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

Work package WP1a – Persistent Organic Pollutants (POP)

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Simplified sample preparation procedure for simultaneous determination of PCBs, BFRs and PAHs in fish

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INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE

Introduction

- Since polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) and polycyclic aromatic hydrocarbons (PAHs) belong, according to EFSA, among food contaminants that should be monitored, the quick, rugged, sensitive and inexpensive analytical method is currently required. [1]
- Analytical methods for determination of various organic contaminants such as PCBs, BFRs and PAHs in environmental and food matrices are typically based on multistep procedures including Soxhlet extraction with a subsequent clean up and fractionation steps. prior to relatively slow gas chromatography (GC) runs using either an electron capture (ECD) or a mass spectrometric (MS) detection in case of halogenated analytes. [2,3]
- PAHs are routinely analysed separately using a liquid chromatography coupled to a fluorescence detector (LC-FLD), but for several non-flurescence PAHs including in the EFSA opinion, a GC-MS analysis is needed. [1,4]

Aim of the study

- To optimise and validate the simplified sample preparation procedure for simultaneous determination of PCBs, BFRs and PAHs in fresh and smoked fish fillets.

Tested matrices

- Fresh fish mussel tissue (Bream - *Abramis brama*)
- Smoked fish (Trout - *Oncorhynchus mykiss*)

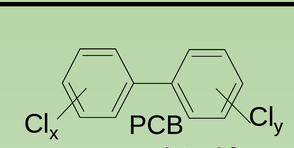
Oncorhynchus mykiss

Abramis brama

Target analytes

Dioxin-like polychlorinated biphenyls (PCBs)

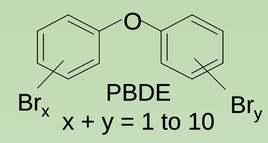
- Non-*ortho* congeners #77, 81, 126, 169
- Mono-*ortho* congeners #105, 114, 118, 123, 156, 157, 167, 189



x + y = 1 to 10

Brominated flame retardants (BFRs)

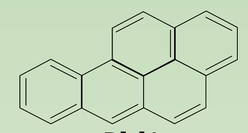
- Polybrominated diphenylethers congener (PBDEs) #28, 47, 99, 100, 153, 154, 183
- Hexabromocyclododecane (HBCD)
- Polybrominated biphenyl (PBB): congener #153



x + y = 1 to 10

Polycyclic aromatic hydrocarbons (PAHs)

Benz(a)anthracene - B[a]A
Benzo(a)pyrene - B[a]P
Benzo(b)fluoranthene - B[b]F
Benzo(c)fluoren - B[c]Fln
Benzo(j)fluoranthene - B[j]F
Benzo(k)fluoranthene - B[k]F
Benzo(g,h,i)perylene - B[ghi]P
Chrysene - Chr
Cyclopenta(c,d)pyrene - CP[cd]P
Dibenz(a,h)anthracene - DB[ah]A
Dibenzo(a,e)pyren - DB[ae]P
Dibenzo(a,h)-pyrene - DB[ah]P
Dibenzo(a,i)-pyrene - DB[ai]P
Dibenzo(a,l)pyrene - DB[al]P
Indeno(1,2,3-cd)pyrene - I[cd]P
5-Methylchrysene - 5 MeChr



B[a]A

Sample preparation procedure

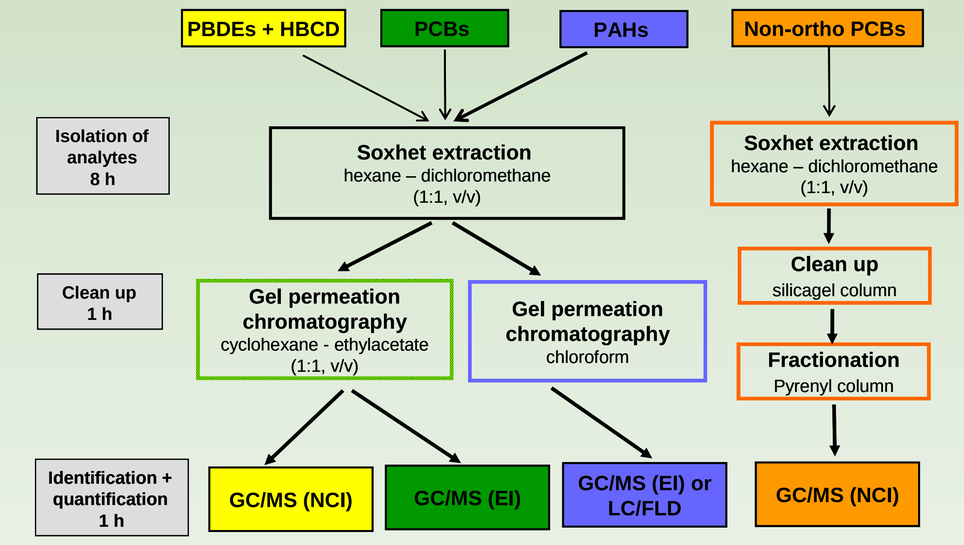


Figure 1: *An example of a „conventional“ sample preparation method for analysis of PCBs, BFRs and PAHs in fish*

