



# Determination of tri-heptabrominated diphenyl ethers in indoor dust by chromatoprobe injection and gas chromatography–mass spectrometry



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## ABSTRACT

This study describes an analytical method that involves ultrasonication extraction and chromatoprobe injection–gas chromatography–mass spectrometry (GC–MS) in the determination of polybrominated diphenyl ethers (PBDEs) in indoor dust. The chromatoprobe injection technique facilitates direct GC–MS analysis of extracts without additional extraction, fractionation or clean-up steps. The instrument detection limits were from 2.60 to 8.08  $\text{pg } \mu\text{L}^{-1}$ . The calibration curves were linear in concentrations between 0.005 and 0.200  $\text{ng } \mu\text{L}^{-1}$  with correlation coefficients of 0.9938–0.9996. The method detection limits were from 283 to 955  $\text{ng } \text{g}^{-1}$  and the recoveries were between 74 and 129%. The analytical method was applied in the determination of tri- to heptabrominated diphenyl ethers (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183) in indoor dust from workplace environments in a university in the Philippines. BDE-47, BDE-99 and BDE-100 were the main congeners detected in the indoor dust samples. The levels of these PBDEs were within the concentration range of those found in indoor dust in other countries.

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## 1. Introduction

Polybrominated diphenyl ethers or PBDEs belong to a group of brominated flame retardant chemicals added in plastic materials, electrical and electronic equipment, upholstery and construction materials to aid these products resist or delay fire. In time, these chemicals are released from flame retardant-treated products and find their way into the different environmental compartments. These chemicals have properties similar to persistent organic pollutants or the historical POP compounds. As such, they may bioaccumulate and persist in the environment where they pose possible ecological and human health risks. Consequently, they are subject to scientific investigations that reveal their occurrence in the environment and potential harmful effects [1–9]. The number of studies on the environmental levels of PBDEs, albeit done mostly in developed countries, has markedly increased in the past years. The analytical determination of PBDEs in various environmental matrices involves standard extraction procedures such as liquid–liquid extraction, solid–phase extraction, Soxhlet extraction, or accelerated solvent extraction followed by gas chromatography with mass spectrometry as the most common detection technique. These analytical methods are reviewed extensively in literature, including recent innovations in analytical methodologies [10–13].

Fig. 1 shows the chemical structure of PBDEs, a class of bromine-containing compounds with 209 congeners. PBDEs are commercially produced as pentabrominated diphenyl ether mixtures (pentaBDE comprising of tetra, penta and hexa congeners), octabrominated

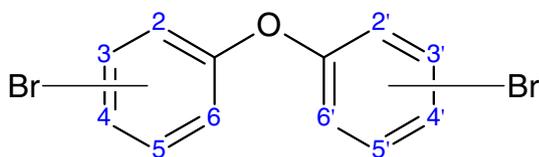
diphenyl ether mixtures (octaBDE comprising of hexa, hepta, octa and nona congeners), and decabrominated diphenyl ether mixture (decaBDE comprising mainly of the fully brominated diphenyl ether with octa and nona congeners as minor components). PBDEs are commonly used as additive flame retardants that are only dissolved in the polymeric material. In contrast, reactive types of brominated flame retardants such as tetrabromobisphenol-A and hexabromocyclododecanes are covalently bonded to polymers. PBDEs, as additive flame retardants, eventually leak out of flame retardant-treated products. In fact, they are now detected in air, water, sediment, human milk and wildlife [1,6,14–21]. Notably, PBDEs were found in air particulates near waste recycling sites and over industrial and urban areas [15,16]. PBDEs are also documented to be present in domestic indoor dust [22]. Today, pentaBDE and octaBDE mixtures are no longer produced while decaBDE production is undergoing a phase-out [2,23,24]. However, flame retardant-treated products made during the years when these chemicals were used still exist in many parts of the world.

Brominated flame retardants may be found in the environment because of trash burning and incineration of waste electronic and electrical equipment or e-wastes. PBDEs, for example, have been detected in air, soil, freshwater fish, chicken and eggs wherein contamination was caused by improper e-waste disposal [15,25–27]. In the Philippines, very little is known of the treatment and disposal of e-wastes. Electronic and electrical equipment that are broken or have become obsolete are commonly stored in homes or offices for extended periods of time. Also, there is limited data on the environmental levels of brominated flame retardants as well as information on the public's potential exposure to these chemicals.

The aim of this study was to determine the occurrence of PBDEs in indoor workplace environments in a university in the Philippines

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**Fig. 1.** General structure of PBDEs. PBDE congeners in this study: 2,4,4'-tribromodiphenyl ether (BDE-28) ; 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) ; 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) ; 2,2',4,4',6-pentabromodiphenyl ether (BDE-100) ; 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) ; 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) ; and 2,2',3,4,4',5',6'-heptabromodiphenyl ether (BDE-183).

where electronic and electrical equipment, both functioning and not, are found. In line with this aim, an alternative method using small sample size, reduced volume of solvent for extraction, and minimal sample preparation was developed for the analysis of PBDEs in indoor dust. The method involved ultrasonication-assisted hexane extraction followed by chromatoprobe injection–GC–MS analysis. The PBDE congeners detected in the dust samples were then confirmed by MSMS analysis. In this study, the levels of tri- to heptabrominated diphenyl ethers in indoor dust in the Philippines were determined for the first time.

