

NEW INTEGRATED STRATEGY FOR QUICK ANALYSIS OF POPs AND PAHs IN FOOD

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CONFIDENCE: CONTaminants in Food and Feed: Inexpensive DETECTION for Control of Exposure.

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CONFIDENCE: Contaminants in food and feed: Inexpensive detection for control of exposure

Improving Food Safety in Europe: developing rapid tests for chemical contaminants in a new European research project

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SEVENTH FRAMEWORK PROGRAMME

Safer food through rapid and cost-efficient tests for chemical contaminants in the food chain. This is the major goal of a new European research project called CONFIDENCE.

Cluster 1: Organic pollutants			Cluster 2: Veterinary pharmaceuticals		Cluster 3: Heavy metals	Cluster 4: Biotoxins		
WP1a POPs	WP1b PFCs	WP1c Pesticides	WP2a Cocci-dio-stats	WP2b Anti-biotics	WP3 Heavy metals	WP4a Alka-loids	WP4b Marine biotox.	WP4c Mycotoxins



CONFIDENCE – Project objectives



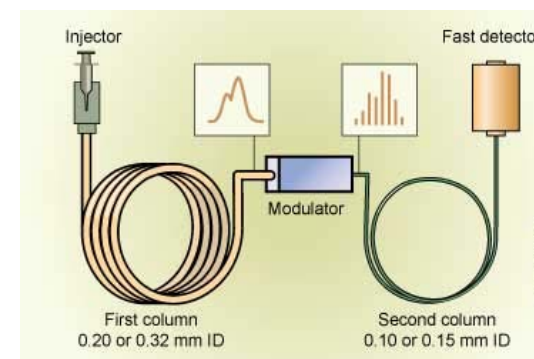
- To develop a simplified sample preparation strategy for simultaneous determination of wide range of contaminants in food and feed focused on fish and cereal based baby food.



- Implementation of a GC×GC–TOFMS for the determination of wide range of contaminants in food and feed.

- Fasten and simplified sample preparation method.
- Decrease the consumption of chlorinated solvents.
- Decrease the financial cost of analysis.

- Obtain high chromatographic resolution and low limits of quantification (LOQ)

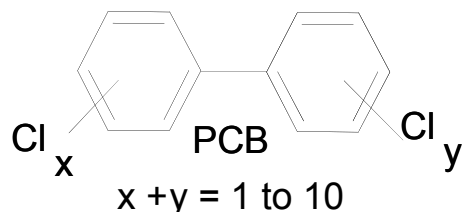
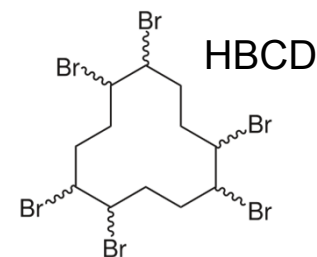
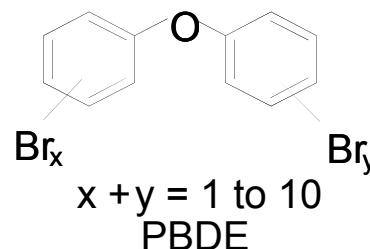


Target analytes – CONFIDENCE project



- PBDE # 28, 47, 99, 100, 153, 154, 183
- HBCD, PBB # 153

16 BFRs



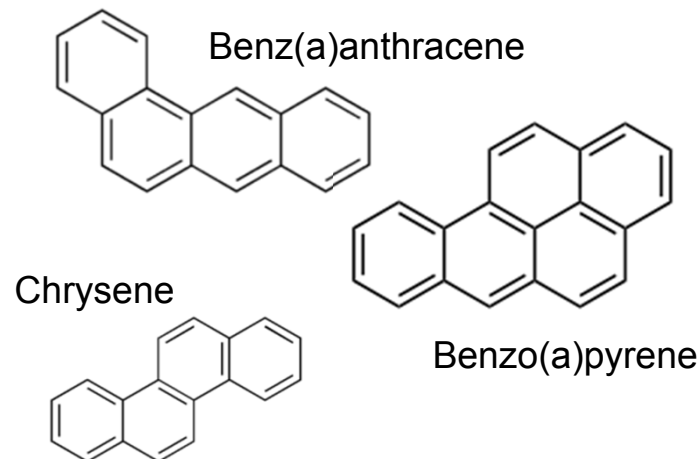
- Non-ortho PCB # 77, 81, 126, 169
- Mono-ortho PCB # 105, 114, 118, 123, 156, 157, 167, 189
- Major PCB # 28, 52, 101, 138, 153, 180

18 PCBs

Benzo(c)fluorene
 Benzo(k)fluoranthene
 Cyklopenta(c,d)pyrene
 Dibenzo(a,e)pyrene
 Dibenzo(a,h)pyrene
 Dibenzo(a,i)pyrene
 Dibenzo(a,l)pyrene
 5-Methylchrysene

Benz(a)anthracene
 Benzo(a)pyrene
 Benzo(b)fluoranthene
 Benzo(j)fluoranthene
 Benzo(g,h,i)perylene
 Chrysene
 Dibenz(a,h)anthracene
 Indeno(1,2,3-cd)pyrene

15+1 EU PAHs



LIMITS AND REGULATIONS



20.12.2006


EN

Official Journal of the European Union

L 364/5

COMMISSION REGULATION (EC) No 1881/2006
of 19 December 2006
setting maximum levels for certain contaminants in foodstuffs
(Text with EEA relevance)

Meetings | Documents | Contacts | Projects May 2, 2010 | Logi




CONVENTION PROGRAMMES COUNTRIES SECRETARIAT PARTNERS

► Convention ► The POPs


☐ **What are POPs?**

Persistent Organic Pollutants (POPs) are organic chemical substances, that is, they are combination of physical and chemical properties such that, once released into the environment:

- remain intact for exceptionally long periods of time (many years);
- become widely distributed throughout the environment as a result of natural processes;



European Food Safety Authority
Committed to ensuring that Europe's food is safe



European Food Safety Authority

The EFSA Journal (2008) 724

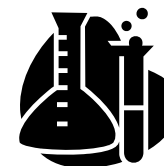
Polycyclic Aromatic Hydrocarbons in Food¹

