



Gas chromatography–triple quadrupole mass spectrometry for the determination of atmospheric polychlorinated naphthalenes

Fang Li^{a,b,1}, Jing Jin^{a,1}, Xiaoli Sun^{a,b}, Xueli Wang^a, Yun Li^a, Syed Mazhar Shah^a, Jiping Chen^{a,*}

^a Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Atmospheric PCNs were detected by isotope-dilution GC–MS/MS.
- The pollution levels of PCNs covering from mono- to octa-CNns were investigated comprehensively in air samples.
- The dioxin-like toxicity and human exposure levels of PCNs in air samples were estimated.

ARTICLE INFO

Article history:

Received 8 April 2014

Received in revised form 28 July 2014

Accepted 29 July 2014

Available online 7 August 2014

Keywords:

Gas chromatography–triple quadrupole mass spectrometry

Polychlorinated naphthalenes

Isotope dilution

Atmosphere

ABSTRACT

Atmospheric polychlorinated naphthalenes (PCNs) ranging from mono-CNns to octa-CNns were detected using isotope-dilution gas chromatography coupled with triple quadrupole mass spectrometry (GC–MS/MS). The developed instrumental method was successfully applied to the determination of PCNs in technical products. It was observed that there were significant differences in concentrations, homologue profiles, chlorinated contents and total toxic equivalents (\sum TEQs) of PCNs for four Halowax products. Subsequently, the validation of the analytical method was evaluated for the determination of PCNs in air samples in terms of method detection limit (MDL), recovery and matrix effect. The results demonstrated that this method could provide satisfactory sensitivity and adequate selectivity with lower cost. It was conducted to comprehensively evaluate the levels, composition patterns, \sum TEQs, and daily intake exposure of PCNs in indoor and outdoor air samples. Concentrations and \sum TEQs of PCNs in air samples ranged 47.7–832.7 pg m^{-3} and 1.31–5.99 fg m^{-3} , respectively, and the predominant homologues were di- and tri-CNns in the gas phase. The results indicated that this analytical method was useful for the accurate and specific evaluation of dioxin-like toxicity and human exposure levels of PCNs in the atmosphere.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds consisting of chlorinated substituted (one up to eight) naphthalene, yielding a complex mixture of 75 possible congeners. PCNs are structurally similar to some polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), showing dioxin-like toxicity. In general, toxicological symptoms caused by PCNs mainly include hepatotoxicity, carcinogenesis, immunotoxic effects and skin defects, such as chloracne and liver disease [1–4]. Owing to such toxicity, persistence, bioaccumulation and long-range transport, PCNs were proposed for inclusion in Annexes A, B, and/or C of the Stockholm Convention on persistent organic pollutants (POPs) in 2011 [5].

Major technical products of PCNs (Halowax, Nibren waxes and Seekay waxes) were widely used in the electric industry, such as flame retardants, dielectric fluids, insulators, etc., and they were also used in dye productions or as wood fungicides [6,7]. Although their production and use were successively prohibited in 1980s, these processes of waste incineration, metal smelting and chemical industrial production can also inadvertently release PCNs into the environment [2]. In recent years, PCNs have been widely detected in biological samples [8,9], soils [10], sediments [11,12], sewage sludge [13], pine needles [14], air [15], foodstuffs [16], and human tissue [17]. For the analysis of PCNs in these matrices, high resolution gas chromatography–high resolution mass spectrometry (HRGC–HRMS) in electron impact or electron capture negative ion mode was the most commonly used instrumental method, because of its high selectivity and low detection limits [5,15,18,19]. However, such technology needs tiresome sample preparation and expensive instrumentation. Therefore, it is essential to explore novel and substitutable instrumental methods for the PCNs analysis in environmental samples.

As well known, the MS/MS technique can reduce the need for extraneous peak identification and minimize the interferences of matrix co-extracts [20], so it

* Corresponding author. Tel.: +86 411 84379562; fax: +86 411 84379562.

E-mail address: chenjp@dicp.ac.cn (J. Chen).

