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Determination of polybrominated diphenyl ethers and polychlorinated biphenyls in fishery and aquaculture products using sequential solid phase extraction and large volume injection gas chromatography/tandem mass spectrometry

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ABSTRACT

A new method was developed to determine polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in fishery and aquaculture products. Samples were extracted by an accelerated solvent extraction system and cleaned up by sequential solid phase extraction (SPE) including dispersive SPE (D-SPE) and tandem SPE. PBDEs and PCBs were analyzed by a large-volume injection gas chromatography triple quadrupole mass spectrometry (LVI-GC–QqQ-MS/MS). Good linearity ($R^2 \geq 0.9958$) was achieved. Method detection limits (MDLs) were 0.16–3.3 pg g^{-1} (wet weight, ww) for PBDEs and 0.13–0.97 pg g^{-1} ww for PCBs. Mean recoveries were 60–140% with relative standard deviations (RSDs) of less than 20% in weever fish, scallop and shrimp samples spiked at a lower level of 13–31 pg g^{-1} ww and a higher level of 50–125 pg g^{-1} ww. Certified reference materials were analyzed with acceptable results. The method reduced solvent consumption, analytical time and labor, and is suitable for the routine analysis of PBDEs and PCBs in fishery and aquaculture products.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants in the environment, and tend to be bioaccumulated within each organism and then biomagnified to much higher levels through the food chain. Human is exposed to these pollutants through inhalation, ingestion, and dermal absorption [1,2]. Consumption of edible fishery and aquaculture products is associated with elevated body burden of PBDEs and PCBs in general population [3,4]. PBDEs and PCBs can cause a range of adverse effects upon human health [1,5–7]. Greater awareness and concerns are rapidly growing about the levels of PBDEs and PCBs in edible fish and other aquaculture species. A sensitive, rapid and cost-effective method is required to monitor these pollutants in these species. Usually, biological tissue samples are extensively processed to eliminate large amounts of lipids and other interferences, so that trace levels of PBDEs and PCBs could be measured in a highly reduced volume. Sample preparation requires several steps, including extraction, cleanup and concentration. The extraction techniques were used such as matrix solid phase dispersion (MSPD) extraction [8,9], Soxhlet extraction [10,11], accelerated solvent extraction (ASE) [10–13] and microwave assisted extraction (MAE) [10]. ASE is more solvent-, time- and labor-saving and has been used more widely than other techniques [10–13]. The extracts were subsequently cleaned up through multiple chromatographic columns with silica, acid silica, florisil and alumina as adsorbents [9,10,12,14,15]. On the basis of column chromatography techniques, fluid management system (FMS) was developed to automatize sample cleanup [12,15]. However, large amounts of solvents were still used to quantitatively recover the target analytes, and limits of quantitation were higher [12,15]. In our lab, cross-contamination was observed in a FMS system, and extra solvents were used to wash the system whenever one sample was processed. In view of the convenience of solid phase extraction (SPE) cartridges (C18 or Oasis® HLB as reverse phase absorbents) to extract PBDEs and PCBs in serum [16,17] and milk samples [14,18], we become interested in using acid silica and basic alumina as normal phase absorbents for dispersive SPE (D-SPE) and/or SPE cartridge preparation to clean up extracts of biological tissue samples.

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Gas chromatography-electron capture detector and gas chromatography–mass selective detector (GC–MSD) in EI mode were used to analyze PBDEs and PCBs with inadequate sensitivity and selectivity [8]. GC–MSD in NCI mode could more sensitively quantify PBDE congeners by monitoring characteristic ions (m/z, 79 and 81) of Br^-, but some of PBDE congeners could not be resolved from other coeluted brominated compounds [14]. Gas chromatography–high resolution mass spectrometry (GC–HRMS) in EI mode is highly sensitive and selective for the analysis of PBDEs and PCBs. However, operation and maintenance are more expensive [19,20]. Gas chromatography–tandem mass spectrometry (GC–MS/MS) could determine PBDEs and PCBs with sensitivity, accuracy and selectivity comparable to GC–HRMS [1,9,14,15]. GC–MS/MS can be performed by both quadrupole ion trap (QIT) and triple quadrupole (QqQ-MS/MS) techniques. GC–QIT has been widely used for studying PBDEs and/or PCBs in adipose tissues, filet and earthworms [9,11,12,15]. GC–QqQ-MS/MS offers a wide dynamic linear range as well as indiscriminate ion detection [8], and is one of the most selective, sensitive and robust techniques for the analysis of PBDEs [21,22]. GC–QqQ-MS/MS was used for the determination of PBDEs and/or PCBs in fish [9], eggs [8] and human breast milk [14,21]. Large-volume GC injection (LVI) with programmable temperature vaporization could decrease detection limits, especially for highly brominated compounds [23].

