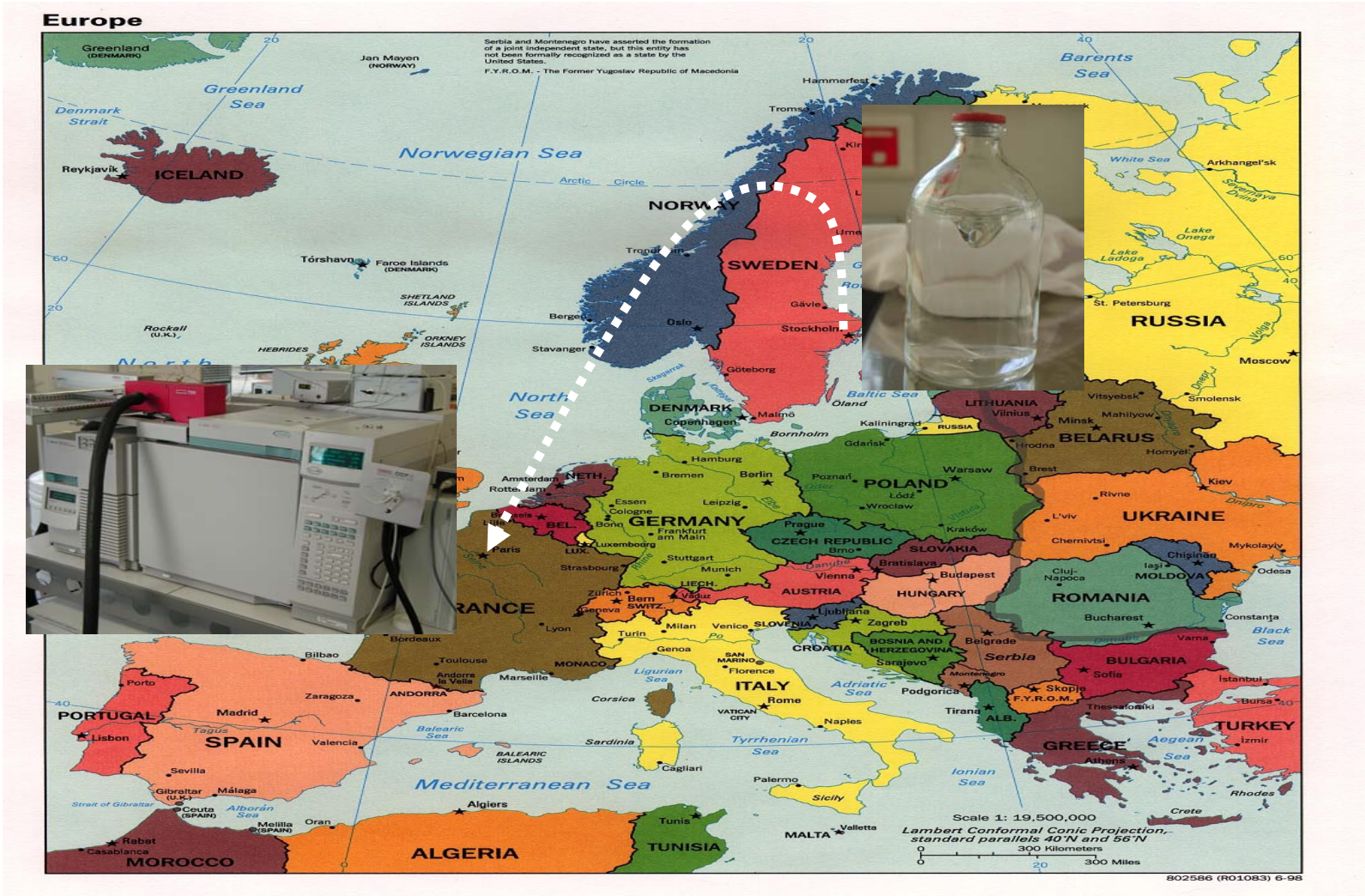




Detection Limits Repeatability

Compounds	Linearity	Detection Limit [ppt]
Naphthalene	0.99846	0.4
A-Methylnaphthalene	0.99829	0.5
2-Methylnaphthalene	0.99886	0.7
Acenaphthylene	0.99928	0.3
Acenaphthene	0.99954	1.3
Fluorene	0.99990	1.9
Phenanthrene	0.99992	0.8
Anthracene	0.99933	1.1
Fluoranthene	0.99990	0.1
Pyrene	0.99994	0.7
Benzo(a)anthracene	0.99727	0.1
Chrysene	0.99895	0.2
Benzo(b)fluoranthene	0.99550	0.2
Benzo(k)fluoranthene	0.99820	0.4
Benzo(a)pyrene	0.99611	1.0
Indeno(1.2.3)pyrene	0.99995	1.3
Dibenz(a.h)anthracene	0.99972	0.3
Benzo(g.h.i)perylene	0.99975	0.2

