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Recent developments in the analysis of polybrominated diphenyl ethers and polybrominated biphenyls in plastic

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Abstract: Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs), heavily used as flame retardant in plastics, are harmful to environment and human health. It is of great importance for method development to determine PBDEs and PBBs in plastics. A review of developments on the analysis of PBDEs and PBBs in plastics is presented in this paper. The analytical procedures including sample pretreatment, extraction, clean-up/fractionation, and detection are carefully discussed. The drawbacks and merits of each method are summarized. The aim of this review is to improve the analytical accuracy, and precision for the determination of PBDEs and PBBs in plastics on the basis of the published papers.

Keywords: mass spectrometry; plastic; polybrominated biphenyl; polybrominated diphenyl ether; review.

Introduction

Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) have been heavily used as additives in plastics of electrical and electronic equipment to improve fire retardancy properties (Wolf et al. 2000, Hoh et al. 2005). Because they are not chemically bound to the polymer, they are prone to volatilize and/or leach out into the air or aquatic environment from landfill (Talsness

2008, Zeleny et al. 2010). PBDEs and PBBs appear to be lipophilic and bioaccumulative in wildlife and human, which leads to adverse physiological effects (Covaci et al. 2007). Therefore, the industrial chemicals of tetra-BDE, penta-BDE, hexa-BDE, and hepta-BDE were added to the Stockholm Convention list of persistent organic pollutants in 2009. The usage of PBDEs in new electric and electronic equipment is prohibited in European Union as of 2006 according to European Commission Directive 2002/95/EC. The usage of PBDEs and PBBs in plastics has also been restricted in other countries such as Australia, Canada, Japan, and China.

The development of analytical methods to enable reliable detection of PBDEs and PBBs in plastics is therefore of great importance for environment protection and human health. Several analytical methods for the determination of PBDEs and PBBs have been published. Some reference materials for the analysis of PBDEs/PBBs in styrenic polymers have been developed to improve the quality of flame retardant analysis (Pöhlein et al. 2009, Roth et al. 2015). Furthermore, an international comparison, conducted by the Organic Analysis Working Group of the Consultative Committee for Amount of Substance-Metrology in Chemistry, was carried out to assess the measurement capabilities of national metrology institutes on the accurate determination of PBDEs and PBBs in plastic (Hoh et al. 2005). Given the instability of the analytes and complexity of matrices, several challenges exist in the method development for accurate quantification of PBDEs and PBBs in plastic. The analytical procedures including sample pretreatment, extraction, clean-up/fractionation, and detection are carefully reviewed in this paper.

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Analytical procedures

The analytical procedures are carried out sequentially by sample pretreatment, extraction, clean-up/fractionation, and detection. Several analytical procedures for the determination of PBDEs/PBBs in plastics were published recently. Relevant references are summarized in Table 1.

Table 1: Overview of typical analytical procedures used for the determination of PBDEs and PBBs in plastics.

Sample	Compounds	Pretreatment (particle size)	Extraction (solvent, time)	Clean-up	Instrument	References
TV, computer housings	Deca-, octa-, penta-BDE Deca-, octa-, hexa-BB	Grind (1000 µm)	Soxhlet (methanol and n-propanol, 3 h)	n.s.	RP-LC-UV	Riess and van Eldik (1998)
Mixed plastics from WEEE	Penta-, octa-, deca-BDE	Grind (120 µm)	Soxhlet [cyclohexane and acetone (1:1), 16 h]	n.s.	GC-ECD	Wäger et al. (2011)
Hard/soft plastic toys	BDE 28, 47, 66, 99, 100, 138, 153, 154, 183, 196, 197, 203, 206, 207, 208, 209, BB 153, 209	Cut into tiny fragments	Soxhlet [acetone and hexane (1:1), 24 h]	Silica/alumina column	GC-MS	Chen et al. (2009)
WEEE	Tetra-, penta-, hexa-, hepta-, octa-BDE	Grind (900 µm)	UAE [pheno/tetrachloroethane (1:1), 30 min, twice]	n.s.	GC-MS	Wu et al. (2007)
WEEE	Di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-BB	Grind (900 µm)	UAE [chloroform/hexane (1:1), 30 min]	Methanol as precipitation solvent	GC-MS	Chen et al. (2012)
HDPE, PS, ABS, PP	Tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-BDE Di-, hexa-, hepta-, octa-, deca-BB PBDE 47, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209, PBB 209	Grind (1000 µm)	UAE (toluene for HDPE, PP and ABS, toluene for PS, 30 min)	Iso-octane as precipitating solvent	HPLC-ICP-MS	Mingwu et al. (2010)
TV, PC monitor	Penta-, octa-, deca-BDE	Grind (1000 µm)	UAE (isopropanol, 5 min)	n.s.	RP-HPLC-UV	Pöhlein et al. (2005)
ABS, PS, HIPS	Octa-, deca-BB Deca-, octa-, penta-BDE Deca-, hexa-, octa-BB	Grind (1000 µm)	UAE (toluene, 20 min)	Iso-octane or 1-propanol as precipitating solvent	GC-MS and GC-ECD	Pöhlein et al. (2008)
HIPS	Hexa-, hepta-, octa-, nona-, deca-BDE	Grind (100–300 µm)	UAE [toluene/THF (1:1), toluene or dichloromethane, 15 min], shaking for 5 min	Methanol as precipitating solvent	GC-ECD	Kim et al. (2012)
HIPS, ABS, SB	Deca-BDE	Grind (5000 µm)	MAE (isopropanol/n-hexane, 30 min, 130°C)	n.s.	HPLC-UV	Vilaplana et al. (2009)
PE, PS	Deca-BDE	Grind (2000–3000 µm)	MAE [toluene/methanol (7.5:2.5), 40 min, 124°C for PE, 111°C for PS]	n.s.	HPLC-DAD	Ranz et al. (2008)
WEEE	Octa-, deca-BDE	n.s.	PLE (THF, 10 MPa, 120°C)	n-Hexane as precipitating solvent	XRF, GC-ECD, GC-HRMS	Sindikü et al. (2015)
WEEE (ABS, HIPS, PC, PPO)	Penta-, octa-, deca-BDE	n.s.	PLE (iso-octane, 10 MPa, 120°C, three cycles)	Gel permeation chromatography	HPLC-UV/ MGPHPLC-UV	Schlummer et al. (2005)
PP, PE, ABS	BDE 47, 183, 206, 209, BB 209	Grind (1000 µm)	PLE (iso-octane, 100 bar, 10 min, three cycles, PP 80°C, PE, ABS 70°C)	n.s.	GC-IDMS	Binici et al. (2013)
WEEE	Octa-, deca-BDE	Grind	PLA (toluene or iso-octane, 130°C)	1-Propanol as precipitating solvent	HPLC-UV/MS	Schlummer et al. (2007)
HIPS	Deca-BDE	n.s.	SFE (65°C, 20 MPa, supercritical CO ₂ to HIPS solution 2:1)	n.s.	HPLC	Peng et al. (2012)

