Journal of Chromatography A, 1216 (2009) 147–153

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Simple approach based on ultrasound-assisted emulsification-microextraction for determination of polibrominated flame retardants in water samples by gas chromatography–mass spectrometry

Ariel R. Fontana[a], Rodolfo G. Wuilloud[a,b,c], Luis D. Martínez[b,d], Jorgelina C. Altamirano[a,b,c,*]

[a] *Laboratorio de Investigaciones y Servicios Ambientales Mendoza, Centro Científico Tecnológico-CONICET-Mendoza, PO Box 131, 5500 Mendoza, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Avda. Rivadavia 1917, CP C1033AAJ Buenos Aires, Argentina*
[c] *Departamento de Química, Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Parque General San Martín, 5500 Mendoza, Argentina*
[d] *Area de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, PO Box 375, 5700 San Luis, Argentina*

ARTICLE INFO

Article history:
Received 7 August 2008
Received in revised form 7 November 2008
Accepted 13 November 2008
Available online 19 November 2008

Keywords:
Polybrominated diphenyl ethers
Brominated flame retardants
Ultrasound-assisted emulsification-microextraction
Water analysis
Gas Chromatography–mass spectrometry

ABSTRACT

A simple, efficient, innovative and environmentally friendly analytical technique was successfully applied for the first time for the extraction and preconcentration of polybrominated diphenyl ethers (PBDEs) from water samples. The PBDEs selected for this work were those most commonly found in the literature in natural water samples: 2,2′,4,4′-tetraBDE (BDE-47), 2,2′,4,4,5-pentaBDE (BDE-99), 2,2′,4,4,6-pentaBDE (BDE-100) and 2,2,4,4′,5,5′-hexaBDE (BDE-153). The extracted PBDEs were separated and determined by gas chromatography–mass spectrometry (GC–MS). The extraction/preconcentration technique is based on ultrasound-assisted emulsification-microextraction (USAEME) of a water-immiscible solvent in an aqueous medium. Several variables including, solvent type, extraction time, extraction temperature and matrix modifiers were studied and optimized over the relative response the target analytes. Chloroform was used as extraction solvent in the USAEME technique. Under optimum conditions, the target analytes were quantitatively extracted achieving enrichment factors (EF) higher than 319. The detection limits (LODs) of the analytes for the preconcentration of 10 mL sample volume were within the range 1–2 pg mL^{-1}. The relative standard deviations (RSD) for five replicates at 10 pg mL^{-1} concentration level were <10.3%. The calibration graphs were linear within the concentration range of 5–5000 pg mL^{-1} for BDE-47 and BDE-100; and 5–10,000 pg mL^{-1} for BDE-99 and BDE-153, respectively. The coefficients of estimation were $\geq$0.9985. Validation of the methodology was performed by standard addition method at two concentration levels (10 and 50 pg mL^{-1}). Recovery values were $\geq$96%, which showed a successful robustness of the analytical methodology for determination of picogram per milliliter of PBDEs in water samples. Significant quantities of PBDEs were not found in the analyzed samples.

1. Introduction

In the last 50 years polymer industry has notoriously grown, providing polymers with particular properties, which have spread and diversified their applications [1,2]. Due to the flammable character of many polymers it is necessary to add flame retardant (FR) compounds in order to complement safety regulation for their commercialization. Among the most commonly used FR, brominated flame retardants (BFRs) has been the most applied group due to the high efficiency of the bromine atoms to capture free radicals generated during the combustion process [1–3]. Polybrominated diphenyl ethers (PBDEs) are included in this group of compounds. PBDEs have become a ubiquitous analyte of the environment because of their widespread use, and their predisposition to be released from the polymeric mass. Furthermore, their concentration levels found in global environment as well as in human and other biota samples have rapidly increased in the last three decades [3]. PBDEs have a non-polar character, which favoured their bioaccumulation in hydrophobic mediums in biota, such us humic substances and fat tissues. In this way, they can easily reach animals and humans via their food chain [4,5]. Several epidemiological studies have shown PBDEs to pose health risks [6–9] such as endocrine disruption and adverse neurobehavioral effects. They also act as feasible reproductive toxicants, and probable carcinogens [9].

---

* Corresponding author at: Laboratorio de Investigaciones y Servicios Ambientales Mendoza, Centro Científico Tecnológico-CONICET-Mendoza, PO Box 131, ZC 5500 Mendoza, Argentina. Tel.: +54 261 524 4064; fax: +54 261 524 4001.
E-mail address: jaltamirano@mendoza-conicet.gov.ar (J.C. Altamirano).

