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# Comparison of in-cell lipid removal efficiency of adsorbent mixtures for extraction of polybrominated diphenyl ethers in fish

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) have become ubiquitous environmental contaminants due to their incorporation into many consumer products. Their ability to bioaccumulate to alarming levels in fat-rich matrices such as fish demands fast and efficient methods to monitor these contaminants. We present an analytical method for selective-pressurised liquid extraction (S-PLE) of PBDEs from fish tissue. Fat removal performance of different mixtures of Florisil, silica gel and sulphuric acid-impregnated silica gel were evaluated using a response surface experimental design approach for determining the optimal fat-retaining mixture for S-PLE. Acid-silica gel had the greatest individual effect on fat retention; with a two-thirds acid-silica one-third Florisil mixture found to be the most efficient (>97%). Method validation was performed using recovery experiments at three spiked concentration levels (0.05, 0.5 and 5 ng $g^{-1}$ ww). Mean recoveries of target analytes in spiked samples ranged from 70 to 124%, with relative standard deviations <27%. The S-PLE lipid removal efficiency combined with the sensitivity of triple quadrupole mass spectrometers provides a fast and comparatively inexpensive analytical method for analysis of PBDEs in fish samples.

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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame-retardant (BFR) compounds used to reduce flammability of products. PBDEs are found in a wide array of consumer products from building materials, textiles, paints and varnishes, to plastics, electronic circuitry and housing, and polyurethane foams such as those used in furniture [1–3]. While PBDEs can enter the environment during the manufacturing processes, PBDEs are additives that are not chemically bound in materials and therefore they are also able to enter the environment via leaching and volatilisation from the products [2–9]. PBDEs are now ubiquitous environmental contaminants that can bioaccumulate through the food chain to potentially harmful levels [10,11]. Increasingly higher levels of PBDEs are found in edible fish and have been identified as a significant source of human exposure [12–17]. Thus, there is growing demand for fast, sensitive and cost-effective analytical methods to monitor these pollutants in fishery and environmental samples.

The most commonly used extraction techniques for analysis of persistent organic pollutants (POPs), such as PBDEs, in solid environmental matrices include Soxhlet, matrix solid-phase dispersion, microwave-assisted extraction, supercritical fluid extraction and pressurised liquid extraction (PLE) [18]. PLE utilises elevated pressure to maintain an extracting solvent in a liquid state at temperatures above its boiling point, significantly reducing extraction time and solvent consumption [18,19]. Following extraction environmental samples often require further sample clean-up steps to remove co-extracted interfering compounds and in the case of fish samples a major interference is co-extracted fats and oils (lipids) [19–21]. The most commonly used methods of non-destructive removal of fat from fish sample extracts are GPC and column chromatography using silica gel, Florisil or alumina with varying degrees of activation [20,21].

Recently, methods have been developed that combine sample clean-up during PLE [22–29]. The methods utilise a layer of adsorbents placed beneath the sample in extraction cells, which retain interfering compounds as the solvent extract passes through them. The technique is referred to as in-cell clean-up, on-line clean-up or more commonly, selective-PLE (S-PLE) [24]. In regard to biological samples, S-PLE utilises a layer of fat-removal (FR) adsorbents such as Florisil, alumina (basic, acidic or neutral), silica gel and sulphuric acid-silica gel [23–30]. PBDEs are resistant to acids and the use of sulphuric acid as a destructive method of lipid removal technique is simple but can cause emulsion problems and is time-consuming [19]. Sulphuric acid maybe added to activated silica gel, usually at

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40% weight per weight (w/w) for destructive fat removal is often used in combination with neutral, and sometimes alkaline, adsorbents (silica gel, alumina or Florisil) in order to increase purification efficiency [19,21,31,32].

The removal capacity of the adsorbent(s) being used allows for an optimal fat to fat-remover ratio (FFR) to be used which helps achieve both minimal fat elution and analyte loss [24,30]. S-PLE has been shown to result in very good recoveries and reproducibility measuring PBDEs in fish samples [24–26,28,33], with the best performing fat-removal adsorbents seeming to be Florisil® [24,26] and mixtures of silica gel and sulphuric acid-impregnated silica gel [33].

Performance comparison between individual fat retainers in S-PLE has been studied [30] and different fat retainer mixtures have been shown to result in efficient fat removal and analyte recoveries [25,33]. However, it appears, to the best of our knowledge, that no study has been undertaken aimed at comparing the performance of different fat-removal mixtures in S-PLE. Thus, the objective of the current study was to compare the performance of different mixtures of three of the best performing FRs (Florisil, silica gel and acid-impregnated silica gel) and develop an S-PLE method for trace analysis of PBDEs of primary interest in fish.

