



Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in seawater samples by membrane-assisted solvent extraction combined with gas chromatography–electron capture detector and gas chromatography–tandem mass spectrometry



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ABSTRACT

A highly efficient and environment-friendly membrane-assisted solvent extraction system combined with gas chromatography–electron capture detector was applied in the simultaneous determination of 17 polychlorinated biphenyls and organochlorine pesticides in seawater samples. Variables affecting extraction efficiency, including extraction solvent used, stirring rate, extraction time, and temperature, were optimized extensively. Under optimal extraction conditions, recoveries between 76.9% and 104.6% in seawater samples were achieved, and relative standard deviation values below 10% were obtained. The limit of detection (signal-to-noise ratio = 3) and limit of quantification (signal-to-noise ratio = 10) of 17 polychlorinated biphenyls and organochlorine pesticides in seawater ranged from 0.14 ng L⁻¹ to 0.36 ng L⁻¹ and 0.46 ng L⁻¹ to 1.19 ng L⁻¹, respectively. Matrix effects on extraction efficiency were evaluated by comparing with the results obtained using tap water. The extraction effect of developed membrane-assisted solvent extraction method was further demonstrated by gas chromatography–tandem mass spectrometry which can provide structural information of the analytes for more accurate identification, and results identical to those produced by gas chromatography–electron capture detector were obtained. These findings demonstrate the applicability of the developed membrane-assisted solvent extraction determination method for coupling to gas chromatography–electron capture detector or tandem mass spectrometry for determining polychlorinated biphenyls and organochlorine pesticides in seawater samples.

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1. Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), which feature high chemical and thermal stability, as well as lipophilicity, are found in the environment as major persistent organic pollutants (POPs) that accumulate in organisms through various food chains [1,2]. Considering the characteristics of POPs, which include long-range transport and adverse effects on reproductive, carcinogenic, immunologic, and neurologic functions in

living organisms and humans, most PCBs and OCPs have been banned globally over the past several decades [3,4]. Nevertheless, POPs remain widely distributed and are routinely detected in the environment, particularly in seawater, surface water, air, fish, food, and humans. Many studies have observed the endocrine-disrupting properties of PCBs and OCPs even at low concentrations [5,6], and these compounds have been accorded increasing international concern on account of their environmental and ecotoxicological behaviors. Therefore, the sensitive analytical methods to trace levels of POPs residues, aid in better understanding of their distribution and exposure risk to living organisms, must be employed.

Sample preparation is often required prior to analysis. PCBs and OCPs analyses are commonly performed by initial partitioning via liquid–liquid extraction followed by enrichment and purification via solid-phase extraction (SPE) coupled to some chromatographic

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method [7]. Although SPE features high automation and purification efficiency, the method requires rigorous pre-conditioning procedures, large volumes of organic solvents, and various stationary phases including C₁₈ and/or NH₂. Multi-residue analysis, on the other hand, is restricted by the physicochemical characteristics of the analytes [8–10]. Other extraction techniques, such as liquid-phase microextraction and stir bar microextraction, present disadvantages of inadequate automation and matrix effects [11,12]. Considering these issues, trends in sample preparation for trace PCBs and OCPs have led to environment-friendly simplification, automation, miniaturization, and simultaneous determination of multi-residue toxic compounds. Membrane techniques, which exhibit the characteristics of low solvent requirement, minimal time consumption for a great quantity of samples, high concentration enrichment factors, remarkable clean-up efficiency, and automation potential, have become increasingly popular for extracting organic compounds in the last several years. Membrane-assisted solvent extraction (MASE), for example, which exhibits advantages of minimal solvent consumption and good practicability for automation, has recently been successfully applied in the trace analysis of organic pollutants, such as organophosphorus pesticides, hydrocarbon contamination, phenols, in different aqueous samples, including lake water, river water, wastewater, juice, and surface and drinking water, among others [13–16]. However, to the best of our knowledge, no reports are available on the application of MASE for seawater sample simultaneous clean-up and pre-concentration of PCBs and OCPs; seawater is fairly different from fresh water as a matrix, and the presence of salt may result in negative effects on extraction efficiency [13].

The present study aimed to construct a MASE method with good enrichment capability and minimal solvent consumption for concentrating 17 PCBs and OCPs in seawater. Parameters including the extraction solvent used, stirring rate, extraction time, temperature, and NaCl concentration were optimized. The MASE method was then coupled to a gas chromatography (GC)–electron capture detector (ECD) or GC–tandem mass spectrometer (MS/MS) for the simultaneous analysis of PCBs and OCPs in aquatic seawater samples.

