



# Simultaneous analysis of organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) from marine samples using automated pressurized liquid extraction (PLE) and Power Prep™ clean-up

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## ARTICLE INFO

### Article history:

Received 16 June 2011

Received in revised form 7 February 2012

Accepted 15 February 2012

Available online 20 March 2012

### Keywords:

Fast analysis  
Marine sample  
Clean-up system  
OCPs and PCBs

## ABSTRACT

An automated pressurized liquid extraction (PLE) method followed by Power Prep™ clean-up was developed for organochlorinated pesticide (OCP) and polychlorinated biphenyl (PCB) analysis in environmental marine samples of fish, squid, bivalves, shells, octopus and shrimp. OCPs and PCBs were simultaneously determined in a single chromatographic run using gas chromatography–mass spectrometry–negative chemical ionization (GC–MS–NCI). About 5 g of each biological marine sample was mixed with anhydrous sodium sulphate and placed in the extraction cell of the PLE system. PLE is controlled by means of a PC using DMS 6000 software. Purification of the extract was accomplished using automated Power Prep™ clean-up with a pre-packed disposable silica column (6 g) supplied by Fluid Management Systems (FMS). All OCPs and PCBs were eluted from the silica column using two types of solvent: 80 mL of hexane and a 50 mL mixture of hexane and dichloromethane (1:1). A wide variety of fish and shellfish were collected from the fish market and analyzed using this method. The total PCB concentrations were 2.53, 0.25, 0.24, 0.24, 0.17 and 1.38 ng g<sup>-1</sup> (w/w) for fish, squid, bivalves, shells, octopus and shrimp, respectively, and the corresponding total OCP concentrations were 30.47, 2.86, 0.92, 10.72, 5.13 and 18.39 ng g<sup>-1</sup> (w/w). Lipids were removed using an SX-3 Bio-Beads gel permeation chromatography (GPC) column. Analytical criteria such as recovery, reproducibility and repeatability were evaluated through a range of biological matrices.

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## 1. Introduction

Polychlorinated biphenyls (PCBs) are a group of persistent contaminants that have high thermal stability and high dielectric constants. They are used in many industrial fields due to their high stability under different conditions, high thermal conductivity, and low electric conductivity [1]. PCB production was banned in the early 1970s in the United States (US) due to the serious effects PCBs have on health and the environment [2]. The US Environmental Protection Agency (EPA) subjects materials with more than 50 µg g<sup>-1</sup> of total PCBs to strict regulations [3]. PCBs are characterized by lipophilicity, resistance to degradation, bioaccumulation and biomagnification in the food chain, resulting in concerns about the effect of exposures to these chemicals on human health [4].

Organochlorinated pesticides (OCPs) are ubiquitous environmental contaminants that tend to accumulate in the food chain and affect ecosystem and human health [5,6], and most organohalogenated compounds, such as PCBs and OCPs, are considered to be

widespread, persistent environmental pollutants. Like PCBs, OCPs have been commercially produced for use in agricultural and industrial applications [7].

The United Nations Environment Programme (UNEP) has identified 12 persistent organic pollutants (POPs), all of which contain chlorine compounds, as top-priority pollutants due to their negative impact on the environment and human health. POPs have been found in fishponds, where they persist for long periods of time and are transferred into food chains, accumulate in marine organisms, and eventually are consumed by humans [8]. Although, humans are exposed to POPs via multiple sources, contaminated fish constitutes one of the major pathways [9]. Therefore, data on the presence of PCBs and OCPs in fish and other edible marine species are important from the ecological and human health points of view [10].

Marine species are used as bioindicators of POPs [11], and their presence in fish and shellfish can be used to assess the pollutants in marine environments [12]. The contaminants in biological samples need to be determined, since little information is available on the routes of exposure of PCBs and OCPs for humans [13]. Previous studies have determined the presence of PCBs and OCPs in marine environmental samples, applying separate extraction and clean-up methods [14–17]. However, few studies on the multi-residue

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analysis of PCBs and OCPs in marine organisms, including fish, squid, bivalves, shells, octopus and shrimp [18] have been reported.