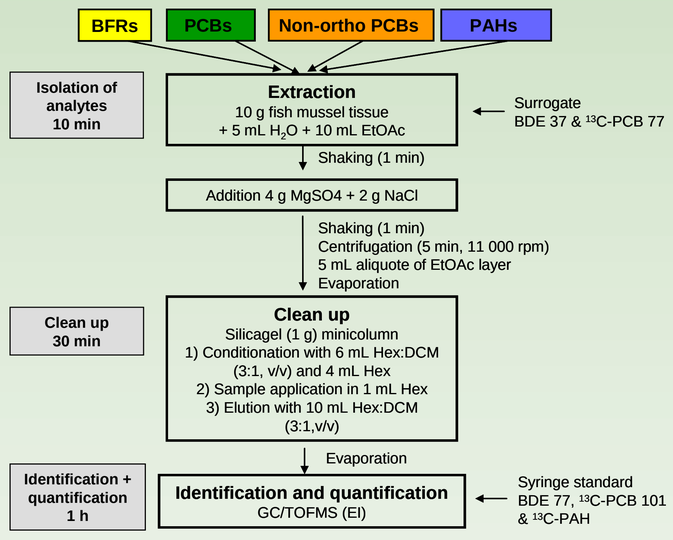


Figure 2: *Optimised final sample preparation method for simultaneous analysis of PCBs, BFRs and PAHs in fish*

Table 1: *Recovery (%) and repeatability RSD (%) of optimised sample preparation method; spiked fish fillet sample - 1 and 10 µg/kg for PCBs and PBDEs (for major PCBs – 5 and 25 µg/kg); 1 and 5 µg/kg for PAHs; n=6*

Analytes		Level 1		Level 2	
		Rec [%]	RSD [%]	Rec [%]	RSD [%]
Mono-ortho PCBs	PCB 105	113	9	108	11
	PCB 114	99	18	100	6
	PCB 118	95	9	87	13
	PCB 123	85	14	79	7
	PCB 156	96	9	77	11
	PCB 157	91	8	95	9
	PCB 167	75	10	76	10
	PCB 189	106	16	93	15
Major PCBs	PCB 138	82	8	78	11
	PCB 153	96	5	74	10
	PCB 180	84	11	77	8
Non-ortho PCBs	PCB 77	88	7	87	6
	PCB 81	91	4	84	5
	PCB 126	77	5	74	11
	PCB 169	105	10	101	11
PBDEs	PBDE 28	82	8	87	7
	PBDE47	86	9	93	7
	PBDE 99	97	7	95	5
	PBDE 100	98	8	107	6
	PBDE 153	95	7	95	6
	PBDE 154	95	8	94	5
	PBDE 183	93	6	94	7
HBCD	all isomers	89	12	85	10
PBB	PBB 153	85	9	82	14

Analytes		Level 1		Level 2	
		Rec [%]	RSD [%]	Rec [%]	RSD [%]
EU PAHs	B[a]A	82	2	88	6
	B[a]P	97	6	96	4
	B[b]F	84	4	86	7
	B[c]Fln	76	6	85	2
	B[j]F	85	4	92	4
	B[k]F	85	5	90	4
	B[ghi]P	96	6	94	4
	Chr	89	6	91	6
	CP[cd]P	83	7	89	5
	DB[ah]A	94	6	95	5
	DB[ae]P	85	3	86	2
	DB[ah]P	83	3	86	3
	DB[ai]P	83	4	85	6
	DB[al]P	90	9	92	6
	I[cd]P	95	4	91	6
	5MeChr	79	6	78	6

Parameters of sample preparation procedures within optimisation

- Pressurized liquid extraction (PLE) with different fat sorbents and their combinations (silicagel, florisil, alumina) – suitable for halogenated compounds (PCBs and BFRs), not for PAHs.
- Ethylacetate extraction derived from QuEChERS

- Tested parameters - different amounts of water and extraction solvent both with and without following clean up step
  - different minicolumn setup - sorbent, solvent for conditionation and elution

- Limits of detection (LOD) of optimised sample preparation method were between 0.1 and 0.5 µg/kg fresh weight for PCBs and BFRs and 0.01 and 0.1 µg/kg fresh weight for PAHs.
- The quality control (for selected PCBs and PBDEs) was finally realized on standard reference material SRM 1947 of Lake Michigan Fish tissue provided by NIST (USA).

GC-TOFMS parameters

- Instrument - Agilent 6890N for GC GC with TOFMS detector (Pegasus III, LECO Corp.)
- Column – BPX-50 (30 m x 250 µm i.d. x 0.25 µm), SGE
- PTV – injected volume 1 × 8 µL
- Column flow - 1.3 mL/min (19 min), @ 50 mL/min to 2 mL/min
- Oven temperature program - 80 C (4.3 min), @ 30 C/min to 220 C, @ 2 C/min to 240 C, @ 10 C/min to 360 C (15 min)
- Acquisition rate – 3 spectra/s
- Mass range – 45–700 u

Conclusions

- Simplified sample preparation method for simultaneous determination of PCBs, BFRs and PAHs in fish fillets was optimised. For validation one dimentional GC-TOFMS was emploied.

Future plans

- To optimise two dimensional column setup, mainly with regard to the most difficult groups of PAHs, different column combinations have been already tested.
- Selected columns for the 1st and 2nd dimension of GC×GC system will be used for validation of entaire analytical procedure, including critical assesment of performance parameters in terms of description of work.
- Optimised GC×GC-TOFMS method will be applied for identification and quantification of all target analytes in real fish fillet samples.

References

1 http://www.efsa.europa.eu/EFSA/efsa_locale-1178620753812_1211902012171.htm (13/01/2010)
2 Naert C., van Peteghem C.: Food Additives and Contaminants, 2007, 24, 1018-1025
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