2. Experimental

2.1. Reagents and materials

Seven PCB congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-138, PCB-180) and ten OCPs (o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, α -HCH, β -HCH, γ -HCH, δ -HCH) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). HPLC-grade *n*-hexane was obtained from Spectrum Chemical Mfg. Corp. (New Brunswick, NJ, USA). HPLC-grade cyclohexane and acetone were purchased from China National Pharmaceutical Group Corporation (Shanghai, China). HPLC-grade isooctane was obtained from Tedia, Company, Inc. (Fairfield, OH, USA). All other reagents were of analytical grade. MASE-membrane bags and accessories were supplied by Gerstel (Mühlheim, Germany). Standard stocking solutions (200 μ g L⁻¹) of PCBs and OCPs were prepared in *n*-hexane. Working solutions were prepared weekly by appropriate dilution of aliquots from stocking solutions.

2.2. Sample preparation

Seawater and tap water samples were collected at the local aquaculture and laboratory, respectively. All samples were collected in amber glass bottles pretreated with acetone, methanol, and water and stored in the dark at 4 °C. Samples were examined

via GC–ECD to confirm the absence of detectable PCBs and OCPs prior to analysis.

2.3. Membrane-assisted solvent extraction

The MASE system was produced by Gerstel (Mühlheim, Germany) and consisted of a 20 mL extraction vial and a dense polypropylene membrane bag attached to a metal funnel with a Teflon ring. The membranes were cleaned with *n*-hexane before use to eliminate contamination of interfering compounds from the membrane materials.

To optimize extraction conditions, the operation was carried out via the this procedure: Membrane bags were first pre-conditioned with the extraction solvent of *n*-hexane:acetone (9:1, v/v) at 40 °C for 10 min. Up to 15 mL of water samples were placed in the 20 mL extraction vial. The membrane bags were then filled with 750 μ L of *n*-hexane:acetone (9:1, v/v) and agitated at 600 rpm for 60 min at 40 °C. After extraction, the extraction solvent in the membrane bag was transferred into a 2.0 mL auto-sampler vial and analyzed by GC–ECD or GC–MS/MS.

Operation optimization of MASE was carried out using seawater and tap water samples to determine matrix effects. Permeation characteristics of MASE for PCBs and OCPs were evaluated in different extraction conditions, including the extraction solvent used, temperature, stirring rate, ionic strength, and extraction time.

2.4. Gas chromatography–electron capture detection

A Shimadzu GC-2010 GC equipped with a 63Ni ECD and chromatographic Supelco SPB-5 (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness) capillary column were used in this study. The system was equipped with a split/splitless injection inlet for analysis. Nitrogen was used as both carrier and makeup gases and applied at constant flow rates of 1.0 and 34 mL min⁻¹, respectively. The column oven temperature program was 100 °C (held for 6 min), raised at a rate of 10 °C min⁻¹ to 160 °C, raised at a rate of 2 °C min⁻¹ to 230 °C, and then raised at a rate of 10 °C min⁻¹ to 280 °C. The ECD temperature was 320 °C. The samples were injected in the split mode (split ratio, 30:1) at an injection temperature of 240 °C.

2.5. Gas chromatography–tandem mass spectrometry

All GC–MS/MS experiments were performed using an Agilent 7890A GC coupled to an Agilent 7000A triple–quadrupole mass spectrometer (Agilent Technologies) operated in multiple reaction monitoring mode (MRM) with electron impact ionization at a collision energy of 20 eV. The GC system was equipped with a 7683B autosampler (Agilent Technologies). For separation, an SPB-5 MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μ m, Supelco) was used. Pulsed splitless mode was used for injection of a volume of 1.0 μ L, and the injection temperature was 250 °C. The temperature program was as follows: 70 °C for 2 min, raised at a rate of 25 °C min⁻¹ to 150 °C, raised at a rate of 3 °C min⁻¹ to 200 °C, and then raised at a rate of 8 °C min⁻¹ to 280 °C, where the temperature was held for 10 min. The MS transfer line and ion source temperatures were set to 300 and 280 °C, respectively. Ar was applied as the collision gas at a flow of 1.5 mL min⁻¹. Helium was applied as the carrier gas at a constant flow of 2.25 mL min⁻¹. GC–MS/MS parameters for separating PCBs and OCPs are shown in Table 1.

2.6. Method validation

Validation of the developed MASE method coupled to GC for the simultaneous determination of 17 PCB and OCP residues was achieved by obtaining the following parameters: matrix-matched

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