Table 1 (continued)

Sample	Compounds	Pretreatment (particle size)	Extraction (solvent, time)	Clean-up	Instrument	References
TV housing plastics (HIPS)	Deca-BDE	n.s.	SFE (65°C, 20 MPa, supercritical CO ₂ to HIPS solution 2:1, 40 min)	n.s.	HPLC-UV	Peng et al. (2014)
Printed wiring boards	Deca-BDE	Grind (250 µm)	Soxhlet (80% THF, 140 min, 110°C or 160°C) or UAE (T70, 30 min)	n.s.	GC-MS	Roth et al. (2013)
ABS, PS	Deca-BDE	Grind (1000 µm)	Soxhlet (70 ml 1-propanol, 4 h, 190°C)	n.s.	HPLC-UV	Altwaiq et al. (2003)
Plastics of consumer products	Octa-BDE, BDE 209	Grind	UAE (10 min)	Sulfuric acid/silica column	HPLC-MS	Gallen et al. (2014)
PVC	Deca-BDE	Grind (1000 µm)	UAE (toluene and hexane, 60 min)	Acidic silica column	GC-MS	Li et al. (2009)
WEEE (HIPS, ABS)	BDE 28, 47, 99, 100, 153, 154, 183 209	n.s.	Soxhlet (isopropanol, 60 min boiling, and 120 min rinsing, 190°C)	n.s.	HPLC-DAD	Huang et al. (2010)

Polymer: ABS, Acrylonitrile butadiene styrene; HDPE, high-density polyethylene; HIPS, high impact polystyrene; PC, polycarbonate; PE, polyethylene; PPO, poly(propylene oxide); PS, polystyrene; PVC, poly(vinyl chloride); SB, styrene butadiene. Solvent: DCM, dichloromethane; THF, tetrahydrofuran. WEEE, waste electric and electrical equipment; RP, reverse phase; HPLC, high performance liquid chromatography; DAD, diode array detector; IDMS, isotope dilution mass spectrometry; HRMS, high resolution mass spectrometry. n.s., not specified.

Sample pretreatment

The plastic samples need to be cut into fragments, then embrittled with liquid nitrogen, and ground to small particles prior to extraction. The effect of particle size on the extraction efficiency was systematically investigated (Vilaplana et al. 2009). It was found that the particle size would have a minor influence on the extraction efficiency when the diameter of the particle was changed from 5 mm to 1 µm.

Extraction

To accurately determine PBDEs and PBBs in plastic, the analytes should be completely extracted from matrix, similarly as in the case of any other matrices. Current available extraction methods include Soxhlet extraction, ultrasonic-assisted extraction (UAE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), and supercritical fluid extraction (SFE).

Soxhlet extraction

Soxhlet extraction, a traditional liquid-solid extraction technique, is widely used because of the advantages of simplicity, low cost, and high efficiency. The combination of polar and nonpolar solvents will improve the extraction efficiency (Boer 1988). Therefore, binary solvent mixtures, such as cyclohexane/acetone and hexane/acetone, are often used as the extraction solvents for the extraction of PBDEs and PBBs from plastics. For example, penta-BDE, octa-BDE, deca-BDE, and deca-BB were successfully extracted by using a mixture of cyclohexane and acetone (1:1) (Wäger et al. 2011).

Ultrasonic-assisted extraction

UAE has several advantages including the saving of solvents, low temperature, and short extraction time, especially suitable for the thermolabile and unstable compounds (Chen et al. 2010). It was demonstrated that UAE had the same extraction efficiency as Soxhlet extraction for the determination of PBDEs and PBBs in waste electric and electrical equipment (Wu et al. 2007).

