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UAE-SPE-UHPLC-UV Method for the Determination of Flame Retardants in Fish Tissues

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Abstract Analytical method for the determination of four flame retardants (FRs) from two groups was proposed. These groups included the brominated flame retardants (BFRs) 3,3′,5,5′-tetrabromobisphenol A (TBBPA) and 1,2,5,6,9,10-hexabromocyclododecane (HBCD); triester organophosphate flame retardants (OPFRs), ethylhexyl diphenyl phosphate (EHDP) and triphenyl phosphate (TPhP). Reversed-phase Ultra HPLC with a UV detector, Hypersil GOLD chromatographic column and two-eluent gradient elution programme was used to obtain the best separations within the shortest possible time. UAE extraction with acetone, ethyl acetate and acetone/ethyl acetate (1:1, *v*/*v*) solvents was proposed. For the removal of fats, addition of sulphuric acid (VI) was conducted as well as solid-phase extraction (SPE) for the final clean-up of the extracts was used. The best recoveries were achieved with acetone/ethyl acetate (1:1, *v*/*v*) mixture of solvents and Bond Elut ENV column for SPE step gave the highest overall recoveries. Method detection limits (MDL) ranged from 0.05 to 0.39 μg g^{-1} and method quantification limits (MQL) ranged from 0.15 to 1.16 μg g^{-1} for all compounds.

Keywords Flame retardants · Fish samples · Ultra HPLC · SPE columns

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Introduction

Flame retardants (FRs) are group of chemicals, which can be added to plastics, wood and other materials in order to reduce their ignition properties. These materials are a part of building components, electronic equipment, aircraft, automobiles and many others. FRs can be differently classified; however, the most common classification is due to the active ingredient. In this classification, the largest group comprises those containing bromine, chlorine, phosphorus, nitrogen and magnesium (Beard 2013). FRs are lipophilic, and their persistence, bioaccumulation and biomagnification can cause harmful effects on humans, animals and plants. The main source of flame retardants in humans is air (inhalation), dust, water, food, and for some person's exposure to the chemicals. More dangerous is exposure to FRs by young children who are less able to detoxification and elimination of environmental pollution from their organisms, which can lead to diseases in adulthood (Kim et al. 2014).

Many of the animals have been subjected to research on the impact of FRs on health. As a result of their exposure to a particular group of compounds many negative effects were observed such as thyroid dysfunction, changes in homeostasis, neurotoxicity, neurobehavioral and reproduction changes (including delayed puberty, reduced pregnancy, changes in menstruation), cancer (including breast cancer) and many others (Kim et al. 2014).

Retardants penetrate to the environment as a result of the release of materials during their use (by thermal desorption, leaching and other), as well as the burning, which causes their release into the air, soil, sewage, sludge, water, and eventually to living organisms such as fish.

As literature survey reveals, in order to analyse fish samples to find FRs, there are few analytical steps that need to be conducted. First of all, fish samples must be collected, then fish tissues are manually extracted and lyophilised and eventually dried with anhydrous sodium sulphate (VI)

Table 1 The best gradient elution programme for Hypersil GOLD column: A—acetonitrile, B—water

Time (min)	Solvent		Flow rate (mL min^{-1})
	A (%)	B (%)	
0.0	45	55	0.3
1.0	85	15	0.3
1.5	100	0	0.5
3.0	100	0	0.5

(Covaci et al. 2009, Ueno et al. 2006, Xia et al. 2011, Xian et al. 2008, Nyholm et al. 2008). After the preliminary preparation, fish tissues were subjected to different extraction procedures. Scientists often used Soxhlet extraction (SE) with different (Covaci et al. 2009, Johnson-Restrepo et al. 2008, Ueno et al. 2006, Xian et al. 2008, Su et al. 2014, Hu et al. 2011, Lankova et al. 2013, He et al. 2013, Zhang et al. 2013, Jeong et al. 2014, Roosens et al. 2008, Roosens et al. 2010, Losada et al. 2009, McHugh et al. 2010). The advantage for this extraction was high recovery values but extraction time was quite long and ranged from 4 to 48 h. Some of the researchers also used classic solvent extraction; nevertheless, recovery values were not always high enough and the consumption of solvents was high (Nyholm et al. 2008, Asante et al. 2013, Kim et al. 2011). Very popular in those kind of matrices was accelerated solvent extraction (ASE, PLE), which can lead to very high recovery values in a short time (Xia et al. 2011, Haukas et al. 2009, Feng et al. 2010, Ilyas et al. 2013, ten Dam et al. 2012, Gao et al. 2014, Sundkvist et al. 2010). Less popular, however, not worse extraction techniques were ultrasound-assisted extraction (UAE) (Remberger et al. 2004), microwave assisted extraction (MAE) (Ma et al. 2013) and matrix solid-phase dispersion (MSPD) (Campone et al. 2010). The research mentioned after the extraction step used mostly gel permeation chromatography (GPC) for the clean-up of the extracts before chromatographic analysis. Some of the scientists used solid-phase extraction (SPE) or saponification in exchange of GPC. For the final analysis, high-performance liquid chromatography (HPLC) or gas chromatography (GC) mostly with mass spectrometry (MS) detection were used.