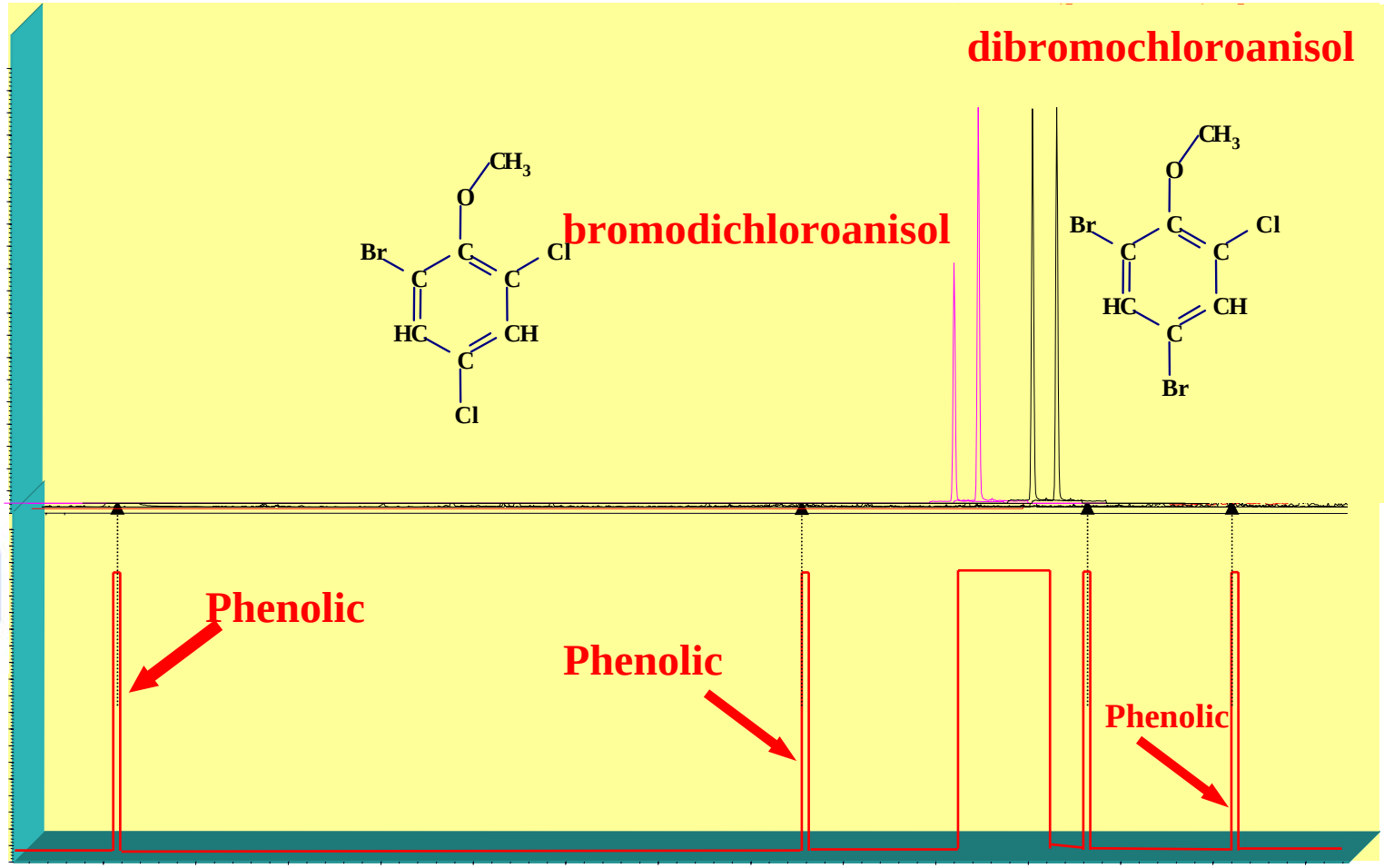
SBSE-TD-GC-MS - On-site SBSE



SBSE-TD-GC-SNIF/MS

MS detection

sniffing detection



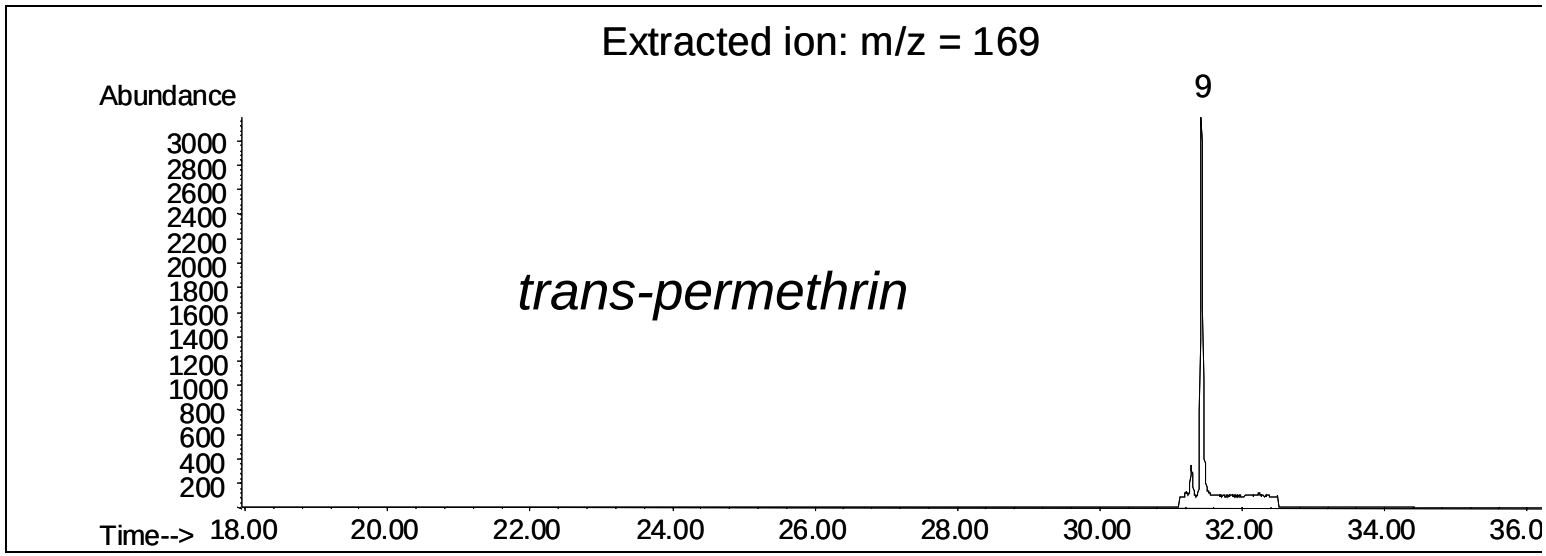
EDCs

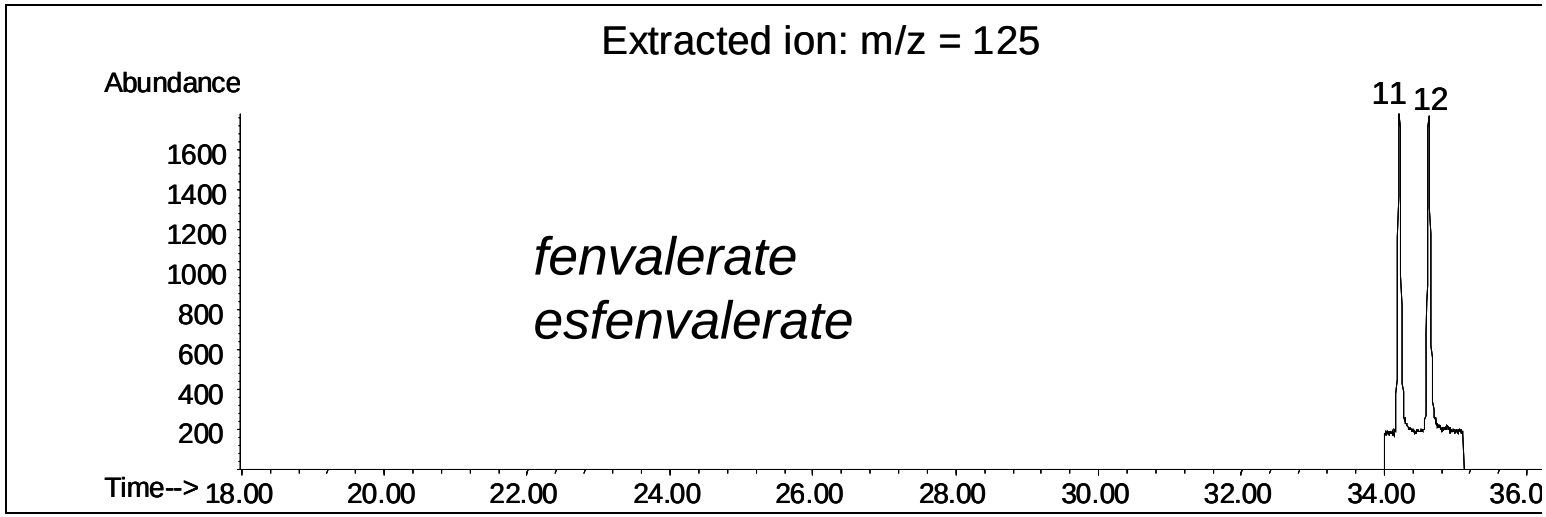
- ***Natural and synthetic hormones***
- ***Phytoestrogens***
- ***Alkylphenols and bisphenol A***
- ***Polycyclic aromatic hydrocarbons (PAHs)***
- ***Polychloro and bromo biphenyls (PCBs, PBrBs)***