Microwave-assisted extraction

MAE has attracted growing interest for assisting the extraction of organic and organometallic compounds

from various matrices (Kot and Namiesnik 2000, Vázquez et al. 2008). Unlike classical heating, microwave heats the whole sample simultaneously without heating the vessel. MAE has the advantage of lower solvent consumption, which lowers the cost and makes the procedure more environment friendly (Chan et al. 2011). For example, rapid extraction of deca-BDE from plastic was achieved by using MAE with binary solvents (toluene:methanol=75:25, v/v) (Ranz et al. 2008). The MAE provides an efficient, fast, and low solvent-consuming method compared with Soxhlet extraction.

Pressurized liquid extraction

PLE, also known as an accelerated solvent extraction, is a technique using elevated temperature and pressure to achieve extraction from solid matrices. It reduces solvent consumption and shortens extraction time, and thus enhances analytical throughput compared with a traditional procedure (Vazquez-Roig and Picó 2015). The extraction efficiencies of different extraction techniques (e.g. PLE, MAE, and UAE) were evaluated regarding the determination of some important brominated flame retardants [e.g. tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and deca-BDE] in waste electric and electrical equipment (Vilaplana et al. 2008). PLE showed high extraction efficiency, especially for the extraction of chemicals with high molecular weight. It has to be noticed that the temperature and pressure should be carefully controlled to avoid the collapse of the plastic structure during PLE (Vilaplana et al. 2008).

Supercritical fluid extraction

SFE is another method to extract PBDEs and PBBs from plastic. With supercritical CO₂ as solvent, more than 97% of the PBDEs were successfully extracted from plastic (Peng et al. 2014). In addition, the extraction efficiency of SFE can be further improved when toluene, acetonitrile, and tetrahydrofuran were used as a modifier (Altwaiq et al. 2003).

Clean-up and fractionation

During the extraction of PBDEs and PBBs from plastic, the polymers may be dissolved in the extract. Usually methanol, isooctane, and n-hexane are used to precipitate the dissolved polymers. Alternatively, gel permeation chromatography provides another approach for the separation

of brominated flame retardants and polymer matrix (Schlummer et al. 2005, Li et al. 2009).

Detection with gas chromatography

Gas chromatography (GC) is a commonly used technique for the determination of PBDEs and PBBs in plastic. In order to inject and separate the compounds with high molecular weights, high temperature is inevitable in GC injection and separation systems. However, several PBDEs (e.g. BDE 209) with high boiling points are thermolabile, which makes it difficult to be detected. Thus, it is important to carefully optimize the operational parameters of GC. Recent studies using the GC technique for the determination of PBDEs and PBBs in plastic are summarized in Table 2.

Injection techniques

The introduction of the sample into the GC column is a very important step because it has a great impact on analytical sensitivity, accuracy, precision, and chromatographic resolution. When developing an injection method, the properties (such as boiling point, thermal stability) of the analytes should be considered. A series of injection techniques including split/splitless injection, on-column injection, and programmable temperature vaporization (PTV) injection have been investigated for the determination of PBDEs and PBBs. Each one has merits and demerits in respect of the cost, detection limit, and discrimination of congeners.

The commonly used GC injection technique for the detection of PBDEs and PBBs is split/splitless injection (Boer and Cofino 2002), in which the analytes are immediately vaporized in the injector inlet and subsequently transferred to the GC column. After injection, the analytes are condensed as a narrow band in the column. A small injection volume (1–3 µl) and high injection temperature (250°C–300°C) are normally applied in this process. However, high temperature in the split/splitless injector would lead to thermal degradation of PBDEs with high molecular weight. Therefore, it is necessary to accurately determine an appropriate temperature of the injection port when split/splitless injection is used. The determination of the splitless time is based on the natures of the analytes and solvent, the volume of sampling, sampling injection rate, and carrier gas flow rate. It was found (Björklund et al. 2004) that the optimal injection temperature for the determination of BDE 209 was 325°C with a

Table 2: GC parameters for PBDEs and PBBs analysis.

Sample	Compounds	Column	Dimension	Injection techniques	Detector	Recovery (%)	RSD (%)	LOD	References
WEEE	Di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-BB	Homemade KL-PBB	15 m×0.2 mm×0.10 μm	Split	El-MS	91.3	4.3	5 mg/kg	Wu et al. (2007)
PVC	Deca-, octa-, hexa-BB	Restek, MXT-1	15 m×0.28 mm×0.1 μm	Pulsed splitless	El-MS	92.5	4.1	100 ng/ml	Li et al. (2009)
	90–115					1.10			
WEEE	Di-, hexa-, hepta-, octa-, deca-BB	Homemade KL-PBB	15 m×0.25 mm×0.10 μm	Split	El-MS	n.s.	n.s.	n.s.	Chen et al. (2012)
Hard plastic toys	Tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-BDE	Agilent, DB-XLB	30 m×0.25 mm×0.25 μm	Splitless	ECNI-MS	n.s.	4.1–15.4	0.05–50 ng/g	Chen et al. (2009)
	Tri- to hepta-BDEs, PBB153								
	Octa- to deca- BDEs, and PBB209								
PP, PE, ABS	BDE 47, 183, 206, 209, and BB-209	Agilent, DB-HT5	10 m×0.25 mm×0.25 μm	n.s.	El-MS/MS	79.6–93.7	3.1–4.8	0.079–0.493 mg/kg	Binici et al. (2013)
ABS, PS, HIPS	Deca-, hexa-, octa-BB,	Phenomenex, 5% phenyl–95% methyl-modified polysiloxane capillary column	15 m×0.32 mm×0.25 μm	Splitless	ECD	84	n.s.	0.1–6.5 ng/ml	Pöhlein et al. (2008)
	Deca-, octa-, penta-BDE					101	1.3–7.4 ng/ml		
Waste TV back plate	Deca-BDE	Frontier Lab, Ultra ALLOY-PBDE	15 m×0.25 mm×0.05 μm	n.s.	El-MS	n.s.	4.3	n.s.	Hosaka et al. (2005)

