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

Work package WP1a – Persistent Organic Pollutants (POP)

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New simple and fast GC-MS/MS method for the simultaneous analysis of various groups of organohalogen pollutants and polycyclic aromatic hydrocarbons

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Introduction

- Since the number of environmental contaminants which undergo the legislative control or are included in the monitoring programs of the European Food Safety Authority (EFSA) and other international bodies still increases the demand for high throughput, selective, sensitive and non–expensive analytical methods arises as well.
- Gas chromatography coupled to triple quadrupole mass spectrometry (GC–MS/MS) represents a powerful tool for highly sensitive and selective determination of various groups of persistent organic polutants (POPs) as well as for polycyclic aromatic hydrocarbons (PAHs).
- With regards to similarities in physico-chemical properties of these chemicals some steps in various “traditional” analytical methods are almost identical. Nevertheless, until now, any uniform analytical flow-chart encompassing all these target analytes has not been introduced into a routine practice.

Aim of the study

- To implement gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) with triple quadrupole ion analyzer for the simultaneous analysis of several groups of emerging POPs and PAHs in fish tissue.
- To achieve low limits of quantifications (LOQs) to obtain relevant data for exposition studies which require quantification of target contaminants in food even at very low levels.
- To extend the list of target analytes defined in the CONffIDENCE project (includes several PCBs, PBDEs and PAHs) to involve also other emerging contaminants (*e.g.*, methylated analogues of PAHs, organochlorinated pesticides (OCPs) and other BFRs) which are recommended for the monitoring not only by EFSA.

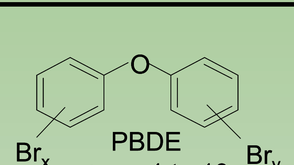
Tested matrices

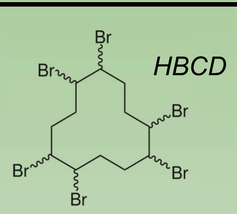
- Fresh fish mussel tissue: Trout *(Salmon trutta)* – 1.6% fat
  Salmon *(Salmon salar)* –13.7% fat

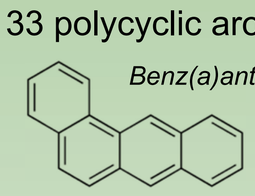
Salmon trutta

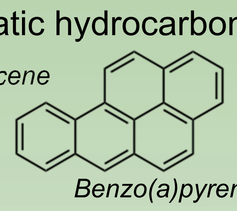
Target analytes

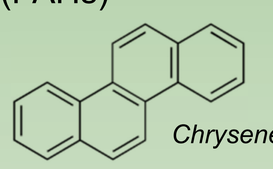
- 18 polychlorinated biphenyls (PCBs)
- 22 organochlorinated pesticides (OCPs)
- 25 brominated flame retardants (BFRs)
- 33 polycyclic aromatic hydrocarbons (PAHs)

