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Simultaneous analysis of polychlorinated biphenyls and polychlorinated naphthalenes by isotope dilution comprehensive two-dimensional gas chromatography high-resolution time-of-flight mass spectrometry

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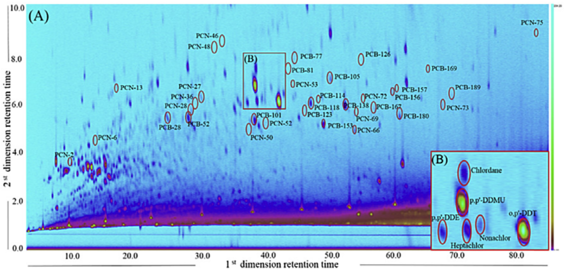
HIGHLIGHTS

- A novel method for simultaneous analysis of 18 PCBs and 16 PCNs was developed using isotope dilution GC × GC-HRTOF-MS.
- Complete separation of all target analytes was achieved with column combination of DB-XLB × BPX-70.
- GC × GC-HRTOF-MS results agreed well with those obtained by GC-HRMS.
- Non-target contaminants including OCPs and PAHs were identified in three species of fish.

GRAPHICAL ABSTRACT



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ABSTRACT

Polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) are listed as persistent organic pollutants (POPs) under the Stockholm Convention. Because they have similar physical and chemical properties, they are coeluted and are usually analyzed separately by different gas chromatography high-resolution mass spectrometry (GC-HRMS) methods. In this study, a novel method was developed for simultaneous analysis of six indicator PCBs, 12 dioxin-like PCBs, and 16 PCNs using isotope dilution comprehensive two-dimensional gas chromatography with high-resolution time-of-flight mass spectrometry (GC × GC-HRTOF-MS). The method parameters, including the type of GC column, oven temperature program, and modulation period, were systematically optimized. Complete separation of all target analytes and the matrix was achieved with a DB-XLB column in the first dimension and a BPX-70 column in the second dimension. The isotope dilution method was used for quantification of the PCBs and PCNs by GC × GC-HRTOF-MS. The method showed good linearity from 5 to 500 pg μL^{-1} for all the target compounds. The instrumental limit of detection ranged from 0.03 to 0.3 pg μL^{-1} for the 18 PCB congeners and from 0.09 to 0.6 pg μL^{-1} for the 16 PCN congeners. Repeatability for triplicate injections was always lower than 20%. The method was successfully applied to the determination of 18 PCBs present at 0.9–2054 pg g^{-1} and 16 PCNs present at 0.2–15.7 pg g^{-1} in three species of fish. The GC × GC-HRTOF-MS results agreed with those obtained by GC-HRMS. The GC × GC-HRTOF-MS method proved to be a sensitive and accurate technique for simultaneous analysis of the selected PCBs and PCNs. With the excellent chromatographic separation offered by GC × GC and accurate mass measurements offered by

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HRTOF-MS, this method allowed identification of non-target contaminants in the fish samples, including organochlorine pesticides and polycyclic aromatic hydrocarbons.

1. Introduction

Polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) are synthetic organic compounds with many distinct congeners. Both classes of chemicals are persistent organic pollutants (POPs), which are characterized by high levels of persistence, toxicity and bioaccumulation, and have adverse effects on biota and human health [1,2]. Both PCBs and PCNs are listed in the Stockholm Convention on POPs, with PCBs being in the original list of chemicals and PCNs added more recently [3,4]. Historically, PCBs and PCNs were widely used in the electrical industry as dielectric fluids in transformers and capacitors, and as cable insulators [5]. Because of this widespread use, they are ubiquitous in many environmental matrices worldwide [6–9], and are even found in the Antarctic [10].

PCBs and PCNs have similar physicochemical properties, and are usually present in the same fraction during sample preparation processes [11]. Moreover, PCNs have similar chromatographic retention behavior to some coplanar PCBs, which makes it difficult to completely separate these compounds chromatographically. Among the 209 PCBs and 75 PCNs congeners, 12 dioxin-like PCBs and 16 PCNs have attracted the most attention because of their possible dioxin-like toxicity [12]. In addition, six indicator PCBs have been found at high levels in various environmental matrices [12]. Consequently, it is of important to be able to separate these specific PCBs and PCNs from other congeners and contaminants. Although there are some high-resolution capillary columns that can separate some of PCB and PCNs congeners, no chromatographic method can unambiguously and simultaneously separate the 12 dioxin-like PCBs, six indicator PCBs, and 16 PCNs from the other PCBs and PCNs [13,14]. Consequently, PCBs and PCNs are usually analyzed separately by gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) in selected ion monitoring mode using ^{13}C isotope dilution for quantification in two injections [11,15]. GC-HRMS instrumentation is expensive, has high operating costs, and requires highly trained personnel to operate it. In addition, multiple injections are needed in GC-HRMS to analyze different classes of compounds. Therefore, alternative methods that can generate results comparable to GC-HRMS are required.