ABS, Acrylonitrile butadiene styrene; HIPS, high impact polystyrene; LOD, limit of detection; PE, polyethylene; PP, polypropylene; PS, polystyrene; PVC, poly(vinyl chloride); RSD, relative standard deviation; WEEE, waste electric and electrical equipment. n.s., not specified.

splitless time of 4 min to ensure that all the components have been transferred into the column. With this experimental condition, the response signal of BDE 209 was increased by about 25% compared with average settings used in an interlaboratory comparison (Boer and Cofino 2002). Also, the dirty liner in the split/splitless injector may cause degradation of PBDEs. Thus the liner should be replaced regularly or appropriately cleaned to reduce the risk of sample degradation (Björklund et al. 2004).

On-column injection is another suitable technique for introducing samples into GC for the analysis of PBDEs and PBBs (Sjödín et al. 1999). In this method, the sample can be directly injected into the GC column with a suitable carrier solvent, or a glass insert fitted into a septum-equipped programmable injector at low temperature. This GC injector can provide reproducible results with low degree of thermal degradation. However, the sample analyzed should be cleaned enough to eliminate noise signal and prolong the lifetime of the column. Meanwhile, in order to prevent excess solvent from flooding the column and overwhelming the detector, the injection volume is limited to 1–2 μl .

In order to avoid degradation of PBDEs, PTV injection was recommended for GC detection. This method overcomes the shortcomings in the traditional injection technology, such as discrimination, thermal degradation, and the adverse effects of non-volatiles present in the sample. An increase of injection volumes (up to 125 μl) in the PTV process can dramatically improve analytical sensitivity. In this case, the extract should be clean enough to avoid interferences during the GC separation process. In the experiment, several parameters including injection rate or flow, injection temperature, vent flow, solvent elimination time, injection volume, transfer time, and transfer temperature in the PTV process are required to be optimized.

Except the aforementioned three injection methods, an automated rotary valve injector was developed for the determination of PBDEs (Björklund et al. 2003). This method can decrease the discrimination of PBDEs with high molecular weight, enlarge the injection volume, and thus improve the analytical sensitivity.

Column

An optimal chromatographic column should have high resolution, high sensitivity, no discrimination of congeners, and short separation time. Generally, GC columns with low-polarity phases were used to separate various PBDEs and PBBs. To analyze PBBs and PBDEs with high molecular mass and high boiling point, nearly 350°C of

column temperature is required. So the stationary liquid in the GC column must resist high temperature. In order to achieve complete separation, several parameters including polarity of the stationary phase, column length, film thickness, and inner diameter should be investigated systematically. A short (10–15 m), nonpolar DB column with a thin (0.1 μm) stationary phase was found to be the most suitable for measuring the entire range (from low to high bromine substitution) of PBDEs (Björklund et al. 2004).

It is difficult to completely separate all PBDE congeners in one GC column. A comprehensive two-dimensional GC was developed for the separation of PBDEs (La Guardia et al. 2006). Because the separation process takes place in two dimensions, each analyte can be identified by two independent retention times. A combination of a medium polar-apolar column was found to be the best for the analysis of PBDEs in a GC \times GC system (Ballesteros-Gómez et al. 2013). Given this, a comprehensive two-dimensional GC would be a suitable approach for analyzing complicated technical mixtures of PBDEs and PBBs in plastics.

Detection technique

Electron capture detector

Electron capture detector (ECD) is a device which is suitable for detecting compounds containing electronegative elements such as bromine. So it is more sensitive for the determination of PBDEs and PBBs compared with other conventional GC detectors. However, the selectivity of ECD is limited (Alaee et al. 2001), because identification is only based on retention time.

Mass spectrometry

Mass spectrometry is typically used as a GC detector for the determination of PBDEs and PBBs in plastics.

Electron ionization (EI) and electron capture negative ionization (ECNI) are common ionization methods in a GC-mass spectrometer (MS) system for the determination of PBDEs and PBBs. In the EI process, the type of ions formed depends on the number of bromine atoms in the molecules of PBDEs. For lower and higher brominated BDEs, the mass spectrum is dominated by ions of $[M]^+$ and $[M-\text{Br}_2]^+$, respectively (Sánchez-Brunete et al. 2006). ECNI, based on the attachment of an electron to an electrophilic molecule, was also used for the detection of PBDEs and PBBs in plastics (Chen et al. 2009). It takes the advantages of high sensitivity and less fragmentation compared with EI. Besides, inductively coupled plasma (ICP), an element-specific detector, was used to couple GC with MS for the

Table 3: HPLC parameters for PBDE and PBB analysis.