¹ The authors contribute equally to this work.

can play an important role in detecting environmental pollutants at trace-levels. As reported, this technique has been successfully applied for the PCBs analysis with a lower cost with satisfactory sensitivity and selectivity [21,22]. In addition, GC-MS/MS is prone to be obtained for most ordinary laboratories. So it is believed that GC-MS/MS will become a promising analytical technique for the determination of PCNs in environmental samples.

As a dominant long-range transportation and propagation route for PCNs on a global scale, air is being paid much attention because air inhalation is one of the most important pathways of human exposure to PCNs. Therefore, monitoring of PCNs in air is of great importance. For air samples, PCNs are distributed between gas and particle phase, and generally present at trace-levels (pg m^{-3}). The concentrations of PCNs in air samples of Lzmir area ranged from 5.2 pg m^{-3} to 162 pg m^{-3} in summer and from 3.7 pg m^{-3} to 229 pg m^{-3} in winter, and this study showed that both of the combustion processes and the historical use were two major sources of PCNs in atmosphere [23]. The Asian region is one of the hotspots for monitoring POPs. Average PCNs concentrations in Japan, Korea and China air were reported to be $9.5 \pm 1.5 \text{ pg m}^{-3}$, $16 \pm 2.4 \text{ pg m}^{-3}$ and $61 \pm 6 \text{ pg m}^{-3}$, respectively [24]. Recent studies showed that the concentration of PCNs ranged from not detection to 26.0 pg m^{-3} in northern South China Sea [25] and from 10 pg m^{-3} to 2460 pg m^{-3} in North China [26]. However, the reports of PCNs concentrations in air samples are still scarce, especially in China. The most frequently analyzed homologues were tri- to octa-CN homologues in these reports without mentioning mono- and di-CN, because of their low toxicity. Although some congeners of mono- and di-CN had low toxic potential, their important contributions to total toxic equivalents ($\sum \text{TEQs}$) of PCNs based on the relative potency factors (RPFs) should not be ignored resulting from its relatively high levels [27]. Therefore, comprehensive analysis of PCNs congeners becomes essential.

This study attempts to employ gas chromatography–triple quadrupole mass spectrometry (GC-MS/MS) technique to investigate the levels of PCNs in air samples. For this purpose, the MS/MS operating parameters were optimized, and the instrumental method was evaluated by analyzing the concentrations and congener compositions of PCNs in four Halowax preparations. The feasibility of the analytical method was validated in terms of method detection limit (MDL), recovery and matrix effect. The developed method was applied for the analysis of PCNs in air samples from different areas/regions, and then the concentrations, composition patterns, $\sum \text{TEQs}$ and daily intake exposure by inhalation were systematically studied.

2. Experimental

2.1. Chemical and materials

Pesticide residue-grade hexane, dichloromethane and nonane were obtained from J.T. Baker (Center Valley, PA, USA). Silica gel with 0.063–0.100 mm was supplied by Merck Chemicals Ltd (Shanghai, China). Alumina was purchased from MP Biomedicals Inc. The standard solutions of PCNs (PCN-MXA and PCN-MXC) were obtained from the Wellington Laboratories Inc. (Guelph, Canada). The standard solutions of isotopically labeled $^{13}\text{C}_{10}$ tetra-octa PCN mixture ECN-5102 ($^{13}\text{C}_{10}$ -CN 27, $^{13}\text{C}_{10}$ -CN 42, $^{13}\text{C}_{10}$ -CN 52, $^{13}\text{C}_{10}$ -CN 67, $^{13}\text{C}_{10}$ -CN 73 and $^{13}\text{C}_{10}$ -CN 75), $^2\text{D}_7$ -CN 2, ^{13}C -PCB 105 and ^{13}C -PCB 126 were purchased from the Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Halowax 1000, 1013, 1014 and 1051 were purchased from the AccuStandard Inc. (New Haven, CT, USA).

2.2. Air sampling

Sampling was conducted in August and September 2013 in two cities in China. Two indoor samples were collected from a workroom (1#) and an e-waste recycling room (2#). Two outdoor samples were collected in downtown of two cities (3# and 4#), respectively. An e-waste site (5#) was located in an e-waste recycling area in the suburb where e-wastes were processed using the primitive method.