The aim of this study was the development of an analytical procedure for the extraction and determination of selected FRs. A new and efficient approach regarding sample clean-up was proposed using the UAE extraction with addition of sulphuric acid (VI) and SPE clean-up. For the determination the UHPLC-UV method was proposed. In this paper, we focused on two brominated flame retardants (BFRs) that are widely used and produced in high amounts—(TBBPA) and (HBCD) and two organophosphate flame retardants (OPFRs)—EHDP and TPhP. The selection of OPFRs for this study was justified by the fact that these are quite new compounds that have been of researchers' interest in biological samples (Chen et al. 2012, Kim et al. 2011, Greaves et al. 2016).

Materials and Methods

Chemical and Reagents

Selected flame retardants were bought from Sigma-Aldrich (Poznan, Poland), HPLC grade water and acetonitrile were purchased from Merck (Darmstadt, Germany) and analytical grade acetone, hexane, acetonitrile (ACN), ethyl acetate

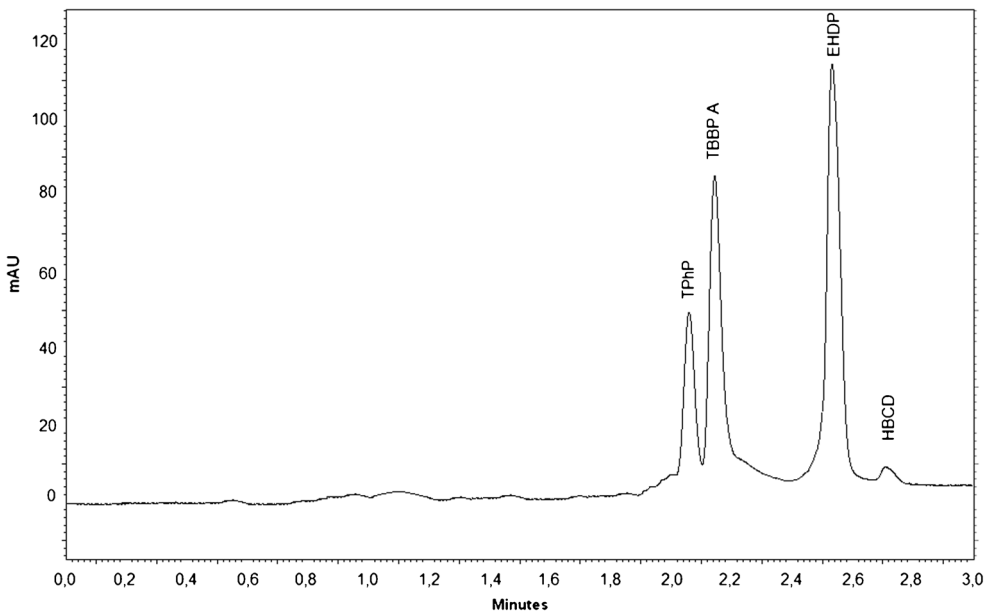

Fig. 1 The chromatogram of standards mixture containing 10 μg mL^{-1} for all FRs performed on the UV detector