Sample	Compounds	Column	Dimension	Detector	Recovery (%)	LOD	References
PE, PS	Deca-BDE	Grace Smart RP 18	150 mm×4.6 mm×5 μm	DAD (200–400 nm)	PE: 95.1±1.3 92.4±1.4 PS: 91.1±1.3 84.5±1.1	2.40 μg/ml	Ranz et al. (2008)
HIPS, ABS	Octa-, deca-BB Penta-, octa-, deca-BDE	Luna 5 μ Phenyl+Hexyl	150 mm×4.6 mm×5 μm	UV (200–400 nm)	n.s.	1.4–4.5 μg/ml	Pöhlein et al. (2005)
TV, computer housings	Deca-, octa-, penta-BDE Deca-, octa-, hexa-BB	Nucleosil ET 250/4/8	250 mm×4 mm×7 μm	UV	n.s.	20–48 μg/ml	Riess and van Eldik (1998)
HIPS, ABS, SB	Deca-BDE	C ₁₈ Hypersyl ODS column	250 mm×4.6 mm×5 μm	UV	n.s.	0.21 μg/ml	Vilaplana et al. (2009)
WEEE (HIPS, ABS)	BDE 28, 47, 100, 99, 154, 153, 183, 209 Octa-BDE, BDE-209	Shimadzu VP-ODS Gemini C ₁₈	250 mm×4.6 mm×5 μm 50 mm×2 mm×3 μm	DAD APCI-MS	78.9–91.3 n.s.	0.05–0.10 μg/g n.s.	Huang et al. (2010) Gallen et al. (2014)
PS	Deca-BDE	C ₁₈ Hypersyl ODS	250 mm×4.6 mm×5 μm	APCI-MS/MS	n.s.	0.011–0.012 μg/ml	Vilaplana et al. (2008)
HDPE, PS, ABS, PP	PBDE 47, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209, PBB-209	Agilent TC-C ₁₈ for PBDEs Waters PAHs for PBB-209	250 mm×4.6 mm×5 μm 250 mm×4.6 mm×5 μm	ICP-MS	84.1–102	5.90–7.55 mg/kg	Mingwu et al. (2010)
WEEE (ABS, HIPS, PC, PPO)	Hexa-, octa-BB Penta-, octa-, deca-BDE	Hypersil ODS	250 mm×4.6 mm×5 μm	APCI-UV/MS	n.s.	Octa-, deca-BDE: 0.01–1 μg/ml penta-BDE, hexa-, octa-BB: >100 μg/ml	Schlummer et al. (2005)

Polymer: ABS, Acrylonitrile butadiene styrene; DAD, diode array detector; HDPE, high-density polyethylene; HIPS, high impact polystyrene; LOD; limit of detection; PC, polycarbonate; PE, polyethylene; PP, polypropylene; PPO, poly(phenylene oxide); PS, polystyrene; SB, styrene butadiene. WEEE, waste electric and electrical equipment. n.s., not specified.

determination of ultra-trace PBDEs in the sewage sludge samples (Vonderheide et al. 2002). It is foreseeable that this method will be applied for analyzing PBDEs and PBBs in plastic samples.

Several mass analyzers are available as a detector of GC system. Quadrupole is a typical mass analyzer for routine analysis of PBDEs and PBBs in plastic (Binici et al. 2013). However, potential interferences from chlorinated compounds may hamper data quality because the mass resolution of quadrupole is not very satisfied. For example, di-BDEs (m/z 325.8942) and penta-chlorinated biphenyl (CB)s (m/z 325.8804) have almost the same masses. A mass analyzer with a high mass resolution of 24,000 is required to distinguish them (Covaci et al. 2003, Eljarrat et al. 2003). The time-of-flight mass analyzer (Ballesteros-Gómez et al. 2013, 2014) was demonstrated to have high mass resolution and high mass accuracy for the determination of PBDEs and PBBs.

Detection with liquid chromatography

Most of PBDEs and PBBs with high molecular weight are thermally labile compounds. However, high temperatures in some of the GC injection and column systems are inevitable in the determination of high molecular weight compounds such as octa-, nona-, and deca-BDE (Björklund et al. 2004). An alternative approach to GC is to utilize liquid chromatography (LC) for the separation. Table 3 summarizes the LC methods used for the analysis of PBDEs/PBBs in plastic samples.

Ultraviolet-visible spectrophotometer (UV) is a commonly used detector for LC. The LC-UV method has advantages of low cost and simplicity of instrumentation, and thus was developed for the determination of PBDEs and PBBs in plastic (Pöhlein et al. 2005, Ranz et al. 2008). However, it suffers from poor selectivity, which limits the application on the analysis of complex samples.

MS is another detector used for LC. MS takes the advantages of high sensitivity, high selectivity, and elucidation capacity of molecular structure. Equipped with atmospheric pressure chemical ionization (APCI) (Zhou et al. 2010, Papachlimitzou et al. 2012) and atmospheric pressure photoionization (APPI) (Debrauwer et al. 2005), LC-MS allows structural identification of PBDEs and PBBs. Notably, LC-MS shows high quantitative accuracy with ICP as an ionization technique. In our lab (National Institute of Metrology, China), an LC-ICP-MS method was developed to determine PBDEs and PBBs (e.g. BDE-47, BDE-183, BDE-206, BDE-209, and PBB-209) in plastic (Mingwu et al. 2010). The results indicated that this method has the

advantages of high sensitivity, high precision, and high accuracy.