Air samples were collected using ECHO Hivol Sampler (TCR, Italy) with a quartz fiber filter (QFF, 101.6 mm diameter, Munktell Filter AB BOX, Sweden) followed by a polyurethane foam plug (PUF, 65 mm diameter, 75 mm thickness, TISCH Environmental INC., USA). Every sampling was operated for 24 h at a flow rate of 200 L min^{-1} to yield a single sample comprising about 288 m^3 of air.

Two samplers were deployed at each location to obtain duplicate samples.

Prior to use, QFFs were baked at 650°C for 10 h, and PUFs were firstly washed with boiled water for 4 h and cold water, and then dried at room temperature, followed by Soxhlet pre-extracted successively with acetone and hexane/dichloromethane (1:1, v/v) for 24 h. Before sampling, PUF was spiked with 8.0 ng of ^{13}C -PCB 105 as a sampling efficiency standard to provide a quantitative measure of analyte losses during the sampling process. After sampling, the QFF and PUF were stored in a glass tube in a -20°C freezer until used for sample preparation and analysis.

2.3. Sample preparation

Prior to extraction, the $^{13}\text{C}_{10}$ -isotopic PCNs mixed standard (4.0 ng) and D_7 labeled CN 2 (4.0 ng) were added to QFF and PUF, respectively, as the surrogate standard to monitor the analytical recovery efficiency. The QFF and PUF loaded PCNs were Soxhlet extracted with hexane/dichloromethane (1:1, v/v) for approximately 16 h, and the extract was concentrated to approx. 1 mL with rotary evaporator. The remaining extract was cleaned up on a multi-layer silica gel column and an alumina column. Such procedures had been described in detail in our early work [28]. Finally, the samples were concentrated near to dryness by a gentle stream of dry nitrogen and the solvent was exchanged to $400 \mu\text{L}$ of nonane containing ^{13}C -PCB 126 (4.0 ng) as the injection internal standard.

2.4. GC-MS/MS analysis

All samples were analyzed with a ThermoFisher Scientific Trace gas chromatograph coupled with triple quadrupole mass spectrometer working in electron impact (EI) mode at 70 eV . The ion source and transfer line temperatures were 250°C and 280°C , respectively. The capillary column was a non-polar $\text{Rtx}^{\text{®}}-5 \text{ MS}$ column ($60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Restek Inc., USA). PCNs congeners were separated using a temperature programme starting at 90°C (held for 2 min), and increased to 200°C at $10^\circ\text{C min}^{-1}$, and then raising to 280°C at 2°C min^{-1} (held for 20 min). All samples were injected in a splitless mode (1 min), and the injection volume was $1 \mu\text{L}$. The injector temperature was 260°C . The carrier gas (helium) was operated at a constant flow mode (1.0 mL min^{-1}).

The quantitative analysis of PCNs was performed in a selected reaction monitoring (SRM) mode by recoding two pairs of SRM ions per congener. The emission current was fixed at $50 \mu\text{A}$. The collision gas for MS/MS experiments was argon (1.5 mTorr).

2.5. Quality assurance and quality control

Peaks were identified by retention time compared to standards and quantified using target/qualifier ion ratios within $\pm 20\%$ of standard values. The quantification of PCNs was made by isotope dilution. The instrumental performance was monitored by quality control standard every ten samples. Solvent blank of hexane and dichloromethane were carried through the whole analytical procedure, and no PCNs congeners were found. QFF and PUF field blanks were prepared for each site, and the concentration of PCNs was also below the method detection limits (MDLs). The reported data on PCNs in this study were not corrected by the blank values and the surrogate recoveries. Sampling recoveries for individual PCNs congeners should fall within the range of 70–150%. The sampling should be reiterated when the recovery was not in the aforementioned range.

Download English Version:

<https://daneshyari.com/en/article/6971296>

Download Persian Version:

<https://daneshyari.com/article/6971296>

[Daneshyari.com](https://daneshyari.com)