Scientific Opinion of the Panel on Contaminants in the Food Chain

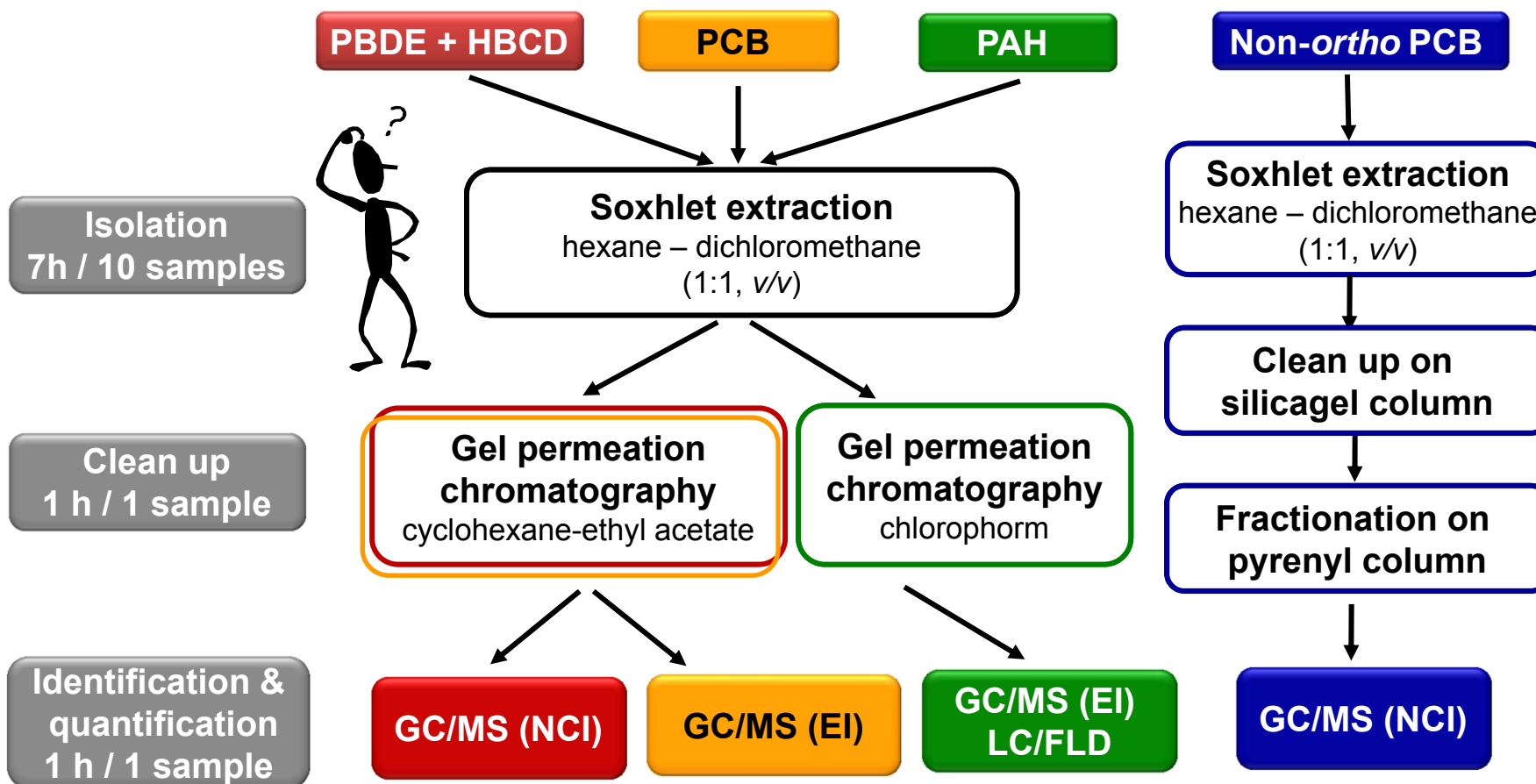
(Question N° EFSA-Q-2007-136)

