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QuEChERS extraction for multi-residue analysis of PCBs, PAHs, PBDEs and PCDD/Fs in biological samples

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ABSTRACT

In this study, a fast and rugged method is presented for the analysis of PCBs, PAHs, PBDEs and PCDD/Fs in biological tissues using a simple Quick, Easy, Cheap, Efficient, Rugged and Safe (*QuEChERS*) extraction and a clean-up by Gel Permeation Chromatography (GPC) and silica Solid Phase Extraction (SPE). Development was performed on blue mussels (*Mytilus edulis*) and Atlantic salmon (*Salmo salar*) for evaluation of two ranges of lipid and water content of biological tissues. Statistical validation was performed with Atlantic salmon samples. Forty-five PAHs were analyzed including the priority list of the US EPA and the European Union with 41 PCBs, 24 PBDEs and 17 PCDD/Fs. Instrumental analyses were performed on Gas Chromatography – High Resolution Mass Spectrometry (GC-HRMS). Accuracy was evaluated for PCBs and PCDD/Fs with a certified reference material furnished by the National Research Council Canada (NRCC) and also compared with results obtained by the conventional Soxhlet extraction. Statistical validation showed recoveries for PCBs, PAHs, PBDEs and PCDD/Fs close to 100% with average Relative Standard Deviation (RSD) lower than 10% and internal standard recoveries in the range of 70% with average RSD ranging from 5–15%. Average calculated Method Detection Limits (MDLs) were lower than 0.05 µg/Kg for PCBs, 0.2 µg/Kg for PAHs and PBDEs and 1 ng/Kg for PCDD/Fs. The method is a faster and cheaper alternative to the time-consuming conventional method that has been used in most environmental laboratories.

1. Introduction

Persistent organic pollutants (POPs) represent a vast category of heterogeneous organic compounds that have been released in the environment, by human activities, and considered as priority pollutants for governmental and regulatory agencies [1]. POPs include organic compounds such as polychlorinated biphenyls (PCBs) [2], polybrominated diphenyl ethers (PBDEs), and the very toxic polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) [3,4]. These pollutants are known to be persistent in the environment and susceptible to be bioaccumulated and bioamplified in the food web [5].

PCBs and PBDEs were produced commercially as synthetic industrial mixtures with different halogenated content in North America [6]. PCBs were mostly used as dielectric fluid in transformers and capacitors, as plasticizers and as fire resistant liquids [7]. PBDEs were used as flame retardant in polymers, textiles, and electronic components [6,8]. PCDD/Fs are undesired by-products issued from waste incineration, from the fabrication of chlorinated organic compounds or from paper bleaching plants [4,9]. Although not considered as POP, polycyclic aromatic hydrocarbons (PAHs) can also be relevant to monitor as that are found in oil and petroleum and can also be released in any incomplete combustion process such as car emission, coil plant, incineration or forest fires [10]. The biomonitoring of PAHs is of particular interest for environmental application to follow industrial and domestic processes using combustion or for oil and petroleum hydrocarbons spill.

Most methods conventionally used to analyze these compounds are time-consuming, require high quantities of toxic chemicals and solvents (toluene, methylene chloride, hexanes, sulfuric acid, silver nitrate and sodium hydroxide) and are expensive. Due to the exceptionally high sensitivity needed for monitoring of PCDD/Fs at trace level, analytical methodologies for PCDD/Fs have been standardized and remained unchanged. However, some new analytical strategies have been proposed in the last few years. For example, the development of a

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faster, cheaper, and more ecofriendly strategy for the sample preparation is of great interest. Also, softer extraction conditions have allowed the detection of PAHs together with the POPs. Moreover, PAHs were too sensitive to resist to the acid clean up used in the conventional preparation method [11].

In 2007 and 2008, reviews summarizing the conventional and the new approaches were published [4,12]. The most commonly used extraction was still the conventional Soxhlet method [4] although time and solvent consuming. Of the other methods, sonication-assisted extraction has been also approved by the US EPA as an alternative extraction method (Method 3550B) [13]. This method is simple but requires the same quantity of solvent than Soxhlet extraction. It has been used for the analysis of PAHs in mussels [14]. Among the newest technologies, Microwave–assisted extraction (MAE) [15], Pressurized liquid extraction (PLE) also labelled ASE by Dionex, and superfluid extraction (SFE) were proposed. MAE [16–18] and PLE [19–22] have been previously adapted for analysis of PCBs, PBDEs, and PCDD/Fs in biota and sediment matrix. All these new extraction strategies allowed faster analysis for POPs and PAHs with less solvent but need costly specialized instrumentations. Also, these techniques require to dry the samples before extraction using drying salt (such as sodium sulphate) [23], ambient drying [24], or freeze-drying [14].

Kalachova and collaborators [11] proposed the use of *QuEChERS* to extract fish and shrimp samples. *QuEChERS,* which stands for Quick, Easy, Cheap, Efficient, Rugged and Safe, was developed and introduced by Anastassiades and collaborators [25] for pesticide analysis in fruits and vegetables with high water content. Exceptionally simple, fast and cheap, this extraction strategy was rapidly extended to other compounds such as quinolones, sulfanilamides, amphenicols [26,27], mycotoxins [28], carbaryl [29], organochlorine pesticides [30], steroids, veterinary and humans drugs [31], and antibiotics [32]. This extraction technique was used for liquid-solid extraction with different matrix such as salmon [33], sediment and fish muscles [34], and soil [31]. *QuEChERS* require no investment, use only small volumes of solvent and is very simple to perform. Also, samples can be extracted without drying process. Higher throughput can be achieved, which is of significant importance when managing an environmental emergency, particularly in aquatic ecosystems due to the high dispersion potency in the hydrologic system.