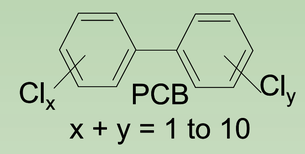








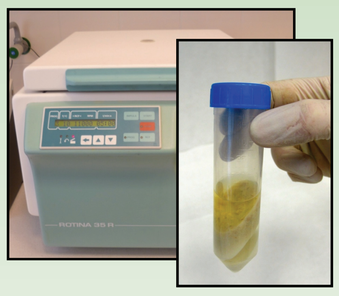




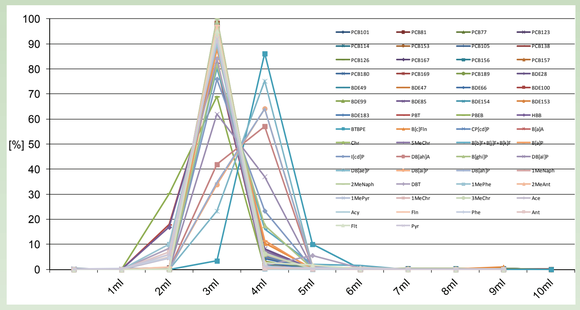
Sample preparation procedure

Extraction
Water & ethyl acetate

Partition
NaCl & $MgSO_4$



Clean-up
Silica minicolumn



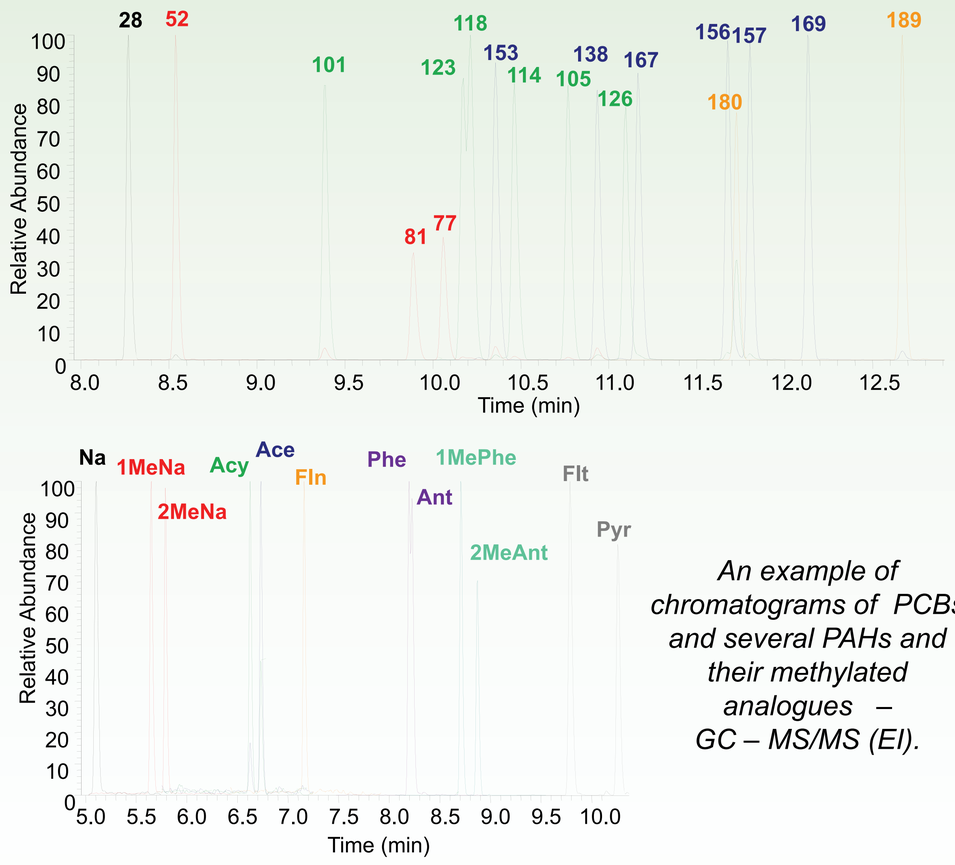
Elution profiles of target analytes

Note: Recoveries of all target analytes after clean-up were higher than 75% except for dieldrine, endrine, β-endosulfane, and endosulfan sulfate which were irreversibly fasten on the silica.

GC-MS/MS analysis

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



PAHs

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

An example of chromatograms of PCBs and several PAHs and their methylated analogues – GC – MS/MS (EI).

- 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 (10min)
- Carrier gas: helium (1.3 mL/min)
- Source temperature: 250°C
- Emission current: 50μA

Thermo Scientific TSQ Quantum XLS triple quadrupole

Table I: Comparison of LOQs achieved using different instrumental techniques. (N/A – not available)

Analytes	Desired LOQ	Achieved LOQ				
	CONffIDENCE	GC-MS/MS (1 μL)	GC-MS (1 μL)	GC-TOFMS (1 μL)	GC-TOFMS (8 μL)	GC×GC-TOFMS (8 μL)
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 PAHs	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
Σdl-PCBs	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 ng TEQ/kg
PBDEs	< 0.2 μg/kg	0.01-0.1 μg/kg	1-5 μg/kg	10-> 10 μg/kg	0.5-10 μg/kg	0.025-5 μg/kg

Conclusions & future plans

- Within this study a sample preparation method previously developed for the determination of PCBs, PBDEs and PAHs in fish tissues was enlarged by other BFRs, OCPs, PAHs and their methylated analogues.
- The irreversible adsorption of dieldrine, endrine, β-endosulfane, and endosulfan sulfate on silica minicolumn was observed.
- GC-MS/MS (EI) was shown to be an effective tool for identification and quantification of all target analytes even at very low levels.
- The LOQs were in the range of 0.005-0.1 μg/kg. The higher values were reached for BDE 183 and some OCPs. The poor sensitivity was also observed in the case of octa-, nona- and decaBDE and decabromodiphenyl ethane for which the CI and shorter GC capillary column (15 m) is recommended.

Acknowledgement

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