Adopted on 9 June 2008

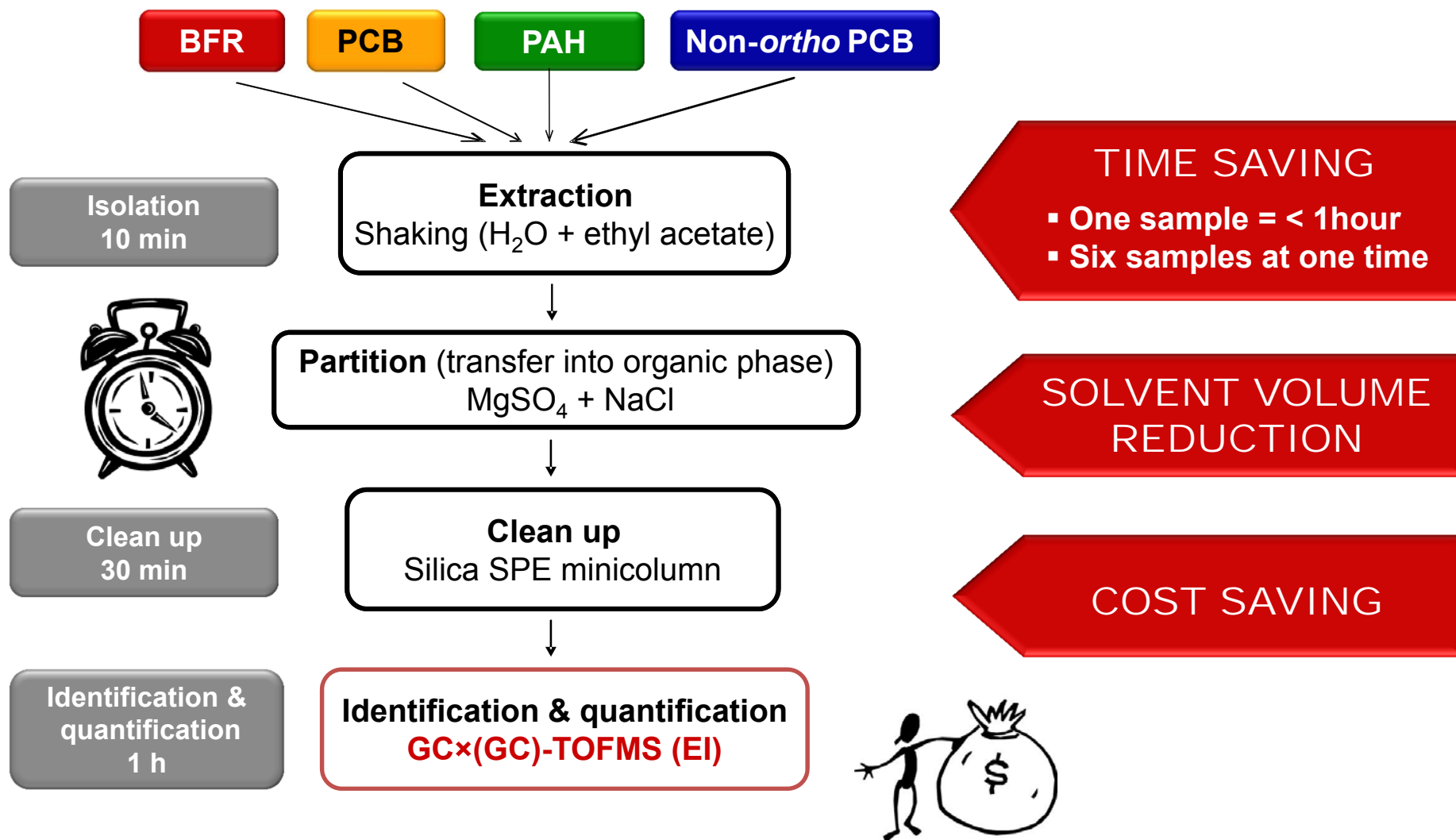
ACREDITATED SAMPLE PREPARATION



Time consuming, laborious, high consumption of chlorinated solvents....

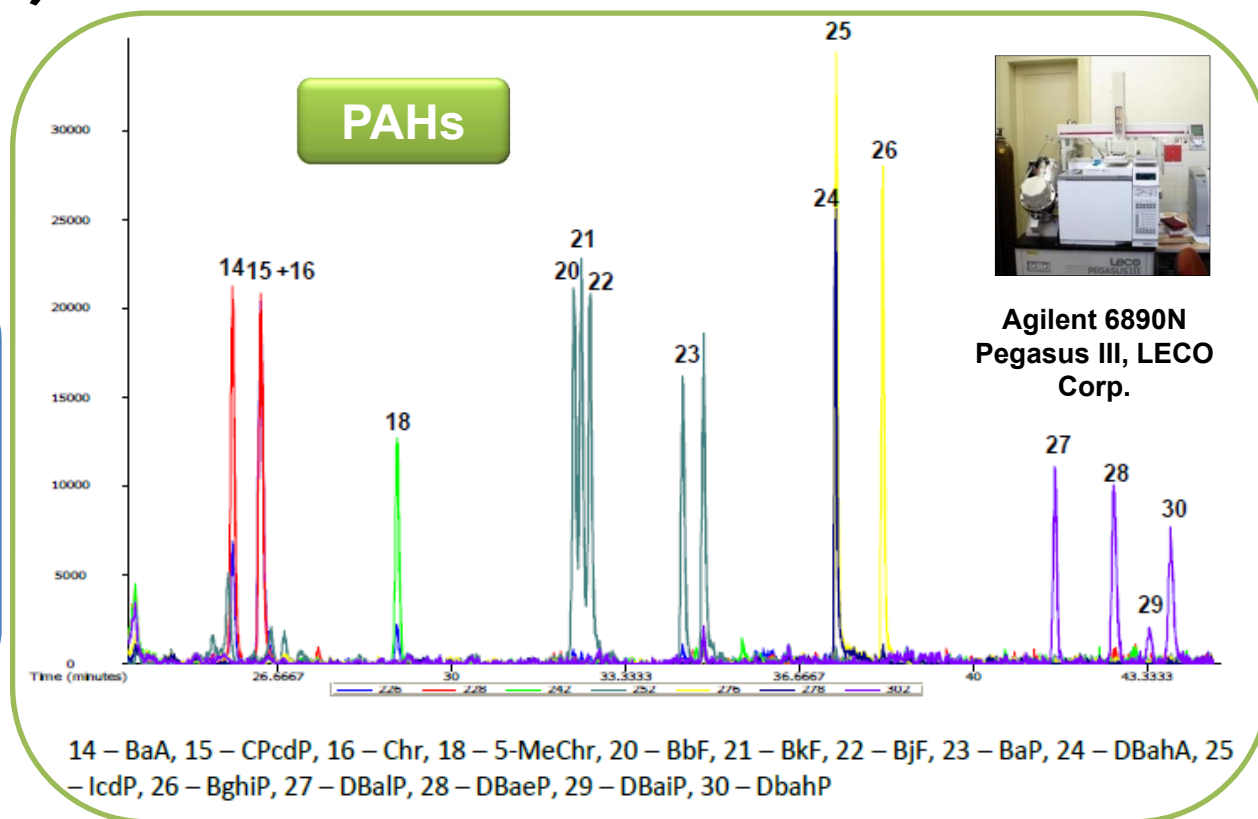
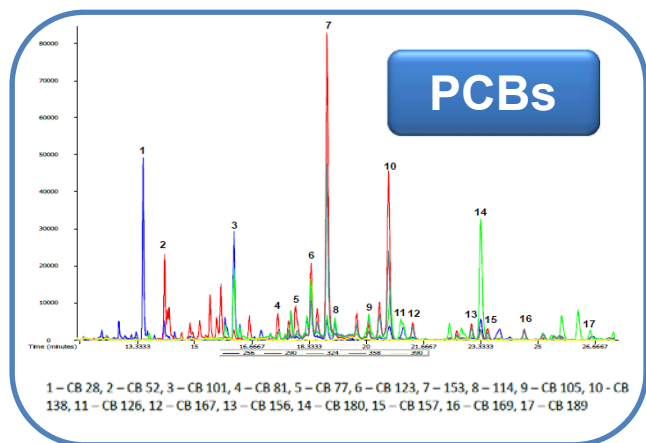