Direct detection methods

Several methods including liquid extraction surface analysis mass spectrometry (Paine et al. 2014), thermal desorption mass spectrometry (Hosaka et al. 2005), direct probe coupled with APCI (Ballesteros-Gómez et al. 2013), APPI (Ballesteros-Gómez et al. 2014), and pyrolysis-GC mass spectrometry (Riess et al. 2000a,b) were developed for direct, fast detection of PBDEs and PBBs in plastic, compromising the analytical accuracy. Also, an electrothermal vaporization coupling with ICP-MS (Okamoto et al. 2010) and X-ray fluorescence (XRF) portable analyzer (Pöhlein et al. 2008) are available for direct determination of bromine in plastics with sufficient sensitivity.

Conclusion

Many methods are available for the determination of PBDEs and PBBs in plastics, considering the trace content and the complexity of the samples. Several challenges need to be carefully handled to achieve successful determination of PBDEs and PBBs in plastics with high accuracy and precision. Suitable grinding of the plastic sample, selective extraction to minimize co-extraction of possibly interfering compounds, and prevention against degradation of measurands (e.g. BDE 209) during the analysis will contribute to the expected result.

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References

- Alaee, M.; Backus, S.; Cannon, C. Potential interference of PBDEs in the determination of PCBs and other organochlorine contaminants using electron capture detection. *J. Sep. Sci.* **2001**, *24*, 465–469.
- Altwaiq, A.; Wolf, M.; van Eldik, R. Extraction of brominated flame retardants from polymeric waste material using different solvents and supercritical carbon dioxide. *Anal. Chim. Acta* **2003**, *491*, 111–123.
- Ballesteros-Gómez, A.; Boer, J.; Leonards, P. E. Novel analytical methods for flame retardants and plasticizers based on gas chromatography, comprehensive two-dimensional gas