Pressurized liquid extraction (PLE) is recognized as an official EPA method (3545) for the determination of POPs in solid samples [19] and biota [20–23]. Bjorklund et al. [24] used PLE to extract PCBs from fat-containing organisms such as fish, while Gomez-Ariza et al. [25] used PLE to extract PCBs from biota samples. Many other studies have applied PLE in sample preparation for environmental analysis [26,27]. Effective analytical methods that can quantitatively evaluate the levels of OCPs and PCBs at low concentrations ( $\text{ng g}^{-1}$ ) are greatly needed.

New analytical extraction techniques that are less tedious and less time-consuming [10,28] have emerged. PLE, which depends on the application of high-pressure and temperature extraction to bring the sample to a temperature greater than the boiling point of the solvent, is one such technique. Liquid–liquid extraction (LLE) is labor-intensive and allows for the extraction of large-volume samples at a low extraction cost. However, the method does not allow for high throughput analysis. Microwave-assisted extraction (MAE) is less automated than SPE. Soxhlet extraction is both time-consuming and labor-intensive, and requires large amounts of solvent. Soxhlet extraction has been used for quantitative determination of POPs [29]. Sample clean-up is the most critical step, since the analytes of interest must be accurately separated from the fatty matrix material. The Power Prep™ system has been used for biotic environmental samples [30–32] and to clean-up samples with low fat contents [33]. Fluid Management Systems' (FMS) Power Prep™ was used to clean biological samples containing low fat contents of polychlorinated dibenzo-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and coplanar PCB compounds [34,35]. To the best of our knowledge, no procedure has been previously reported for simultaneous automated extraction and clean-up of these groups using PLE and Power Prep™. Moreover, simultaneous determination of OCPs and PCBs in a single chromatographic run has not been reported using GC–MS–NCI.

## 2. Experimental

### 2.1. Marine samples

Marine samples of fish, squid, bivalves, shells, octopus and shrimp collected from the local fish market in Kuwait were analyzed to evaluate the performance of automated PLE extraction and automated Power Prep™ clean-up. Fresh samples (5 g) of each species were mixed with anhydrous sodium sulphate. Aliquots of  $25 \text{ ng mL}^{-1}$  of surrogate standard mixture ( $^{13}\text{C}_{12}$ -labeled PCB) and  $50 \text{ ng mL}^{-1}$  of mirex internal standard (I.S.D.) were added to each extracted sample.

### 2.2. Chemicals and standards

All solvents were pesticide-grade. Hexane and dichloromethane were supplied by Merck (Darmstadt, Germany). Nitrogen gas was used to concentrate the extract. The evaporator (Heidolph-Verwenden, Germany) and anhydrous sodium sulphate (EMD-Chemical, Darmstadt, Germany) were purchased from Sigma Aldrich Chemie GmbH in Steinheim, Germany. SX-3 Bio-Beads (200–400 mesh), purchased from Bio-Rad Laboratories GmbH, in Munich, Germany. The PCBs (EC-4133) contained the following congener numbers: 2,4,4',5-tetraCB (74); 2,3,4,5-tetraCB (70); 2,2',3,5',6-pentaCB (95); 2,2',4,5,5'-pentaCB (101); 2,2',4,4',5-pentaCB (99); 2,2',3,4,5'-pentaCB (87); 2,3,3',4,6-pentaCB (110); 2,2',3,5,5',6-hexaCB (151); 2,2',3,4',5',6-hexaCB (149); 2,3',4,4',5-pentaCB (118); 2,2',4,4',5,5'-hexaCB (153); 2,3,3',4,4'-pentaCB (105); 2,2',3,4,4',5'-hexaCB (138); 2,2',3,3',4,6-