## 2. Materials and Methods

### 2.1. Chemicals, Standards and Materials

All glassware, unless volumetric or otherwise stated, was washed with AR grade acetone (Chem-Supply) and baked at 450 °C for ≥12 h. A standard solution of target PBDEs (BDE-CSM, Congeners of Primary Interest) containing BDE-28, -47, -99, -100, -153, -154 and -183 at 20 μg mL$^{-1}$ and BDE-209 at 200 μg mL$^{-1}$ in 8:2 isooctane:toluene (AccuStandard, USA) was used for spiking and calibration. Internal standards (ISTDs) were BDE-37 and BDE-77 at 50 μg mL$^{-1}$ in isooctane (AccuStandard) and 25 μg mL$^{-1}$ $^{13}$C-labelled BDE-209 in toluene (Wellington Laboratories). Certified analyte concentrations in all standards were provided by respective manufacturers. Florisil (60–100 mesh; Grace Davison Discovery Sciences) and silica gel (40–63 μm; Acros Organics) were activated before use by heating for 12 h at 450 and 200 °C, respectively. 40% (w/w) acid-silica gel was prepared by slowly adding an appropriate amount of sulphuric acid (Castle Hill) to cooled activated silica gel.

### 2.2. Sample Collection and Preparation

The fry of sandy sprat (*Hyperlophus vittatus*) used for method development were 5–8 cm long and weighed approximately 1.2–1.5 g wet weight (ww). 1 g of fish sample (lyophilised, freeze-dried) was pulverised to fine powder with the addition of 3 g acid-washed sand, 1 g Hydromatrix (diatomaceous earth, Agilent) and 2 g activated silica gel (40–63 μm, Davison Discovery Sci.) in a Rocklabs® bench top ring mill.

### 2.3. Pressurised Liquid Extraction (PLE)

PLE was performed on a Dionex ASE 200 Accelerated Solvent Extraction (ASE) system using published conditions [24,34]. Polar modifiers are required to adequately extract PBDEs, increasing the fat removing capacity of adsorbents decreases [24]. Equal portion hexane:DCM mixtures have been shown to perform well in S-PLE of fat-rich sample matrices [25,28,35]. ASE 200 conditions were 100 °C, 1500 psi, 5 min static time with three static cycles, flush volume of 60%, and 120 s purge time. All cells were prepared from the bottom: a cellulose filter (Thermo Fischer Scientific), 9 or 10 g layer of adsorbent(s), a cellulose filter (second), pulverised sample mixture, hydromatrix (diatomaceous earth, Agilent) before another cellulose filter (third).

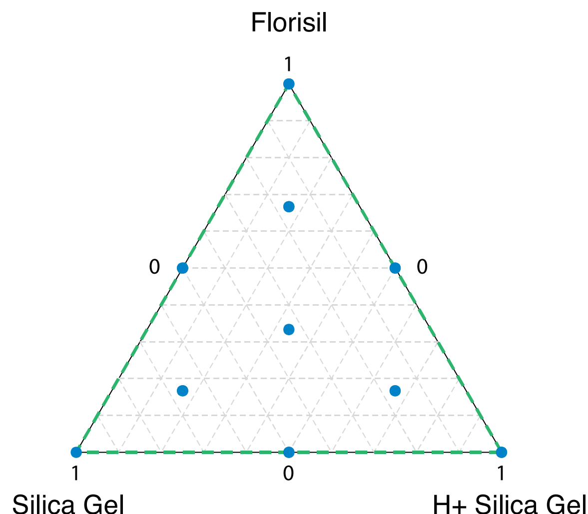


**Fig. 1.** Augmented simplex centroid design plot. Blue dots represent component proportions.

### 2.4. Extractable Lipid Determination

Extractable lipid content was determined gravimetrically after PLE in the absence of in-cell adsorbents. Three replicate weighed samples were loaded into 22 mL PLE cells above a single cellulose filter and approximately 4 cm of Hydromatrix. Extracts were evaporated to dryness at 40 °C (Biotage® Turbovap® LV evaporator) under gentle $N_2$ stream, placed in an oven at 90 °C for 4 h before measuring the lipid mass. The mean mass per gram was used to determine appropriate adsorbent mass required for S-PLE using an FFR of 0.0078 [24].

### 2.5. Selection of Best Adsorbent Mixture for S-PLE

A response surface experimental design approach was utilised to assess the relationship between extracted lipids and FR adsorbent composition (milligramme lipids extracted per gram dw of fish sample). Three FR adsorbents selected for performance assessment were Florisil, silica gel and 40% acid-silica gel. The mixture design for the experiment was set up using Minitab®17 statistical software. A three-component augmented simplex centroid design comprising 10 points and zero process variables was tested in duplicate and randomised order (Fig. 1). Experimental results were analysed using Minitab® 17 statistical software for which main effects and contour plots of response.

### 2.6. Method Validation

Method validation was performed via evaluation of recovery and precision of fish samples spiked at three concentration levels using optimised S-PLE adsorbent mixture. 1 g dw (5 g ww) composite fish samples were spiked in triplicate with 0.25, 2.5 and 25 ng of each target PBDE (2.5, 25 and 250 ng for BDE-209). The spiking levels used represent fish tissue concentration levels of 0.05, 0.5 and 5 ng g$^{-1}$ ww (0.5, 5 and 50 ng g$^{-1}$ ww for BDE-209). Method blanks and matrix blanks, containing 1 g dw whitebait, were also prepared in triplicate and analysed alongside spike samples. Method blanks were used to evaluate the overall preparation

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