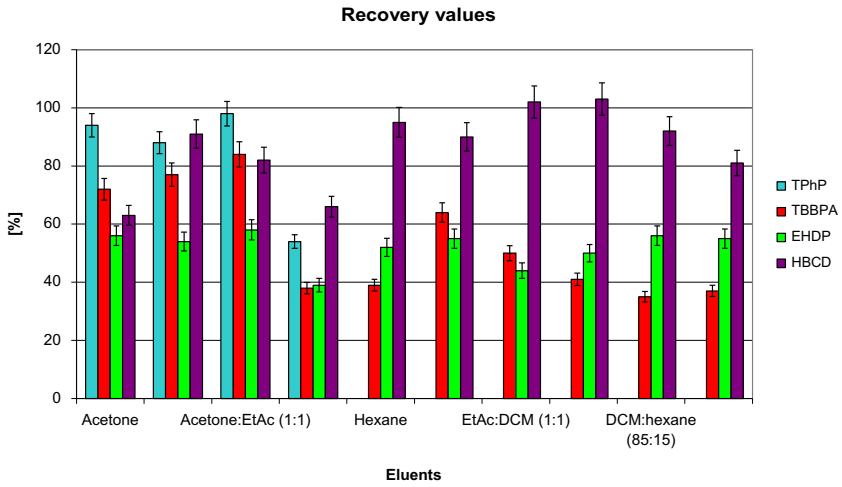

Fig. 2 Recovery values for the UAE extraction followed by addition of sulphuric acid (VI) and SPE clean-up

(EtAc), dichloromethane (DCM) and sulphuric acid (VI) (98%) were acquired from Chempur (Piekary Śląskie, Poland).

Stock solutions (1 mg mL^{-1}) of HBCD, TBBPA and TPhP were prepared by dissolving 10 mg of the appropriate standard in 10 mL of acetonitrile (HPLC grade). The stock solution (1 mg mL^{-1}) of EHDP was prepared by dilution of the appropriate volume of standard (10 mg mL^{-1}) in acetonitrile (HPLC grade) to the final concentration. Stock solutions of all FRs were stable for over 3 months at 4 °C. Working solutions were prepared daily by mixing the appropriate volume of each stock solution with acetonitrile (HPLC grade).

Instrumentation

The Ultra HPLC system included two L-2160U pumps (LaChrom Elite, Merck Hitachi), a L-2350 column oven, a L-2200U autosampler and a L-2400U UV detector (LaChrom Ultra, Merck Hitachi). The data was collected with EZChrom Elite software. An analytical, reversed-phase column Hypersil GOLD™ (50 mm × 2.1 mm, 1.9 μm) from Thermo Fisher Scientific Inc. was used. The UAE extraction was conducted by ultrasound bath from Polsonic (Poznań, Poland) and the frequency of ultrasound was 40 kHz. The SPE was performed using J.T. Baker spe-12G (Deventer, Netherlands).

Chromatographic Separations

The determination of selected flame retardants was performed at temperature of 25 °C using Ultra HPLC equipment and the UV detector. A gradient comprised of two solvents was used, where solvent A was acetonitrile and B was water, both HPLC grade. The solvent gradient was slightly changed from the previous work (Kowalski and Mazur 2014). The column eluent was detected and quantitated at the characteristic detection wavelength for each flame retardant using the UV detector.

UAE Extraction and Clean-Up

For the purpose of this study lyophilised muscle tissues from Herring (*Clupea harengus*, North Sea*)* were received from Gdansk University of Technology. One gram of those samples was spiked with 1 mL of appropriate concentration of standards (2 μg mL^{-1}) and left to dry. In the next step, samples were extracted with different solvents and their mixtures (10 mL): acetone, hexane, EtAc, DCM, acetone:hexane (1:1, *v*/*v*), DCM:hexane (15:85, *v*/*v*), DCM:hexane (85:15, *v*/*v*), EtAc:DCM (1:1, *v*/*v*), acetone:EtAc (1:1, *v*/*v*), acetone:EtAc (20:80, *v*/*v*) at the ambient temperature (ca 22 °C). The UAE extraction was conducted in two steps, each of them lasted 15 min, after that extracts were filtrated. The extracts achieved were then evaporated to dryness under the nitrogen stream at ambient temperature (ca 22 °C), and reconstituted to 1 mL with DCM. Subsequently, 0.5 mL of concentrated sulphuric acid (VI) was added to the samples to remove fats from extracts. The organic layer were then transferred to another bottle, evaporated to dryness under the nitrogen

Table 2 Recoveries for FRs using UAE extraction of three solvents ($n = 3$)

Solvents	Recoveries (%) (% RSD)			
	TPhP	TBBPA	EHDP	HBCD
Acetone	94 (7.6)	72 (6.7)	56 (5.3)	63 (4.2)
EtAc	88 (8.5)	77 (6.1)	54 (6.0)	91 (8.5)
Acetone:EtAc (1:1)	98 (6.6)	84 (7.4)	58 (5.2)	82 (6.8)