- chromatography, and direct probe coupled to atmospheric pressure chemical ionization-high resolution time-of-flight-mass spectrometry. *Anal. Chem.* **2013**, *85*, 9572–9580.
- Ballesteros-Gómez, A.; Brandsma, S.; Boer, J.; Leonards, P. Direct probe atmospheric pressure photoionization/atmospheric pressure chemical ionization high-resolution mass spectrometry for fast screening of flame retardants and plasticizers in products and waste. *Anal. Bioanal. Chem.* **2014**, *406*, 2503–2512.
- Binici, B.; Bilsel, M.; Karakas, M.; Koyuncu, I.; Goren, A. C. An efficient GC-IDMS method for determination of PBDEs and PBB in plastic materials. *Talanta* **2013**, *116*, 417–426.
- Björklund, J.; Tollbäck, P.; Dyremark, E.; Östman, C. Automated rotary valve injection for polybrominated diphenyl ethers in gas chromatography. *J. Sep. Sci.* **2003**, *26*, 594–600.
- Björklund, J.; Tollbäck, P.; Hiärne, C.; Dyremark, E.; Östman, C. Influence of the injection technique and the column system on gas chromatographic determination of polybrominated diphenyl ethers. *J. Chromatogr. A* **2004**, *1041*, 201–210.
- Boer, J. Chlorobiphenyls in bound and non-bound lipids of fishes; comparison of different extraction methods. *Chemosphere* **1988**, *17*, 1803–1810.
- Boer, J.; Cofino, W. P. First world-wide interlaboratory study on polybrominated diphenylethers (PBDEs). *Chemosphere* **2002**, *46*, 625–633.
- Chan, C.-H.; Yusoff, R.; Ngoh, G.-C.; Kung, F. W.-L. Microwave-assisted extractions of active ingredients from plants. *J. Chromatogr. A* **2011**, *1218*, 6213–6225.
- Chen, S.-J.; Ma, Y.-J.; Wang, J.; Chen, D.; Luo, X.-J.; Mai, B.-X. Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. *Environ. Sci. Technol.* **2009**, *43*, 4200–4206.
- Chen, X.; Wang, W.; Li, S.; Xue, J.; Fan, L.; Sheng, Z.; Chen, Y. Optimization of ultrasound-assisted extraction of Lingzhi polysaccharides using response surface methodology and its inhibitory effect on cervical cancer cells. *Carbohydr. Polym.* **2010**, *80*, 944–948.
- Chen, Y.; Li, J.; Chen, L.; Chen, S.; Diao, S. W. Brominated flame retardants (BFRs) in waste electrical and electronic equipment (WEEE) plastics and printed circuit boards (PCBs). *Procedia Environ. Sci.* **2012**, *16*, 552–559.
- Covaci, A.; Voorspoels, S.; Boer, J. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples—a review. *Environ. Int.* **2003**, *29*, 735–756.
- Covaci, A.; Voorspoels, S.; Ramos, L.; Neels, H.; Blust, R. Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *J. Chromatogr. A* **2007**, *1153*, 145–171.
- Debrauwer, L.; Riu, A.; Jouahri, M.; Rathahao, E.; Jouanin, I.; Antignac, J.-P.; Cariou, R.; Bizec, B.; Zalko, D. Probing new approaches using atmospheric pressure photo ionization for the analysis of brominated flame retardants and their related degradation products by liquid chromatography-mass spectrometry. *J. Chromatogr. A* **2005**, *1082*, 98–109.
- Eljarrat, E.; Cal, A.; Barceló, D. Potential chlorinated and brominated interferences on the polybrominated diphenyl ether determinations by gas chromatography-mass spectrometry. *J. Chromatogr. A* **2003**, *1008*, 181–192.
- Gallen, C.; Banks, A.; Brandsma, S.; Baduel, C.; Thai, P.; Eaglesham, G.; Heffernan, A.; Leonards, P.; Bainton, P.; Mueller, J. F. Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci. Total Environ.* **2014**, *491*, 255–265.
- Hoh, E.; Zhu, L.; Hites, R. A. Novel flame retardants, 1,2-bis(2,4,6-tribromophenoxy) ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States' environmental samples. *Environ. Sci. Technol.* **2005**, *39*, 2472–2477.
- Hosaka, A.; Watanabe, C.; Tsuge, S. Rapid determination of decabromodiphenyl ether in polystyrene by thermal desorption-GC/MS. *Anal. Sci.* **2005**, *21*, 1145–1147.
- Huang, F.; Meng, X.; Chen, L.; Xiang, N.; Liu, Y.; Li, G. A novel sample pretreatment method for the analysis of polybrominated diphenyl ethers in polymers of waste electrical and electronic equipment (WEEE). *Chinese J. Chem.* **2010**, *28*, 1475–1481.
- Kim, D.; Park, S.; Choi, Y.; Lee, S. K. Optimization of solvent for the determination of polybrominated diphenyl ethers in high-impact polystyrene by GC/ECD. *Bull. Korean Chem. Soc.* **2012**, *33*, 3485–3488.
- Kot, A.; Namiesnik, J. The role of speciation in analytical chemistry. *Trend Anal. Chem.* **2000**, *19*, 69–79.
- La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247–6254.
- Li, Y.; Hashi, Y.; Liu, Y.; Li, H.-F.; Lin, J.-M. Comparison and optimization of several pretreatment techniques for determination of decabrominated diphenyl ether in polymer samples by gas chromatography mass spectrometry. *Anal. Sci.* **2009**, *25*, 523–527.
- Mingwu, S.; Chao, W.; Yongjuan, J.; Xinhua, D.; Xiang, F. Determination of selected polybrominated diphenylethers and polybrominated biphenyl in polymers by ultrasonic-assisted extraction and high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Anal. Chem.* **2010**, *82*, 5154–5159.
- Okamoto, Y.; Komori, H.; Kataoka, H.; Tsukahara, S.; Fujiwara, T. Direct determination of bromine in plastics by electrothermal vaporization/inductively coupled plasma mass spectrometry using a tungsten boat furnace vaporizer and an exchangeable sample cuvette system. *Rapid Commun. Mass Spectrom.* **2010**, *24*, 1265–1270.
- Paine, M. R.; Rae, I. D.; Blanksby, S. J. Direct detection of brominated flame retardants from plastic e-waste using liquid extraction surface analysis mass spectrometry. *Rapid Commun. Mass Spectrom.* **2014**, *28*, 1203–1208.
- Papachlimitzou, A.; Barber, J. L.; Losada, S.; Bersuder, P.; Law, R. J. A review of the analysis of novel brominated flame retardants. *J. Chromatogr. A* **2012**, *1219*, 15–28.
- Peng, S.; Liang, S.; Yu, M. Extraction of polybrominated diphenyl ethers from plastic solution by supercritical carbon dioxide anti-solvent. *Procedia Environ. Sci.* **2012**, *16*, 327–334.
- Peng, S.; Liang, S.; Yu, M.; Li, X. Extraction of polybrominated diphenyl ethers contained in waste high impact polystyrene by supercritical carbon dioxide. *J. Mater. Cycles. Waste* **2014**, *16*, 178–185.
- Pöhlein, M.; Llopis, A. S.; Wolf, M.; van Eldik, R. Rapid identification of RoHS-relevant flame retardants from polymer housings by ultrasonic extraction and RP-HPLC/UV. *J. Chromatogr. A* **2005**, *1066*, 111–117.