This study was aimed to develop a new sample preparation method by using D-SPE and lab-made tandem SPE cartridges. The method was used to process fish, shell and shrimp samples for simultaneously analyzing 39 PBDE and 51 PCB congeners by an optimized LVI-GC–QqQ-MS/MS system.

2. Experimental

2.1. Chemicals and materials

Native standard solutions of PBDEs (BDE-AAP-A-15X) and PCBs (C-WNN, and C-WCFS) were from AccuStandard, Inc. (New Heaven, USA). BDE-AAP-A-15X contained 3 mono-BDE congeners (BDE-1, 2 and 3, 1.5 $\mu g\,ml^{-1}$ for each), 7 di-BDE congeners (BDE-7, 8, 10, 11, 12, 13 and 15, 1.5 $\mu g\,ml^{-1}$ for each), 8 tri-BDE congeners (BDE-17, 25, 28, 30, 32 33, 35 and 37, 1.5 $\mu g\,ml^{-1}$ for each), 6 tetra-BDE congeners (BDE-47, 49, 66, 71, 75 and 77, 1.5 $\mu g\,ml^{-1}$ for each), 7 penta-BDE congeners (BDE-85, 99, 100, 116, 118, 119 and 126, 2.25 $\mu g\,ml^{-1}$ for each), 5 hexa-BDE congeners (BDE-138, 153, 154, 155 and 166, 3.0 $\mu g\,ml^{-1}$ for each) and 3 hepta-BDE congeners (BDE-181, 183 and 190, 3.75 $\mu g\,ml^{-1}$ for each). C-WNN contained CB-8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209 at a level of 10 $\mu g\,ml^{-1}$ for each. C-WCFS contained CB-31, 33, 49, 56, 60, 70, 87, 95, 97, 99, 110, 132, 141, 149, 151, 156, 158, 174, 177, 194, 201, 203, 183 and 74 at a level of 25 $\mu g\,ml^{-1}$ for each. EC-5379-1/10X-EN-1948-4 (CB-28L, 52L, 101L, 138L, 153L and 180L, ≥99.0%, 0.1 $\mu g\,ml^{-1}$ in nonane for each) and EC-1410 (CB-209L, ≥99.0%, 40 $\mu g\,ml^{-1}$ in nonane) were from Cambridge Isotope Laboratories, Inc. (Andover, USA). EO-4999 (BDE-3L, ≥99.0%, 50 $\mu g\,ml^{-1}$ in nonane), EO-5001 (BDE-15L, ≥99.0%, 50 $\mu g\,ml^{-1}$ in nonane), and EO-5277 (BDE-28L, 47L, 99L, 100L, 153L, 154L, 183L and 209L, ≥99.0%, 1 $\mu g\,ml^{-1}$ in nonane for each) were also from Cambridge Isotope Laboratories, Inc. (Andover, USA). CB-198 (10 $\mu g\,ml^{-1}$) was purchased as an injection internal standard from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Freeze-dried fish tissue (WMF-01) for organic contaminant analysis was purchased from Wellington Laboratories Inc. (Ontario, Canada) as certified reference materials (CRM). Hexane and dichloromethane (Optima® grade) were from Fisher Scientific (New Jersey, USA). Silica gel (0.063–0.100 mm, 100–200 mesh) was from Merck (Darmstadt, Germany). Nonane (anhydrous, ≥99.0%), basic alumina (150 mesh) and anhydrous sodium sulphate (≥99.0%) were from Sigma Aldrich (Steinheim, Germany).