- ***Dioxins anf furans***
- ***Polybrominated biphenyl ethers (PBDEs)***
- ***Organotin compounds***
- ***Phthalates***
- ***Pesticides***
- ***….***

Typical example: Pyrethroids

Pyrethroids	*Log Ko/w*	*Retention time (min)*	*SIM ions*	*SIM group*
Cis-Resmethrin	7.11	27.79	*123*/128	1
Trans-Resmethrin	7.11	27.97	*123*/128	1
Bifenthin	8.15	28.87	*181*/165	2
Fenpropathrin	5.62	29	*97*/181	2
λ-Cyhalothrin	6.85	30.4	*181*/197	3
Acrinathrin	6.73	30.73	*181*/93	3
Cis-Permethrin	6.18	31.4	183/*163*	4
Trans-permthrin dimethyl d6 (I.S.)		31.54	183/*169*	4
Trans-permethrin	6.18	31.58	183/*163*	4
Cypermethrin I	6.38	32.73	*181*/163	5
Cypermethrin II	6.38	32.89	*181*/163	5
Cypermethrin III	6.38	33.01	*181*/163	5
Cypermethrin IV	6.38	33.07	*181*/163	5
Fenvalerate	6.76	34.33	*125*/167	6
Esfenvalerate	6.76	34.75	*125*/167	6
Deltamethrin	6.18	35.92	*181*/253	7