0021-9673/$ – see front matter
doi:10.1016/j.chroma.2008.11.034

As a consequence of the occurrence of PBDEs in the environment, there is a growing interest in developing analytical methods for determining them in these types of samples [10–12]. Sample preparation plays an important role in the determination of PBDEs in environmental samples because of the matrixes complexity and the low concentration of these analytes. Highly selective and sensitive analytical techniques are required for their unequivocal identification and determination. In this way, capillary gas chromatography (GC) with electron-capture (ECD) or mass spectrometry (MS) detection are the chosen techniques for this type of analysis [3]. Since PBDEs concentration levels in natural water samples are regularly low ($\leq$80 ng L^{-1}) it is necessary to count on highly efficient preconcentration techniques for their determination by GC [13–15]. The extraction of PBDEs from environmental water samples has been usually carried out by using conventional liquid–liquid extraction (LLE), solid-phase microextraction (SPME) or stir bar sorptive extraction (SBSE) [16–20]. In the past few years new extraction techniques, especially in the microextraction category, have gained interest. Efforts have been placed on the miniaturization of the LLE extraction procedure by greatly reducing the required organic solvent amount. In this way, Jeannot and Cantwell have developed a liquid-phase microextraction (LPME) technique, which is based on analyte partition between a drop of organic solvent (extraction phase) and the aqueous sample bulk [21]. Microextraction techniques are fast, simple, inexpensive, environmentally friendly and compatible with many analytical instruments [22]. Up to now, several different types of LPME have been developed including, single drop microextraction (SDME) [23], hollow fiber LPME [24], headspace LPME [25] and dynamic LPME [26]. Nevertheless, some drawbacks, such as instability of droplet and relative low precision are often reported [27]. The application of ultrasonic (US) radiation is an efficient tool to facilitates the emulsification phenomenon and accelerate the mass-transfer process between two immiscible phases. This leads to an increment in the extraction efficiency of the technique in a minimum amount of time [28,29]. The most widely accepted mechanism for US-assisted emulsification is based on the cavitation effect. It is based on the implosion bubbles generated by the cavitation phenomenon, which produces intensive shock waves in the surrounding liquid and high-velocity liquid jets. Such microjets can cause droplet disruption in the vicinity of collapsing bubbles and thus, improve emulsification by generating smaller droplet size of the dispersed phase right after disruption [28]. Submicron droplet-size leads to significant enlargement of the contact surface between both immiscible liquids improving the mass-transfer between the phases. The combination of micro-extracting systems and ultrasounds radiation provides an efficient preconcentration technique, such as USAEME for determining analytes at trace level. In fact, this preconcentration technique has been developed by Regueiro et al. [30], who successfully applied it to determine synthetic musk fragrances, phthalate esters and lindane in aqueous samples. They demonstrated that USAEME is an efficient, simple, rapid and non-expensive extraction technique for GC analysis.

The purpose of the present work is to demonstrate that such an innovative and environmentally friendly technique (USAEME) can be successfully applied for extraction and preconcentration of PBDEs from water samples and further determination by GC–MS. To this end, and based on PBDEs relative abundance in environmental samples, four of the most commonly studied PBDEs in this type of samples were selected from the 209 possible congeners: 2,2′,4,4′-tetraBDE (BDE-47), 2,2′,4,4,5-pentaBDE (BDE-99), 2,2′,4,4,6-pentaBDE (BDE-100) and 2,2,4,4′,5,5′-hexaBDE (BDE-153). Several factors, including solvent type, extraction time and temperature and matrix modifiers were studied and optimized over the relative response of the PBDEs. The analytical performance of USAEME–GC–MS methodology was evaluated in terms of detection limits (LODs), repeatability and linear working range and also was evaluated the enrichment factor (EF) of the USAEME technique. The type of samples analyzed includes tap, lake and river water.

2. Experimental

2.1. Reagents

The standards of PBDEs were purchased from Accustandard (New Haven, CT, USA) and consisted of: 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). The physicochemical properties of these four PBDEs are given in Table 1. Decachloro biphenyl (PCB-209) was used as internal standard (IS), and was purchased from Dr. Ehrenstorfer (Augsburg, Germany). The PBDEs standards were stored in the dark at −20 °C. Stock solutions of PBDEs and internal standard were prepared in methanol at concentration levels of 1 μg mL^{-1}. Further dilutions were prepared monthly in methanol and stored in brown bottles at −20 °C.

Methanol, dichloromethane, chloroform and trichloroethylene were purchased from Merck (Darmstadt, Germany) and carbon tetrachloride was purchased from Sigma–Aldrich (Steinheim, Ger-

Table 1
GC–MS parameters and physicochemical properties of target PBDEs.

Analyte	t'_R (min)	Target ion (m/z)	Confirmation ions (m/z)	b.p. (°C)	log K_{ow} [38]
BDE-47	0.80	485.7	483.7, 325.8	396	6.81
BDE-100	0.89	403.7	563.6, 405.7	434	7.24
BDE-99	0.92	403.7	563.6, 405.7	416	7.32
BDE-153	1.08	483.6	643.5, 485.6	453	7.90

t'_R: relative retention times to PCB-209; b.p.: boiling point; log K_{ow}: octanol/water partition coefficient.

Table 2
USAEME–GC–MS analytical performance[a].

PBDE	RSD (%)	EF	Linear range (pg mL^{-1})	r^2	LOD (pg mL^{-1})
BDE-47	8.3	333	5–5000	0.9987	2
BDE-100	9.4	328	5–5000	0.9988	2
BDE-99	9.8	324	5–10,000	0.9984	1
BDE-153	10.4	319	5–10,000	0.9985	1

Extraction conditions: sample volume: 10 mL; extraction solvent: 100 μL CH_3Cl; extraction time, 5 min; centrifugation time: 2 min; extraction temperature: 35 °C.

[a] 95% confidence interval; $n = 5$.