2.2. Preparation of standard solutions

Three sets of calibration standard solutions (CSS-BDE, CSS-C-WNN and CSS-C-WCFS) were prepared in a mixture of nonane and hexane (1:4, v/v). Concentrations of CSS-BDE were in a range of 0.5–100 $ng\,ml^{-1}$ for mono- to tetra-BDE congeners, 0.75–150 $ng\,ml^{-1}$ for penta-BDE congeners, 1–200 $ng\,ml^{-1}$ for hexa-BDE congeners, and 1.25–250 $ng\,ml^{-1}$ for hepta-BDE congeners. In each level of CSS-BDE, $^{13}C_{12}$-labeled PBDEs were 10 $ng\,ml^{-1}$ for each congener and CB-198 was 5 $ng\,ml^{-1}$. Concentrations of CSS-C-WNN and CSS-C-WCFs were in a range 0.1–100 $ng\,ml^{-1}$. In each calibration level, $^{13}C_{12}$-labeled PCB congeners were at a level of 5 $ng\,ml^{-1}$ for each congener and CB-198 was 5 $ng\,ml^{-1}$. BDE-AAP-A-15X, C-WNN and C-WCFS were diluted in nonane as matrix spiking solutions at levels of 5 $ng\,ml^{-1}$ for each PCB congeners and 5–12.5 $ng\,ml^{-1}$ for PBDEs. The $^{13}C_{12}$-labeled standard solutions were diluted in nonane as internal standards at levels of 5 $ng\,ml^{-1}$ for PCBs and 10 $ng\,ml^{-1}$ for PBDEs. CB-198 (10 $\mu g\,ml^{-1}$) was diluted in a mixture of nonane and hexane (1:4, v/v) to a level of 5 $ng\,ml^{-1}$ as injection internal standard. After preparation, all standard solutions were stored at 4 °C.

2.3. Preparation of SPE cartridges

Silica gel, basic alumina and anhydrous sodium sulfate were rinsed with dichloromethane (20 ml per gram). Silica gel was activated at 180 °C for 1 h, and basic alumina was at 600 °C for 24 h. Anhydrous sodium sulfate was baked at 400 °C for 1 h. One hundred grams of activated silica gel were thoroughly mixed with 78.6 g concentrated sulfuric acid to produce 44% acid silica gel. Five grams of acid silica gel were packed into a 12 ml SPE cartridge and topped with 1 g granular anhydrous sodium sulfate, and two layers were separated by a polypropylene frit. Similarly, 5 g of activated basic alumina, a polypropylene frit and 1 g anhydrous sodium sulfate were used to prepare the alumina SPE cartridge. After preparation, all SPE cartridges were immediately vacuum packaged for use within three months.

2.4. Sample collection and preparation

All fish and fishery products were purchased from local supermarkets. After shipped to the lab, all samples were stored at −25 °C until chemical analysis. Weever, freshwater shrimp and scallop were used as representative matrices to prepare quality control materials.

Sample preparation is described in Figure S1 (Supplementary materials). The edible parts of the samples were homogenized with an IKA T-18 Basic Ultra Turrax Homogenizer (IKA®-Werke GmbH & Co. KG Staufen, Germany). Ten grams of homogenized samples were lyophilized in a freeze dryer (Christ Gamma 1-16/2-16, Osterode am Harz, Germany) at −52 °C and 0.03 mbar for 24 h.

For recovery measurement, the representative matrices (10 g ww) were freeze dried and spiked with 25 μl (a lower level) or 100 μl (a higher level) of matrix spiking solutions, and 20 μl of internal standards. The real samples were freeze dried and each spiked with 20 μl of internal standards. After spiking, the samples were blended with 2.0 g hydromatrix (Agilent, Santa Clara, USA), and transferred into a 22 ml ASE extraction cell. The extraction was completed in an ASE 200 system (DIONEX, Sunnyvale, USA). Hexane and dichloromethane (1:1, v/v) were used as extraction solvents, temperature was set at 100 °C, pressure at 1500 psi, flush volume at 100% of extraction cell volume, heating time at 6 min,