Pyrethroids	*R^2*	*Repeatability (%)*			*Detection limit (ng/L)*				*Quantitation Limit (ng/l)*
		TDS	*S/SL*	*LD*	*TDS*	*S/SL*	*LD (1µL)*	*LD (10 µL)*	*TDS*
Cis-Resmethrin	0.990	14.7	12.1	4.8	0.1	0.5	16.4	1.5	0.4
Trans-Resmetrhin	0.981	13.5	17.5	3.1	0.2	0.7	17.1	1.6	0.5
Bifenthin	0.997	5.6	19.8	9.2	0.02	0.09	2.4	0.2	0.05
Fenpropathrin	0.994	6.8	11.4	8.4	0.3	1.3	20.5	2.2	1.1
λ-Cyhalothrin	0.992	12.2	9.9	7.0	0.1	0.6	7.7	0.7	0.3
Acrinathrin	0.990	3.9	6.5	7.7	0.9	3.0	40.8	4.0	2.9
Cis-Permethrin	0.990	9.4	11.6	8.7	0.8	1.2	28.8	2.8	2.6
Trans-permethrin	0.993	4.2	9.4	9.7	0.6	1.6	22.6	2.1	1.9
Cypermethrin I	0.997	3.8	9.5	6.1	0.2	1.6	15.1	1.6	0.6
Cypermethrin II	0.991	4.6	7.1	6.5	0.2	1.6	16.4	1.5	0.6
Cypermethrin III	0.995	9.4	5.3	4.9	0.2	1.1	17.0	1.6	0.6
Cypermethrin IV	0.995	5.6	9.3	10.3	0.2	1.8	17.0	1.6	0.7
Fenvalerate	0.993	10.7	8.6	9.5	0.3	2.0	31.1	3.2	1.0
Esfenvalerate	0.990	3.9	9.5	10.4	0.8	3.4	51.9	5.0	2.7
Deltamethrin	0.990	4.7	7.3	9.9	1.4	6.4	73.4	7.1	4.7


Extracted ion: m/z = 169
Abundance
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
Time-->
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
34.00
36.0
9
trans-permethrin


Extracted ion: m/z = 125
Abundance
1600
1400
1200
1000
800
600
400
200
Time-->
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
34.00
36.0
11
12
fenvalerate
esfenvalerate

Aqueous Samples.

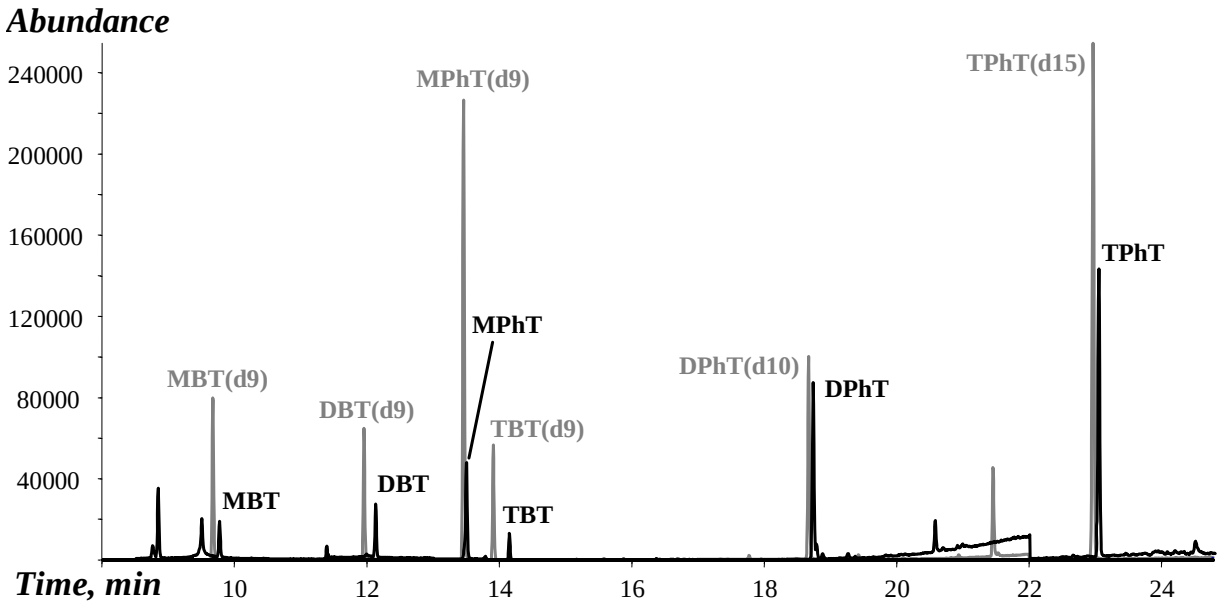
In situ derivatization to increase log P