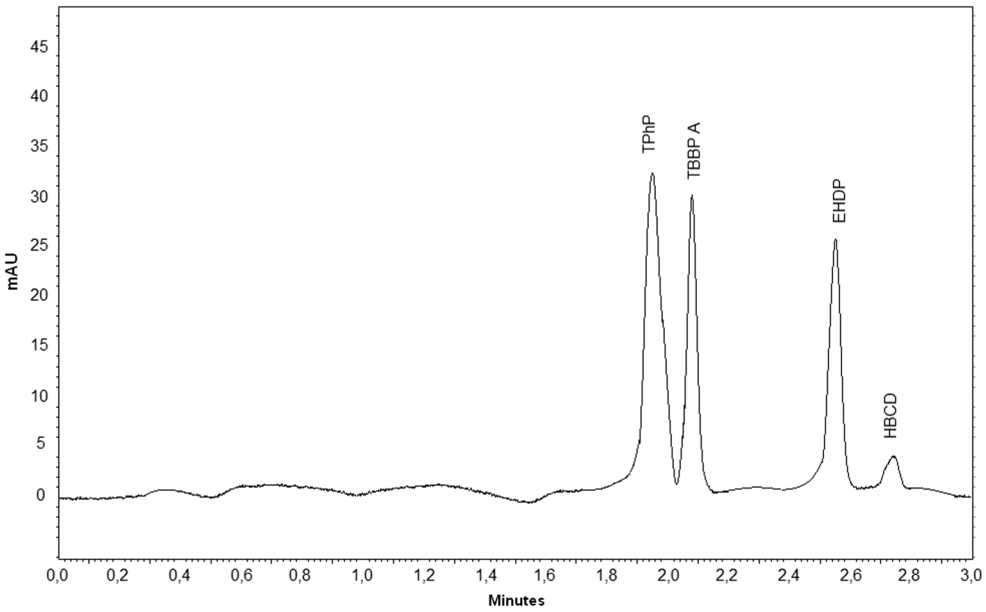

Fig. 3 Chromatogram of fish extract after UAE extraction with acetone:EtAc (1:1) and SPE clean-up

stream, reconstituted in 1 mL of ACN and next 15 mL H_2O was added to each sample before the SPE clean-up step. The extraction procedure was repeated three times for each sample (n = 3).

The SPE procedure was carried out using Bond Elut ENV (6 mL, 500 mg) columns, which were conditioned with 6 mL of EtAc, 6 mL of ACN and 6 mL of H_2O. Afterwards, the sample was passed through the column (1 mL min^{-1}). In the next step, column was dried for 5 min and analytes were extracted with 8 mL of EtAc. The extracts achieved were evaporated to dryness under the nitrogen stream and dissolved in 1 mL of ACN prior to the chromatographic determination.

Results and Discussion

A two-solvent gradient elution programme was used to obtain satisfactory separations for selected flame retardants. The lowest analysis time was achieved using Hypersil GOLD™ (50 mm × 2.1 mm, 1.9 μm) as an analytical column and water and acetonitrile as eluents. The gradient elution programme for the determination of flame retardants is presented in Table 1. The separations of all compounds were satisfactory and the gradient elution programme allows use of a short analysis time (less than 3.0 min) (Fig. 1). For proposed chromatographic system, chromatographic parameters including retention factor (k), resolution (R_s) and selectivity factor (α) were determined—TPhP (k = 1.06), TBBPA (k = 1.25, R_s = 0.71, α = 1.19), EHDP (k = 2.52, R_s = 5.14, α = 2.01) and HBCD (k = 2.91, R_s = 1.42, α = 1.15).

For the UAE extraction, different solvents were tested to obtain the best recoveries for spiked fish samples. Moreover, classic solvent extraction was also tested, however was rejected from further analysis, due to longer time, higher usage of solvents and lower recovery values achieved for each solvent's mixture (TPhP—23–51%, TBBPA—5–60%, EHDP—21–27%, HBCD—58–107%). Within solvents tested for UAE extraction were: acetone, hexane, EtAc, DCM, acetone:hexane (1:1, v/v), DCM:hexane (15:85, v/v), DCM:hexane (85:15, v/v), EtAc:DCM (1:1, v/v), acetone:EtAc (1:1, v/v), acetone:EtAc (20:80, v/v). Different time and volume of solvents were tested in the first attempts. After several adjustments, the best results were obtained when

Table 3 Parameters of calibration curves, linearity ranges and LOD and LOQ values