'-hexaCB (132); 2,3,3',4,4',6-hexaCB (158); 2,2',3,4',5,5',6-heptaCB (187); 2,2',3,4,4',5',6-heptaCB (183); 2,2',3,3',4,4'-hexaCB (128); 2,2',3,3',4',5,6-heptaCB (177); 2,2',3,3',4,4',6-heptaCB (171); 2,3,3',4,4',5-hexaCB (156); 2,2',3,4,4',5,5'-heptaCB (180); 2,3,3',4,4',5',6-heptaCB (191); 3,3',4,4',5,5'-hexaCB (169); 2,2',3,3',4,4',5-hexaCB (170); 2,2',3,3',4,5,5',6,6'-nonaCB (208); 2,2',3,3',4,4',5,6'-octaCB (195); 2,2',3,3',4,4',5,5'-octaCB (194); 2,2',3,3',4,4',5,5',6-nonaCB (206) and decaCB (209). A  $^{13}\text{C}_{12}$ -labeled PCB mixture (EC-4058) was obtained from Cambridge Isotope Laboratories, and contained the following congener numbers: 2,2',3,4,4',5'-hexaCB ( $^{13}\text{C}_{12}$ , 99%) (138); 2,2',4,4',5,5'-hexaCB ( $^{13}\text{C}_{12}$ , 99%) (153); 2,2',3,4,4',5,5'-pentaCB ( $^{13}\text{C}_{12}$ , 99%) (180); and decaCB ( $^{13}\text{C}_{12}$ , 99%) (209). A standard stock solution of  $128.8 \text{ ng mL}^{-1}$  was used to prepare the standard working calibration solutions for most of the PCB compounds.

The OCPs used for the analysis were  $\alpha$ -HCH;  $\beta$ -HCH;  $\gamma$ -HCH;  $\delta$ -HCH; heptachlor; aldrin; heptachlor epoxide; T-chlordane; endosulfan-I; cis-chlordane; T-nonachlor; dieldrin; p-p-DDE; endrin; endosulfan-II; cis-nonachlor; p-p-DDD; endrin aldehyde; p-p-DDT; endrin ketone and methoxychlor. The OCPs were obtained from AccuStandard (M-680P) in New York, USA. A standard stock solution of  $25 \mu\text{g mL}^{-1}$  of each OCP compound was used to prepare the standard working calibration solutions.

### 2.3. PLE system

Automated PLE extraction was used (FMS, Waltham, MA, USA). A stainless-steel extraction cell was supported with Teflon end-caps and filters. The PLE system was controlled by means of a PC using DMS 6000 software that shows the real-time temperature and pressure. The pump, flow rate, solvent, time, valve state and cooling were adjusted during the extraction run by the software. Extraction was carried out under pressure at a temperature above the solvent's boiling point to maintain the liquid state of the organic solvent, which keeps the solvent below critical condition, as well as maintaining viscosity and salivation power. Under the selected conditions, the extraction efficiency was enhanced, and the amount of solvent required was minimized.

### 2.4. Automated Power Prep™ system

Automated clean-up was performed using the Power Prep™ system (FMS, Waltham, MA, USA). The system is controlled by software through a control module. The valves, pump, pressure modules, and flow were controlled automatically by the software. The internal pressure which did not exceed 35 psi and was monitored by pressure gauges. The system includes 3–6 way electrostatic valves driven by the PC's software. Valve modules (V1–V6) select the solvent and columns. PCB and OCP clean-up was conducted using a disposable silica column (6 g) packed with PTFE tubes sealed in Mylar packaging supplied by FMS. Two different solvent compositions were used to elute the analytes from the pre-packed silica column, i.e., (A) 80 mL hexane and (B) 50 mL of a 1:1 (v/v) hexane:DCM mixture.

### 2.5. GC–MS–NCI conditions

PCBs and OCPs were quantified on an Agilent 5973 inert mass selective detector, an Agilent Technology 6890 network gas chromatography (GC) system coupled with mass spectrometry (MS) with a negative chemical ionization (NCI) ion source. The system was operated in selective ion monitoring (SIM) mode, and  $1 \mu\text{L}$  of sample solution was injected into the GC in the auto-sampler's splitless mode. The capillary column was a DB-5MS (30 m  $\times$  0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness). The initial oven temperature was  $50^\circ\text{C}$ , which was held constant for 5 min. It was then

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