- ***$NaEt_4B$ (pH control)***
- ***Cl COOEt (pyridine/ethanol)***
- ***$(CH_3COO)_2O$ (pH 12)***
- **…**

Organo-Sn Speciation

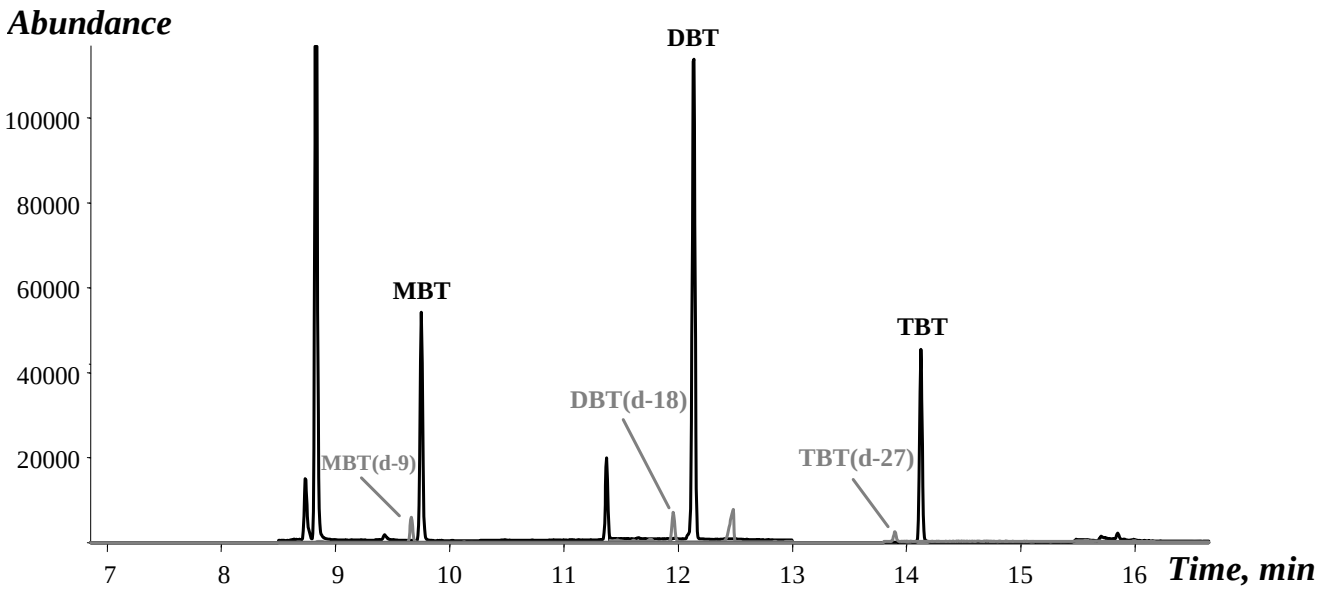
- ***SPME - capillary GC/ICPMS***
- ***SBSE – capillary GC/ICPMS***
- ***In-situ derivatisation - SPME - RTL - ID - capillary GC/MS***

  - sub ng/L for water samples
  - µg/kg for sediment samples
  - robust and fully validated (accreditation)