INTEGRATED SAMPLE PREPARATION

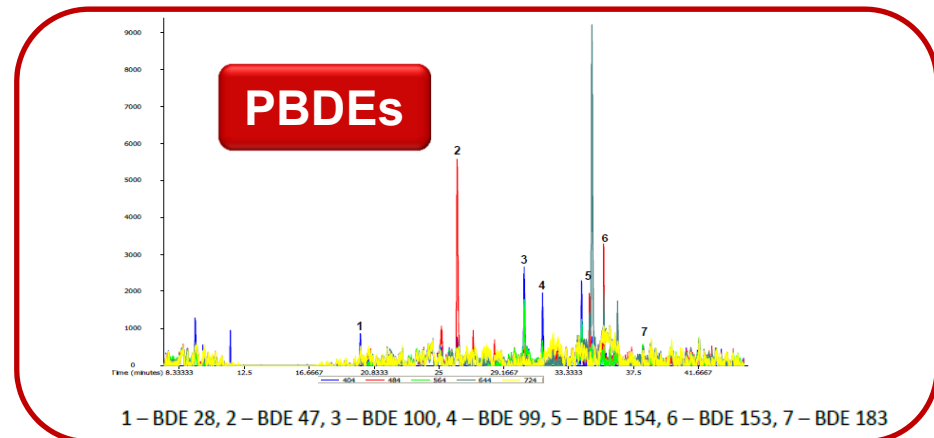
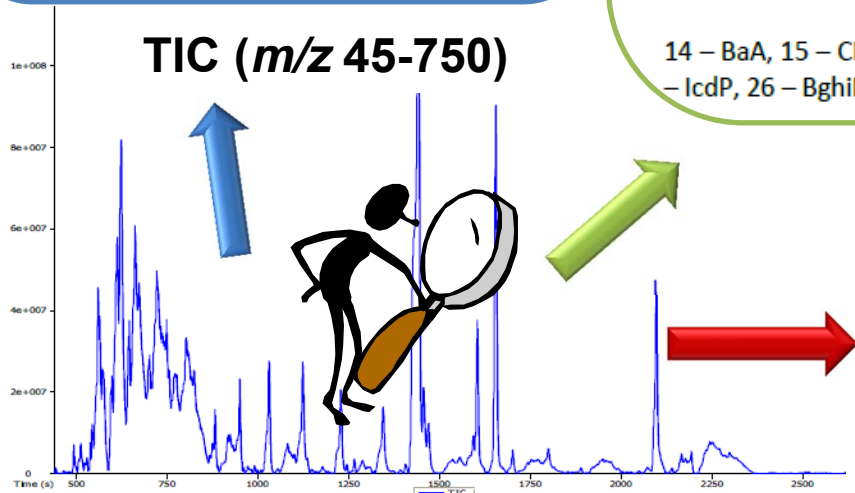


GC-TOFMS (EI) – fish muscle tissue

Spiked with PAHs, PCBs
and PBDEs at 1 µg/kg.
Injected equivalent of matrix
80 mg.



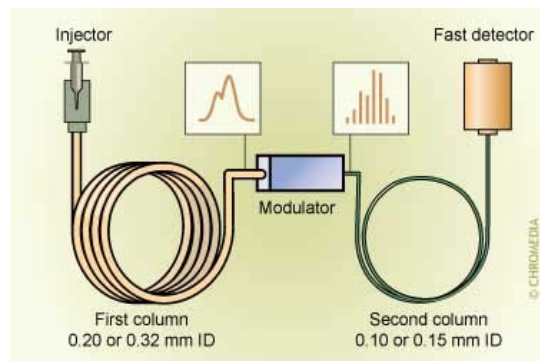
Agilent 6890N
Pegasus III, LECO
Corp.



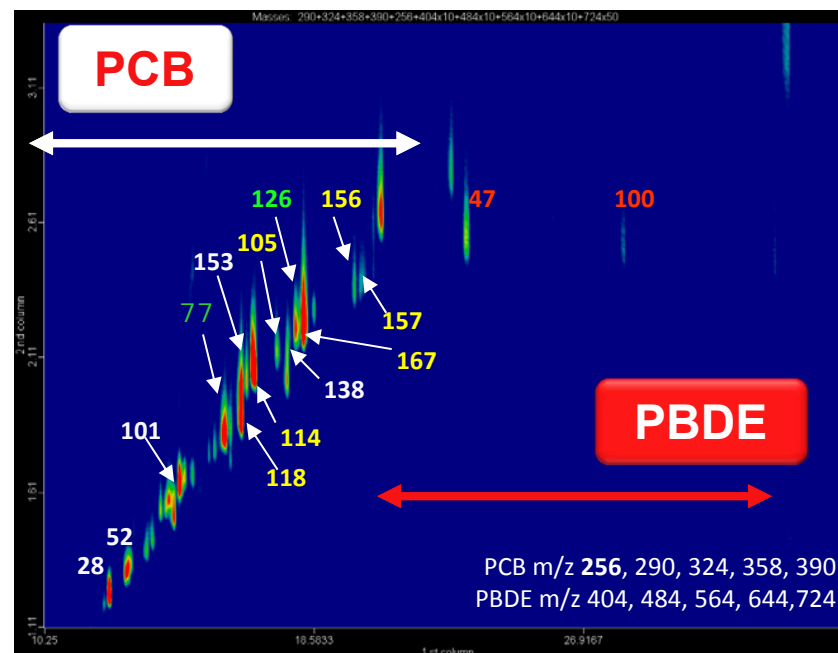
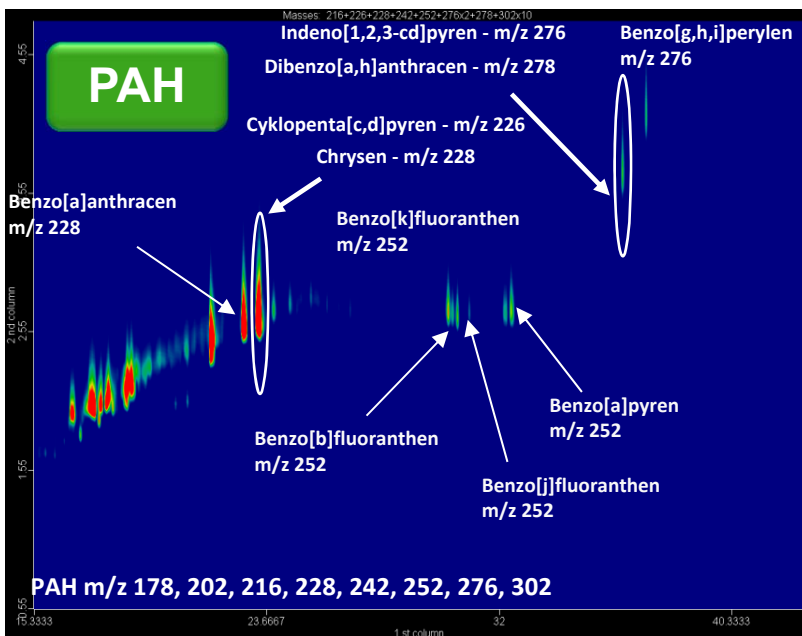
GC×GC-TOFMS (EI) – fish muscle tissue



Agilent 6890N
Pegasus III,
LECO Corp.