This paper presents a *QuEChERS* extraction method for the analyses of PCBs, PAHs, PBDEs and PCDD/Fs. The method includes 17 PCDD/Fs, 41 PCBs, 45 PAHs and 24 PBDEs and has been tested for salmon and mussel samples. Clean-up was performed by automated GPC followed by silica SPE for PCBs, PAHs and PBDEs. Dioxins and furans were further purified on alumina oxide column. This approach reduces the matrix effect normally observed in these types of samples while improving recoveries, and detection limits and respect the criteria of the European Commission No 333/2007 indicating that method should respect LOQ < 0.9 μg/kg and recoveries ranging 50–120% for benzo(a)pyrene.

2. Materials and methods

2.1. Standards

Three groups of certified standards, 24 PBDEs, 41 PCBs and 44 PAHs, were used.

Individual PBDEs congeners – 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209 (purity > 98%) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Labelled injection ^{13}C-PBDE standards (77, 99, 154 and 207) and ^{13}C-PBDE surrogates (28, 47, 100, 153, 183 and 209) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Calibration curve were prepared in toluene, stored in the freezer (T=−20 ± 5 °C), and as follow for PBDEs: 0.5; 5.0; 25.0; 100.0 ng/mL.

Individual PCBs congeners – 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208, and 209 (all with declared purity > 98%) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Labelled injection ^{13}C-PCB standards (47, 101, 170 and 209) and ^{13}C-PCB surrogates (28, 52, 111, 153, 178, 194 and 208) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Calibration curve were prepared in isooctane, stored in the freezer (T=−20 ± 5 °C), and as follow for PCBs: 0.25; 1.0; 10.0; 50.0 and 200.0 ng/mL.

The certified standards of individual PAHs: naphtalene, 2-methylnaphtalene, 1-methylnaphtalene, 2-chloronaphtalene, 1-chloronaphtalene, 1,3-dimethylnaphtalene, acenaphtylene, acenaphtene, 2,3,5-trimethylnaphtalene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, 2-methylfluoranthene, benzo(c)phenanthrene, benzo(a)antracene, 3-methylchrysene, 2-methylchrysene, 6-methylchrysene, 5-methylchrysene, 4-methylchrysene, 1-methylchrysene, 1-nitropyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j) fluoranthene, 7,12-dimethylbenz(a)anthracene, benzo(e)pyrene, benzo(a)pyrene, perylene, 3-methylcholanthrene, dibenzo(a,j)anthracene, indeno(1,2,3-cd)pyrene, dibenzo(a,c)anthracene, dibenzo(a,h)anthracene, benzo(g,*h*, i)perylene, anthanthrene, dibenzo(a,e)fluoranthene, dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a, i)pyrene, and dibenzo(a,h)pyrene (purity > 98%) were supplied by Accustandard (ChromSpec, Ontario, Canada). Labelled injection PAHs standards (D_8- acenaphtylene, D_{10}-phenanthrene, D_{10}-fluoranthene, D_{12}-benzo(a)anthracene, D_{12}-benzo(e)pyrene, and D_{12}-benzo(g,*h*, i)perylene) and deuterated and ^{13}C-PAHs surrogates (D_{10}–2-methylnaphtalene, D_{10}-acenapthene, $^{13}C_6$-anthracene, D_{10}-pyrene, D_{12}-chrysene, $^{13}C_4$-benzo(a)pyrene, and D_{10}-dibenz(a,h)anthracene) were supplied by Accustandard (New Haven, USA). Calibration curve were prepared in isooctane, stored in the freezer (T=−20 ° ± 5 C), and as follow for PAHs: 1.0; 5.0; 10.0; 50.0; 100.0 and 150.0 ng/mL.

Individual PCDD/Fs congeners – 2,3,7,8-TCDF; 1,2,3,7,8-PeCDF; 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; OCDF; 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD, and OCDD (purity > 98%) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Labelled injection ^{13}C-PCDD/Fs standards (1,2,3,4-TCDD; 2,3,4,7,8-PeCDF; 1,2,3,7,8,9-HxCDD, and 1,2,3,4,7,8,9-HpCDF) and ^{13}C-PCDD/Fs surrogates (2,3,7,8-TCDF; 1,2,3,7,8-PeCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDF; 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD, and OCDD) were supplied by Wellington Laboratories (Guelph, Ontario, Canada). Calibration curve were prepared in isooctane, stored in the freezer (T=−20 ± 5 °C), and as follow for PCDD/Fs: 0.25; 1.0; 5.0 and 25.0 ng/mL.

The certified reference material (CRM) CARP-2 was supplied by the National Research Council Canada (NRCC) (Ottawa, Ontario, Canada), was stored at 4 ± 2 °C, and contains PCBs, organochlorine pesticides, and PCDD/Fs.

2.2. Chemicals, reagents and other material

n-Hexanes, methylene chloride, and isooctane were pesticide grade and supplied by Fisher Scientific. Ethyl acetate was HPLC/residue analysis grade and supplied by EMD. Silica (particle size 100–200) supplied by Selecto Scientific Inc. was dried at 110 °C overnight and deactivated by adding 2% of deionized water, shaking overnight, and finally stored in a desiccator. Granular sodium sulphate was ACS grade (10–60 mesh, EMD) and dried at 500 °C overnight, and stored in a desiccator before use. Sodium chloride crystals were ACS grade and were supplied by EMD. Glass column (7 mm i.d.) for adsorption chromatography was obtained from Supelco Analytical.