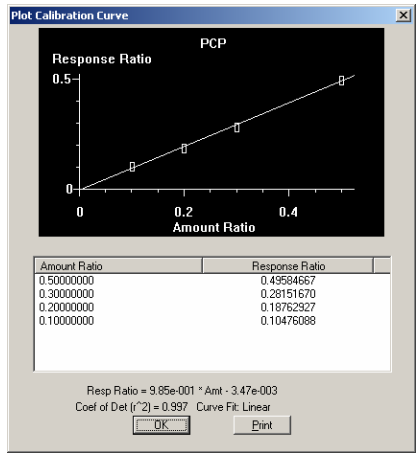


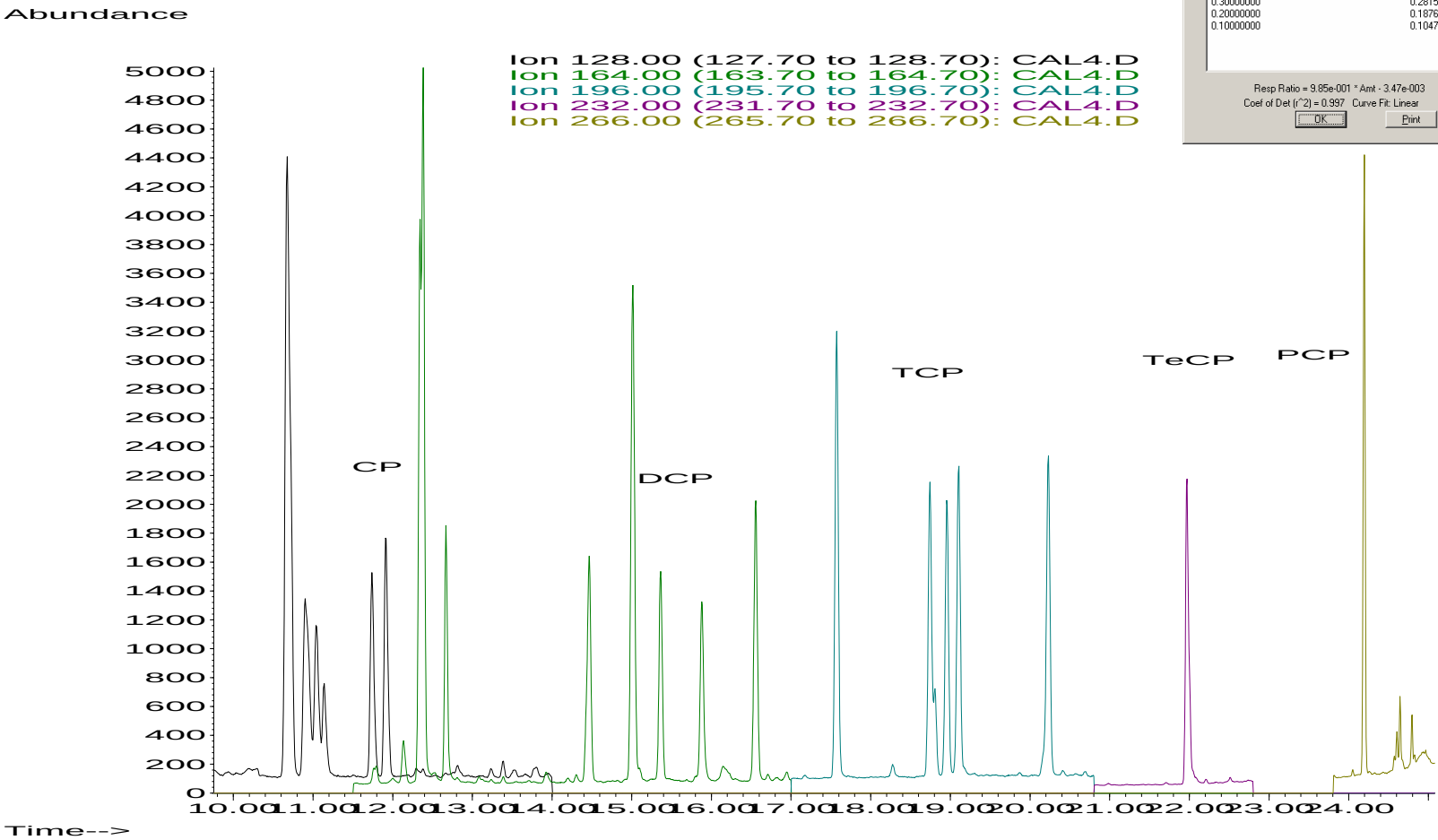
Water at 20 ng/L

PACS-2



In-situ acetylated Cl-phenols – ng/L !