BPX 50 (30 m × 0.25 mm × 0.25 μm)
HT 8 (1 m × 0.1 mm × 0.1 μm)



Yellow – mono-ortho PCB Green – non-ortho PCB
White – major PCB Red – PBDE

▲ Bream (*Abramis brama*)

Target analytes II

PBDE # 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, ...
 HBCD, PBB # 153, PBT, PBEB, HBB, BTBPE, DBDPE



16 BFRs

Non-ortho PCB # 77, 81, 126, 169
 Mono-ortho PCB # 105, 114, 118, 123, 156, 157, 167, 189
 Major PCB # 28, 52, 101, 138, 153, 180

18 PCBs

α-, β-, γ-HCH,	β-endosulfane	
Hexachlorobenzene	Endosulfansulfate	
Heptachlor	Aldrine	
Cis-HEPO	Dieldrine	
Trans-HEPO	Endrine	
Cischlordan	op-DDE	pp-DDD
Oxychlordan	pp-DDE	op-DDT
Transchlordan	op-DDD	pp-DDT
α-endosulfane		

22 OCPs

Benzo(c)fluorene
 Benzo(k)fluoranthene
 Cyklopenta(c,d)pyrene
 Dibenzo(a,e)pyrene
 Dibenzo(a,h)pyrene
 Dibenzo(a,i)pyrene
 Dibenzo(a,l)pyrene
 5-Methylchrysene

15+1 EU PAHs

Dibenzothiophene DBT

Benz(a)anthracene
 Benzo(a)pyrene
 Benzo(b)fluoranthene
 Benzo(j)fluoranthene
 Benzo(g,h,i)perylene
 Chrysene
 Dibenzo(a,h)anthracene
 Indeno(1,2,3-cd)pyrene

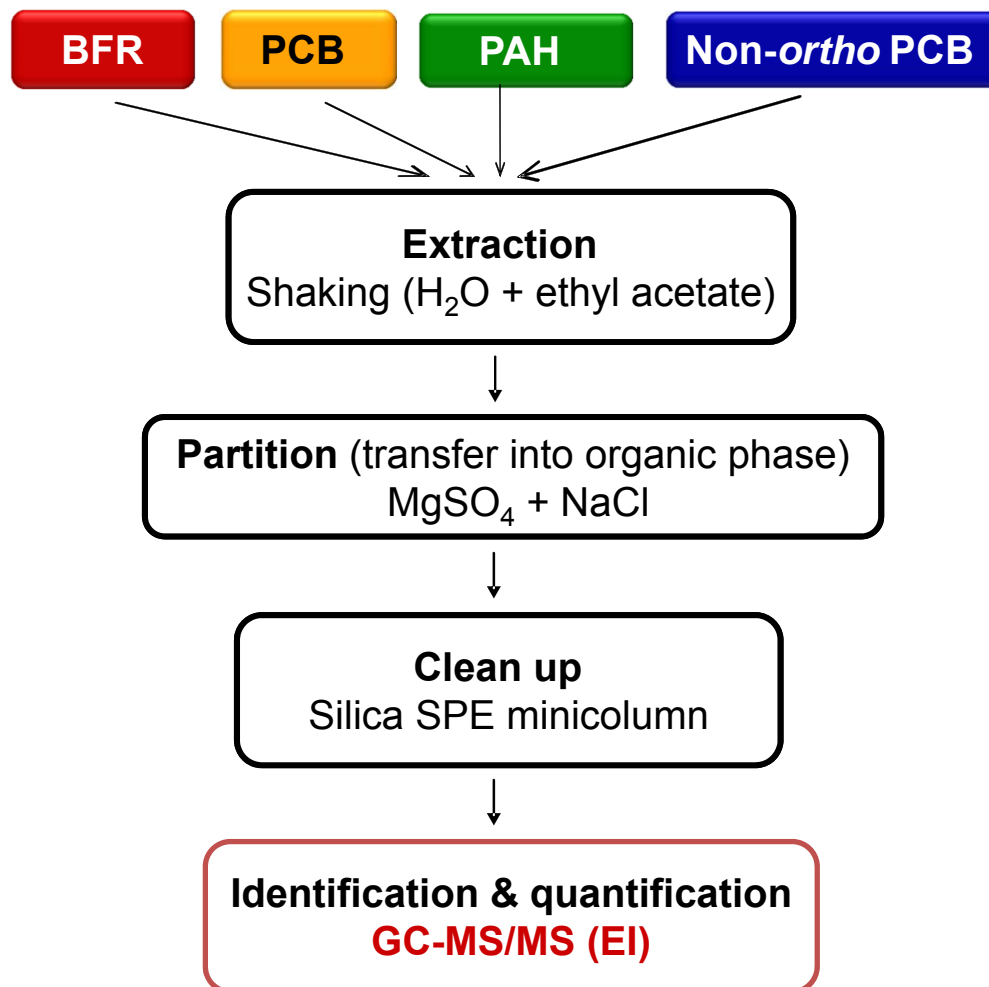
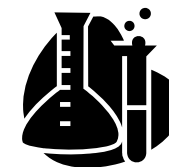
Acenaphthene
 Acenaphthylene
 Anthracene
 Fluoranthene
 Fluorene
 Naphthalene
 Phenanthrene
 Pyrene

16 US EPA PAHs

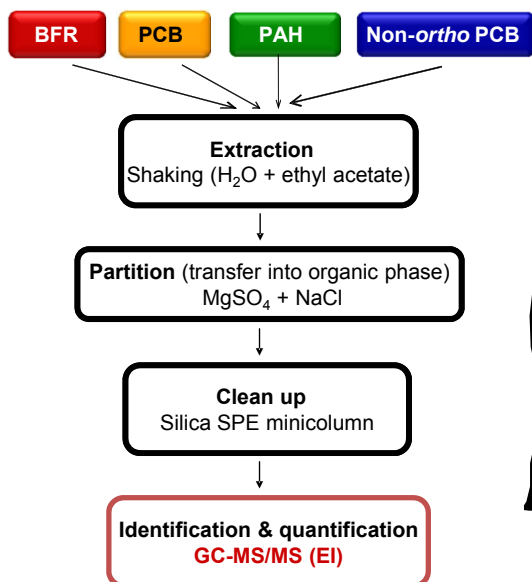
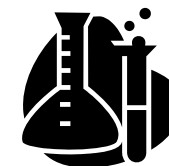
2-methylantracene
 1-methylchrysene
 3-methylchrysene
 5-methylchrysene
 1-methylnaphthalene
 2-methylnaphthalene
 1-methylphenanthrene
 1-methylpyrene