The most promising alternative is comprehensive two-dimensional gas chromatography (GC × GC), which can produces two-dimensional chromatograms. This method uses a modulator to connect two columns with different polarities, and has the potential to improve separation of the target compounds [16–18]. Narrow peaks (50–200 ms) are obtained from fast separation in the second dimension, and require fast detectors with high scan rates and full scan acquisition [19]. GC × GC coupled with high-speed low-resolution (LR) time-of-flight (TOF)-MS has been used for the separation and determination of several environmental contaminants in complex samples, and offers high separation power through combination of the chromatographic and mass spectral resolution [20–25]. Hoh et al. developed a GC × GC high-speed LRTOF-MS method for analyzing polychlorinated dibenzodioxins and furans (PCDD/Fs) at an acquisition rate of 50 Hz [26]. This separated the PCDD/Fs from PCBs, and gave a detection limit for tetrachlorodibenzo-*p*-dioxin of 0.25 pg. However, GC × GC-LRTOF-MS is not successful with trace amounts of compounds (pg L^{-1}) in highly complex matrices with low mass resolution. Shunji et al. reported a GC × GC high-resolution TOF-MS (GC × GC-HRTOF-MS) method for PCDDs and PCDFs with a resolving power of 5000, acquisition range of m/z 35–500, and acquisition rate of 25 Hz [27]. The high mass resolution and mass accuracy of HRTOF-MS allowed for discrimination of any interferences from the target compounds in environmental samples. However, GC × GC-HRTOF-MS with a low data acquisition rate (25 Hz) may increase errors in the quantification. GC × GC-HRTOF-MS with a faster data acquisition rate (>100 Hz) could maximize compound separation, eliminate matrix interferences, and greatly improve the selectivity [28]. To the best of our knowledge, simultaneous analysis of different classes of compounds in various matrices using high speed GC × GC-HRTOFMS has not been reported.

The objectives of this study were to develop a GC × GC-HRTOF-MS method for simultaneous determination of PCBs and PCNs, including the 12 dioxin-like PCBs, six indicator PCBs, and 16 PCNs congeners, in one injection. The GC × GC and HRTOF-MS parameters were optimized to obtain separation of the targeted congeners and exclude possible interferences. The GC × GC-HRTOF-MS results were compared with those obtained by GC-HRMS. Meanwhile, the identification and screening of non-target contaminants in the fish samples were conducted using GC × GC-HRTOF-MS.

2. Materials and methods

2.1. Chemicals and standards

US Environmental Protection Agency (EPA) Method 1668C standard solutions, including PCB 1668C-PAR, labeled calibration and cleanup solution (1668C-LCS), injection standard spiking solution (1668C-IS), and PCN-MXA and PCN-MXC (containing 16 PCN congeners), were used for spiking and calibration and were obtained from Wellington Laboratories (Guelph, Canada). ECN-5102 and ECN-5260 were purchased from Cambridge Isotope Laboratories (CIL; Tewksbury, MA). All solvents were pesticide residue analysis grade. Five solutions of unlabeled (native) compounds were prepared for construction of a calibration curve with concentrations between 5 pg μL^{-1} and 500 pg μL^{-1}. Solutions of ^{13}C-labeled internal standards were prepared at 100 pg μL^{-1}.

2.2. Sample preparation

Three different types of fish (yellow croaker, thornback and flatfish) were all lean fish and collected from Bohai Bay, China in July 2013, wrapped in aluminum foil, and stored at −20 °C until analysis. Each fish sample (fish muscle with skin not attached) was homogenized and freeze-dried. Fish samples were prepared and analyzed by GC × GC-HRTOF-MS and GC-HRMS. The results are all presented in picograms of the target compound per gram of fish fresh weight (fw). The sample extraction and cleanup procedures followed US EPA Method 1668 and have been described in detail previously [11,28,29]. Briefly, a 10 g (dry weight) fish sample was spiked with 1 ng of $^{13}C_{12}$-labeled PCB internal standards (1668C-LCS) and $^{13}C_{10}$-labeled PCN internal standards (ECN-5102). The sample was then extracted with a 1:1 mixture of dichloromethane and *n*-hexane using an ASE 350 extraction unit (Dionex, CA, USA) at