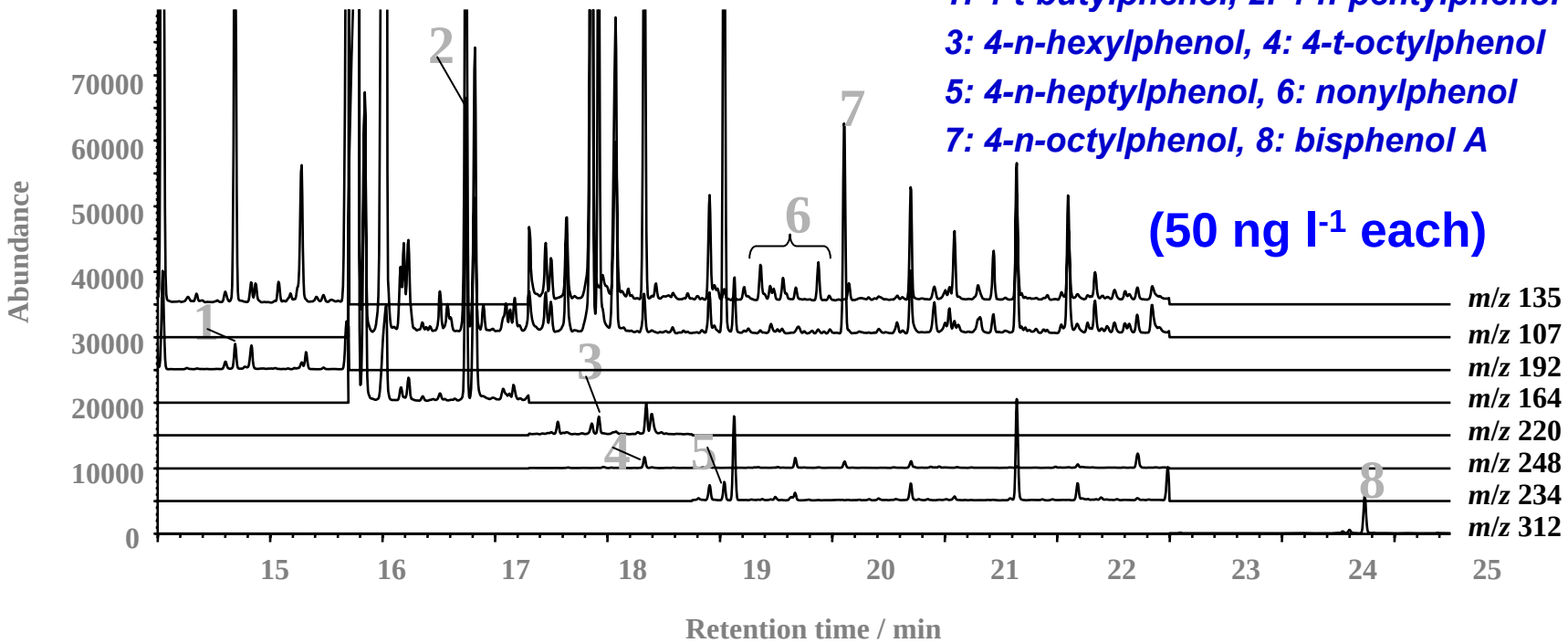
In-situ Derivatisation-SBSE-TD-GC-MS(SIM) Analysis of Alkylphenols in water *

Sample volume 10 mL, 60 min extraction
K_2CO_3 0.5g, acetic anhydride 0.5 mL
cal: 1.0 – 1000 ng L^{-1} (7 points) → r^2 > 0.9981
sensitivity (MDL (n = 6), 3.0SD) → 0.11 – 3.6 ng L^{-1}
recovery (10 ng L^{-1}) → 85-106 % (RSD < 3-11 %, n = 6)

* S. Nakamura *et al*, *J. Chromatogr. A*, 1038 (2004) 291

1: 4-t-butylphenol, 2: 4-n-pentylphenol
3: 4-n-hexylphenol, 4: 4-t-octylphenol
5: 4-n-heptylphenol, 6: nonylphenol
7: 4-n-octylphenol, 8: bisphenol A

(50 ng l^{-1} each)



Agilent Technologies


Thank you
for your
attention