8 Methyl - PAHs

METHOD INNOVATION



METHOD INNOVATION

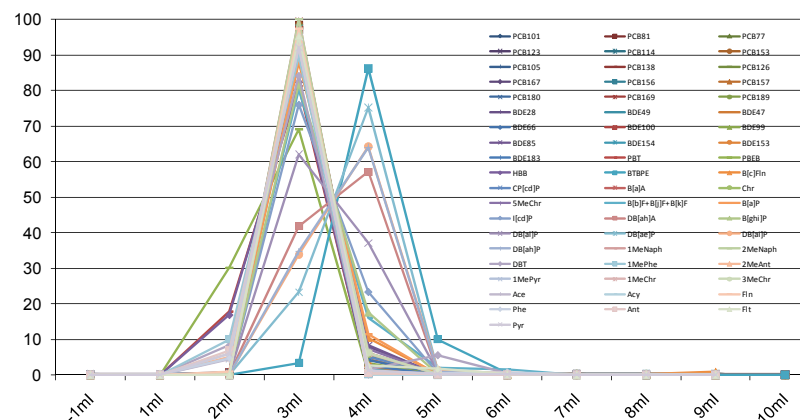


■ Clean up - silica SPE minicolumn

- Elution profiles
- Recoveries



~~Dieldrin
Endrin
β-endosulfane
Endosulfansulfate~~



■ GC-MS/MS (EI) method development

- Capillary column
- Injection parameters
- Oven temperature program
- Ion transitions, collision energies...

*Thermo Scientific TSQ Quantum
XLS triple quadrupole*



Column: Rxi-17Sil-ms (30m × 0.25mm × 0.25μm)
 Injection: PTV splitless (1μL)
 Oven temperature: 80°C (2min), @30°C/min to 240°C,
 @ 10°C/min to 340°C (20min)
 Carrier gas: helium (1.3mL/min)
 Source temperature: 250°C
 Emission current: 50μA

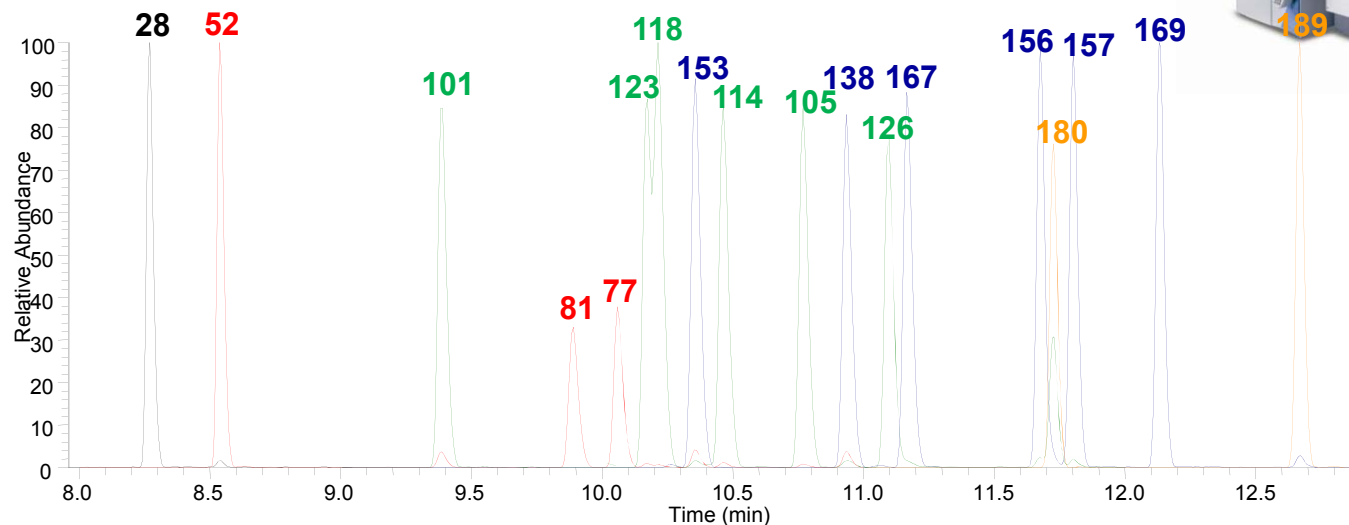
GC-MS/MS (EI) – PCBs + OCPs

Thermo Scientific TSQ
Quantum XLS triple
quadrupole



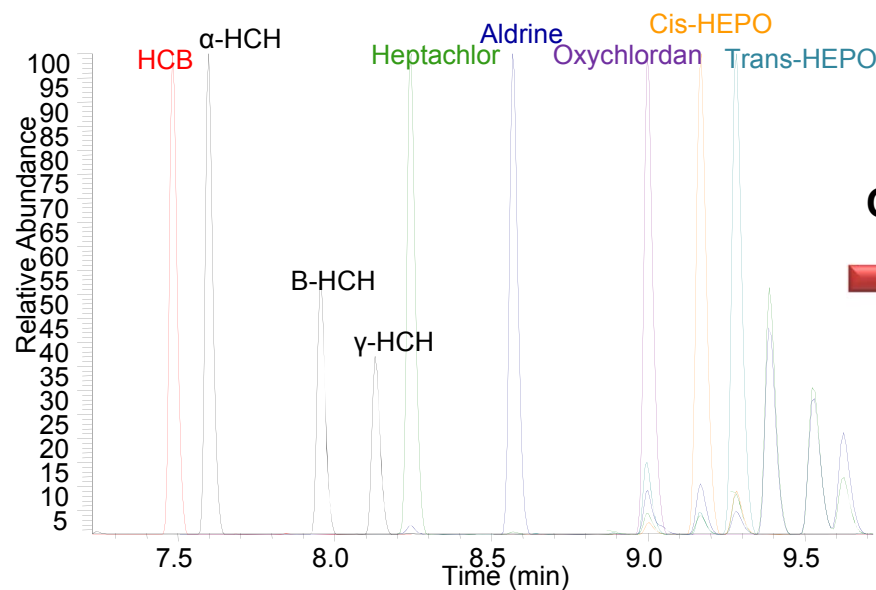
PCBs

- SRM 255.860 > 185.901
- SRM 291.900 > 221.899
- SRM 323.800 > 253.901
- SRM 357.840 > 287.881
- SRM 391.810 > 321.839



OCPs

- SRM 216.890 > 180.909
- SRM 248.840 > 213.859
- SRM 271.870 > 236.889
- SRM 262.910 > 190.929
- SRM 352.830 > 252.879
- SRM 386.790 > 262.859
- SRM 182.910 > 154.929