## 2. Materials and methods

### 2.1. Standards and reagents

Analytical standards were obtained from AccuStandard (New Haven, CT, USA): 50.03  $\mu\text{g mL}^{-1}$  2,4,4'-tribromodiphenyl ether (99.3%, BDE-28), 50.12  $\mu\text{g mL}^{-1}$  2,2',4,4'-tetrabromodiphenyl ether (100%, BDE-47), 50.06  $\mu\text{g mL}^{-1}$  2,2',4,4',5-pentabromodiphenyl ether (100%, BDE-99), 50.0  $\mu\text{g mL}^{-1}$  2,2',4,4',6-pentabromodiphenyl ether (100%, BDE-100), 50.36  $\mu\text{g mL}^{-1}$  2,2',4,4',5,5'-hexabromodiphenyl ether (99.3%, BDE-153), 50.38  $\mu\text{g mL}^{-1}$  2,2',4,4',5,6'-hexabromodiphenyl ether (100%, BDE-154), and 50.06  $\mu\text{g mL}^{-1}$  2,2',3,4,4',5',6'-heptabromodiphenyl ether (100%, BDE-183). The internal standard hexabromobenzene (99.8%) was purchased from Sigma Aldrich (St. Louis, MO, USA). HPLC-grade n-hexane (99.8% as C6 isomers) was purchased from JT Baker (Philipsburg, NJ, USA). Standard solutions and sample fortifications

were prepared using n-hexane. The high purity standards and solvent were used without further purification.

### 2.2. Sampling, sample preparation and extraction

The sampling of indoor dust was carried out in September 1–4, 2009. Indoor dust samples were collected from filters of air-conditioning units in 15 locations in offices, libraries, and computing laboratories inside the University of the Philippines Diliman campus in Quezon City, Philippines. These sites were known to have computers in use or in storage within the room or facility. An indoor dust sample was also taken from a room in one of the university hostels where no computer is installed. Using clean test tube brushes, dust particles were scraped from air-conditioner filters into a white paper. The filters were mostly made of a fine wire mesh. The dust samples were transferred into aluminum foil-covered 20 mL vials (RPI Corporation, Mt. Prospect, IL, USA) and stored in the freezer until analysis.

Sixteen indoor dust samples were collected. One of these samples was analyzed in triplicate, 7 samples were analyzed in duplicates and 8 samples only had enough amounts for a single analysis. The indoor dust samples were mechanically homogenized. A 0.1 g of each sample was weighed and extracted with 2.5 mL n-hexane using a Power Sonic 410 ultrasonicator (Hwashin Technology, Gyeonggi-do, Korea) for 30 min at room temperature. One mL of the extract was mixed with 2  $\mu\text{g}$  of hexabromobenzene prior to chromatoprobe injection and GC–MS analysis.

Because a certified reference material was not available in this study, the recovery was measured using indoor dust samples previously cleaned by exhaustive n-hexane extraction. The cleaned dust was spiked with 2500  $\text{ng g}^{-1}$  of the tri- to heptabrominated diphenyl ether standards. Method blanks and the spiked indoor dust samples underwent the ultrasonication extraction procedure and GC–MS analysis.

### 2.3. Gas chromatographic–mass spectrometric determination

The GC-ion trap MS system used was a Varian-450 GC connected to a Varian-240 MS (Varian Inc., Palo Alto, California, USA). A 15-mm Varian microvial containing 4  $\mu\text{L}$  extract was loaded in a chromatoprobe that was positioned through an adaptor into the Varian 1079 injector. The injection temperature program was 60  $^{\circ}\text{C}$  for 2 min, heated to

**Table 1**  
Optimum MSMS parameters.

PBDE IUPAC no.	Segment time (min)	Segment range (m/z)	Parent mass (m/z)	Product mass (m/z)	Isolation window (m/z)	Excitation storage level (m/z)	Excitation amplitude (V)
BDE-28	8.00–9.80	200–416	406	246	12.0	154.7	2.5
BDE-47	9.80–10.60	250–496	486	326	14.0	185.2	2.0
BDE-100	10.60–11.10	330–576	566	406	14.0	215.7	2.3
BDE-99	11.10–12.00	330–576	566	406	14.0	215.7	2.3
BDE-154	12.00–12.80	400–654	644	484	14.0	245.4	2.5
BDE-153	12.80–15.00	400–654	644	484	14.0	245.4	2.5
BDE-183	15.00–16.83	400–734	724	564	14.0	275.9	3.2

**Table 2**  
Retention times, quantification ions, detection limits and recoveries.

PBDE IUPAC no.	Retention time, min	MW	Quantification ion, m/z	Qualifying ions, m/z	Instrument detection limits, $\text{pg } \mu\text{L}^{-1}$		Percent recoveries (SD, n = 3)
					LOD	LOQ	
BDE-28	9.24	406.9	406	248, 246	7.41	24.70	129 (7)
BDE-47	10.05	485.6	486	488, 326	5.25	17.50	74 (12)
BDE-100	10.91	564.7	566	564, 406	8.08	26.92	75 (16)
BDE-99	11.24	564.7	566	564, 406	8.08	30.23	100 (5)
BDE-154	12.32	643.6	644	484, 642	3.31	11.04	97 (3)
BDE-153	13.08	643.6	644	484, 646	5.37	17.90	102 (9)
BDE-183	16.02	722.5	724	564, 722	2.60	8.67	98 (5)

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