- Pöhlein, M.; Bertran, R. U.; Wolf, M.; van Eldik, R. Versatile and fast gas chromatographic determination of frequently used brominated flame retardants in styrenic polymers. *J. Chromatogr. A* **2008**, *1203*, 217–228.
- Pöhlein, M.; Bertran, R. U.; Wolf, M.; van Eldik, R. Preparation of reference materials for the determination of RoHS-relevant flame retardants in styrenic polymers. *Anal. Bioanal. Chem.* **2009**, *394*, 583–595.
- Ranz, A.; Maier, E.; Trampitsch, C.; Lankmayr, E. Microwave-assisted extraction of decabromodiphenylether from polymers. *Talanta* **2008**, *76*, 102–106.
- Riess, M.; van Eldik, R. Identification of brominated flame retardants in polymeric materials by reversed-phase liquid chromatography with ultraviolet detection. *J. Chromatogr. A* **1998**, *827*, 65–71.
- Riess, M.; Ernst, T.; Popp, R.; Muller, B.; Thoma, H.; Vierle, O.; Wolf, M.; van Eldik, R. Analysis of flame retarded polymers and recycling materials. *Chemosphere* **2000a**, *40*, 937–941.
- Riess, M.; Thoma, H.; Vierle, O.; van Eldik, R. Identification of flame retardants in polymers using curie point pyrolysis-gas chromatography/mass spectrometry. *J. Anal. Appl. Pyrol.* **2000b**, *53*, 135–148.
- Roth, T.; Wolf, M.; Pöhlein, M.; van Eldik, R. Analysis of flame retardants and elements of concern in printed wiring boards with respect to origin and year of construction. *Anal. Bioanal. Chem.* **2013**, *405*, 7215–7229.
- Roth, T.; Bertran, R. U.; Latza, A.; Andörfer-Lang, K.; Hügelschäffer, C.; Pöhlein, M.; Puchta, R.; Placht, C.; Maid, H.; Bauer, W.; van Eldik, R. Preparation of candidate reference materials for the determination of phosphorus containing flame retardants in styrene-based polymers. *Anal. Bioanal. Chem.* **2015**, *407*, 3023–3034.
- Sánchez-Brunete, C.; Miguel, E.; Tadeo, J. L. Determination of polybrominated diphenyl ethers in soil by ultrasonic assisted extraction and gas chromatography mass spectrometry. *Talanta* **2006**, *70*, 1051–1056.
- Schlummer, M.; Brandl, F.; Mäurer, A.; van Eldik, R. Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *J. Chromatogr. A* **2005**, *1064*, 39–51.
- Schlummer, M.; Gruber, L.; Mäurer, A.; Wolz, G.; van Eldik, R. Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management. *Chemosphere* **2007**, *67*, 1866–1876.
- Sindik, O.; Babayemi, J.; Osibanjo, O.; Schlummer, M.; Schluep, M.; Watson, A.; Weber, R. Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria. *Environ. Sci. Pollut. R.* **2015**, *22*, 14489–14501.
- Sjödén, A.; Hagmar, L.; Klasson-Wehler, E.; Kronholm-Diab, K.; Jakobsson, E.; Bergman, A. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ. Health Persp.* **1999**, *107*, 643–648.
- Talsness, C. E. Overview of toxicological aspects of polybrominated diphenyl ethers: a flame-retardant additive in several consumer products. *Environ. Res.* **2008**, *108*, 158–167.
- Vázquez, A. S.; Costa-Fernandez, J. M.; Encinar, J. R.; Pereiro, R.; Sanz-Medel, A. Bromine determination in polymers by inductively coupled plasma-mass spectrometry and its potential for fast first screening of brominated flame retardants in polymers and paintings. *Anal. Chim. Acta* **2008**, *623*, 140–145.
- Vazquez-Roig, P.; Picó, Y. Pressurized liquid extraction of organic contaminants in environmental and food samples. *Trend Anal. Chem.* **2015**, *71*, 55–64.
- Vilaplana, F.; Karlsson, P.; Ribes-Greus, A.; Ivarsson, P.; Karlsson, S. Analysis of brominated flame retardants in styrenic polymers: comparison of the extraction efficiency of ultrasonication, microwave-assisted extraction and pressurised liquid extraction. *J. Chromatogr. A* **2008**, *1196*, 139–146.
- Vilaplana, F.; Ribes-Greus, A.; Karlsson, S. Microwave-assisted extraction for qualitative and quantitative determination of brominated flame retardants in styrenic plastic fractions from waste electrical and electronic equipment (WEEE). *Talanta* **2009**, *78*, 33–39.
- Vonderheide, A. P.; Montes-Bayón, M.; Caruso, J. A. Development and application of a method for the analysis of brominated flame retardants by fast gas chromatography with inductively coupled plasma mass spectrometric detection. *J. Anal. At. Spectrom.* **2002**, *17*, 1480–1485.
- Wäger, P. A.; Schluep, M.; Müller, E.; Gloor, R. RoHS regulated substances in mixed plastics from waste electrical and electronic equipment. *Environ. Sci. Technol.* **2011**, *46*, 628–635.
- Wolf, M.; Riess, M.; Heitmann, D.; Schreiner, M.; Thoma, H.; Vierle, O.; van Eldik, R. Application of a purge and trap TDS-GC/MS procedure for the determination of emissions from flame retarded polymers. *Chemosphere* **2000**, *41*, 693–699.
- Wu, H.-Q.; Huang, X.-L.; Huang, F.; Lin, X.-S. Determination of polybromodiphenyl ethers and polybromobiphenyls in electrical and electronic equipments by gas chromatography-mass spectrometry. *Chinese J. Anal. Chem.* **2007**, *35*, 325–329.
- Zeleny, R.; Voorspoels, S.; Ricci, M.; Becker, R.; Jung, C.; Bremser, W.; Sittidech, M.; Panyawathanakit, N.; Wong, W.; Choi, S. Evaluation of the state-of-the-art measurement capabilities for selected PBDEs and decaBB in plastic by the international intercomparison CCQM-P114. *Anal. Bioanal. Chem.* **2010**, *396*, 1501–1511.
- Zhou, S. N.; Reiner, E. J.; Marvin, C.; Helm, P.; Riddell, N.; Dorman, F.; Misselwitz, M.; Shen, L.; Crozier, P.; MacPherson, K. Development of liquid chromatography atmospheric pressure chemical ionization tandem mass spectrometry for analysis of halogenated flame retardants in wastewater. *Anal. Bioanal. Chem.* **2010**, *396*, 1311–1320.

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