Other OCPs



GC-MS/MS (EI) - BFRs

Thermo Scientific TSQ
Quantum XLS triple
quadrupole



PBDEs

SRM 405.800 > 245.851

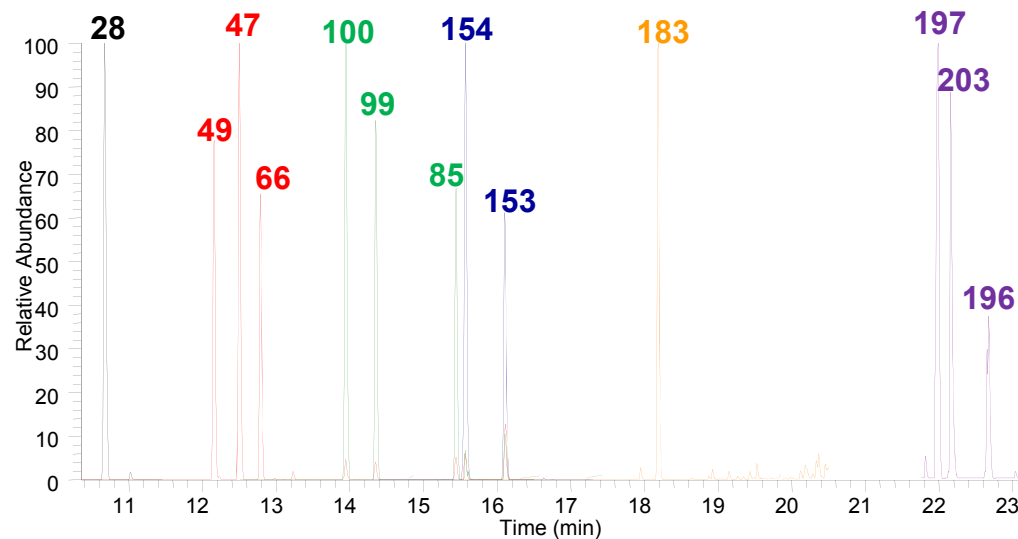
SRM 483.810 > 323.810

SRM 561.780 > 401.779

SRM 641.730 > 481.729

SRM 719.740 > 559.739

SRM 803.700 > 643.699



Poor sensitivity

BDE 206

BDE 207

BDE 209

Other BFRs

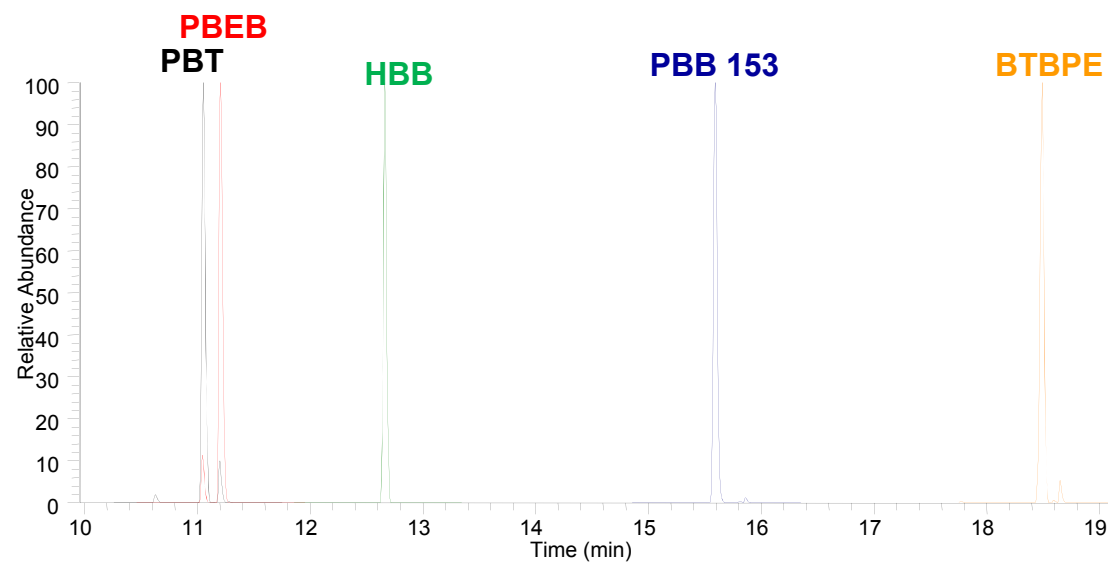
SRM 406.700 > 246.671

SRM 486.440 > 405.719

SRM 551.560 > 470.569

SRM 627.700 > 467.899

SRM 356.680 > 277.379



Poor sensitivity

OBIND

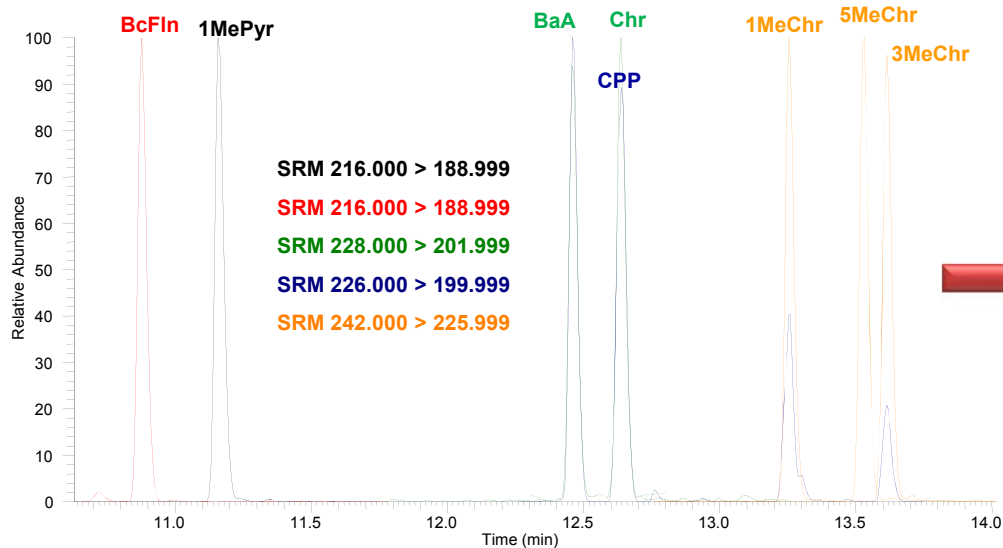
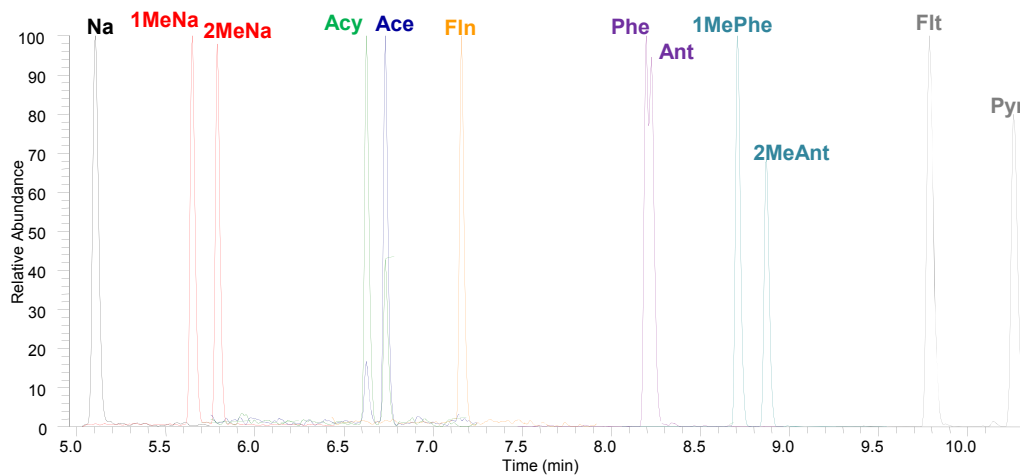
DBDPE