Analyte	Linear range (g g^{-1})	Slope (a)	S_a	Intercept (b)	S_b	S_{xy}	R^2 (n = 6)	MDL (μg g^{-1})	MQL (μg g^{-1})
TPhP	0.52–20	21,514	2501	−3888	25,059	32,305	0.9610	0.17	0.52
TBBPA	0.15–20	83,353	4401	9141	43,591	55,110	0.9917	0.05	0.15
EHDP	0.12–20	87,112	2922	113,343	35,780	47,774	0.9955	0.04	0.12
HBCD	0.31–50	6903	711	−38,580	21,537	29,334	0.9593	0.10	0.31

the UAE extraction lasted 2 × 15 min and for each sample 2 × 10 mL of appropriate solvent mixture was used. Obtained extracts could not be further processed (even SPE clean-up or UHPLC analysis) without the removal of fats that were in high content in obtained extracts. Several methods were tested and only one gave satisfactory results. Literature survey reveals that most often used technique was saponification. However, with non-polar FRs, this method did not give satisfactory results, since together with fats some of the FRs were also removed from the samples and recovery values achieved were under 20% for all FRs. Another method for removal of lipids that only few references described was the use of concentrated sulphuric acid (VI). Therefore, the second attempt was to use this acid to remove fats from prepared samples. The addition of 0.5 mL of sulphuric acid (VI) to 1 mL of the extract followed by shaking for a few minutes removed fats from organic layer without removing analysed FRs. Therefore, organic layer was taken to the next step of sample preparation. However, the SPE clean-up is not totally necessary, but without this step some matrix effects occur on chromatograms. In order to achieve high recovery values, the organic layer from the extracts was dried under the nitrogen stream and then reconstituted in 1 mL of ACN. Then, 15 mL of distilled water was added in order to conduct the proper SPE clean-up. Two SPE columns were tested: Bond Elut ENV (6 mL, 500 mg) and Oasis HLB (6 mL, 500 mg). Conditioning and elution process were described in material and methods. Higher recovery values were achieved using Bond Elut ENV columns. Recovery values achieved including all analytical steps and different UAE solvents are presented in Fig. 2.

The satisfactory results were achieved for three solvents: acetone, EtAc and acetone:EtAc (1:1, *v*/*v*) using Bond Elut ENV columns (Table 2). However, the highest recoveries were achieved for the mixture of acetone/EtAc (1:1, *v*/*v*) from those tested in this research.

The chromatogram of final extract using whole analytical procedure for the UAE extraction and clean-up is presented in Fig. 3.

Standard curves were determined using linear regression: $y = axe + b$, where: y: peak area, a: slope, x: respective concentration and b: intercept. The parameters of calibration curves obtained were calculated and presented in Table 3. The method detection limit (MDL) and method quantification limit (MQL) values were determined using the parameters of the obtained standard curves for each analyte. The MDL was calculated as MDL = 3.3 s/a, where s is the standard deviation of the blank samples and a is the slope. The MQL value was determined as MQL = 3 MDL. The MDL and MQL values obtained by this method were recalculated including the appropriate recovery level of analyte from fish samples. Therefore, calculated values included all steps introduced to the analytical procedure.

Conclusions

A new, very fast and sensitive method has been developed for the determination of four flame retardants in fish samples using Ultra HPLC equipment and UV detection. All FRs can be determined with good separation and within 3 min using this chromatographic system.

The combination of a fast UHPLC-UV system together with an optimised UAE extraction technique with SPE clean-up procedure was verified as selective, efficient, and precise. All compounds studied can be extracted from lyophilised fish samples with different content of fat that can be removed using sulphuric acid (VI). The extraction method proposed can obtain high recovery values with different combinations of solvents acetone, EtAc and acetone:EtAc (1:1, *v*/*v*); however, the best recoveries were achieved using mixture of acetone/EtAc (1:1, *v*/*v*). For the SPE extraction, Bond Elut ENV columns have been proposed as they achieved the highest recovery values. Low values of MDL and MQL, as well as wide linear range of the developed method are satisfactory for the determination of FRs. Therefore, this method with optimised extraction procedure can be used for the analysis of different fish samples.

To conclude, the optimised UAE extraction with SPE clean-up procedure and the Ultra HPLC method for determination of the selected FRs have been successfully applied to the analysis of fish samples.

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Compliance with Ethical Standards

Conflict of Interest Bartosz Kowalski declares that he has no conflict of interest. Magdalena Płaszczyk declares that she has no conflict of interest.

Ethical Approval All applicable international, national, and/or institutional guidelines for the care and use of animals were followed.

Informed Consent This article does not contain any studies with human subjects.

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