GC-MS/MS (EI) - PAHs

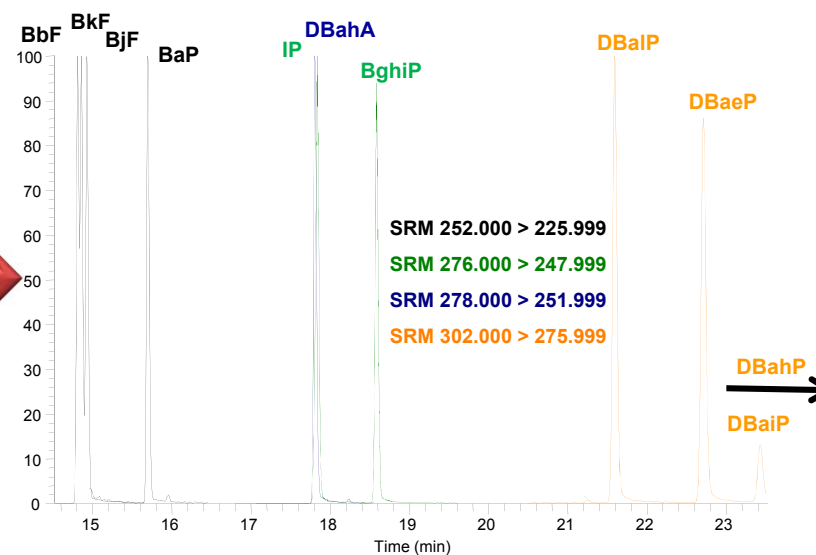
Thermo Scientific TSQ
Quantum XLS triple
quadrupole



- SRM 128.000 > 76.999
- SRM 141.000 > 114.999
- SRM 152.000 > 101.999
- SRM 153.000 > 125.999
- SRM 165.000 > 138.999
- SRM 178.000 > 151.999
- SRM 192.000 > 151.999
- SRM 202.000 > 164.999



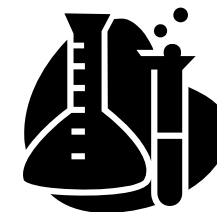
- SRM 216.000 > 188.999
- SRM 216.000 > 188.999
- SRM 228.000 > 201.999
- SRM 226.000 > 199.999
- SRM 242.000 > 225.999



- SRM 252.000 > 225.999
- SRM 276.000 > 247.999
- SRM 278.000 > 251.999
- SRM 302.000 > 275.999



VALIDATION STUDY



Procedure blank

- With each batch of six samples, the procedure blank was prepared.

Recovery (%) and repeatability RSD (%)

- Fish muscle tissue spiked with all target analytes at two concentration levels (n=6).
- Level 1 and 2 = 1 and 5 $\mu\text{g}/\text{kg}$

LOQ ($\mu\text{g}/\text{kg}$), linearity (R^2), ...

Final independent control - trueness



Trout



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1947

Lake Michigan Fish Tissue

Standard Reference Material (SRM) 1947 is a frozen fish tissue homogenate, which was prepared from fish from Lake Michigan, and is intended primarily for use in evaluating analytical methods for the determination of selected trace elements, methylmercury, total mercury, polychlorinated biphenyl (PCB) congeners, and



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 1974b

Organics in Mussel Tissue (*Mytilus edulis*)

Standard Reference Material (SRM) 1974b is a frozen mussel tissue homogenate intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in marine bivalve mollusk tissue and similar matrices. All of the constituents for

LIMITS OF QUANTIFICATION (LOQ)

Analytes	Desired LOQ CONFIDENCE	Achieved LOQ				
		GC-MS/MS (1µL)	GC-MS (1µL)	GC-TOFMS (1µL)	GC-TOFMS (8µL)	GC×GC- TOFMS (8µL)
B[a]P	2.0 µg/kg	0.01 µg/kg	0.05 µg/kg	1 µg/kg	0.1 µg/kg	0.01 µg/kg
Other PAH	N/A	0.005-0.5 µg/kg	0.05-0.5 µg/kg	1-10 µg/kg	0.1-0.5 µg/kg	0.01-0.1 µg/kg
Σ dl -PCB	2 ng TEQ/kg	1.1 ng TEQ/kg	56 ng TEQ/kg	559.7 ng TEQ/kg	12.9 ng TEQ/kg	1.3 TEQ/kg
PBDE	< 0.2 µg/kg	0.01-0.1µg/kg	1-5 µg/kg	10 - >10 µg/kg	0.5-10 µg/kg	0.025-5 µg/kg



**Thermo Scientific TSQ
Quantum XLS triple
quadrupole**



**Agilent 6890N
Agilent 5975 Inert XL MS**



**Agilent 6890N
Pegasus III, LECO
Corp.**



CONCLUSIONS & FUTURE PLANS



- A simple, fast and cheap method for simultaneous determination of PAHs, PCBs, OCPs and BFRs has been optimized and validated.
- 6 fish muscle tissue samples can be processed within 1 hour.
- No special equipment brand/model is required for realization of the analysis.
- GC-fast TOF MS was used at first, nevertheless, other common GC-MS systems – e.g. equipped with MS/MS QqQ mass analyzers can be used for examination of sample extracts.
- No “confirmation” method is needed; analytes can be conclusively identified, as well as quantified.



Thank you for your kind attention....



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