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An efficient GC–IDMS method for determination of PBDEs and PBB in plastic materials

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ABSTRACT

In this study, a fast, inexpensive, simple and reliable analytical method, involving pressurized solvent extraction (PSE) system and gas chromatography, coupled to an ion trap tandem mass spectrometry (GC–ITMS–MS), has been developed. It was validated for determination of 2,2′,4,4′-tetrabromodiphenyl (BDE-47), 2,2′,3,4,4′,5′,6-heptabromodiphenyl (BDE-183), 2,2′,3,3′,4,4′,5,5′,6-nonabromodiphenyl (BDE-206) and decabromodiphenyl (BDE-209) ethers and decabromobiphenyl (BB-209) in polypropylene (PP), polyethylene (PE) and acrylonitrile butadiene styrene (ABS) polymeric matrix. Certified reference materials (CRM) were used to assess the trueness of the method. Quantification of the analytes was performed by a primary method, i.e. isotope dilution mass spectrometry (IDMS). An important advantage of the method is speed. While the analysis of a single sample could take one and half hours, analyses of six samples take 5 h. This is due to the automated PSE system, which allows extraction of six samples simultaneously. Automated system increases the repeatability and reduces analyst dedication and human error input. Recoveries between 79.6% and 93.7% were obtained. GC/ITMS–MS presented high selectivity by eliminating matrix effect so that the LOD values of 0.079–0.493 mg/kg in polymeric matrix were obtained. The method was applied to various selected electrical and electronic products. Sum of the mass fractions of PBDE and PBB analytes in the materials was determined to be under 1000 mg/kg, which is the limit defined by directives.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) constitute a large group of brominated flame retardant (BFRs) additives, which are used as building and insulation materials, in textile, vehicle and electrical and electronic equipments to diminish the possibility, and if takes place, intensity of fire [1–3]. At higher temperatures, BFRs prevent chemical reactions that may cause fire by releasing bromine atoms, which are effective at capturing free radicals formed by combustion reactions [4,5]. Compounds used as additive are easily released to the environment [6], which cause adverse effects on human health and the environment due to their lipophilic and bioaccumulative nature [7–11]. Restrictions on the use of certain hazardous substances in electrical and electronic equipments (RoHS) by the European Commission Directive 2002/95/EC [12] prohibits the use of certain polybrominated flame retardants in electrical and electronic devices. Moreover, the European Regulation 850/2004, implementing the Stockholm Convention on persistent organic pollutants (POPs), (Commission Decision 2005/618/EC) [13] sets "maximum limits" for the total sum of polybrominated diphenyl ethers (PBDE) as 0.1 g/100 g (expressed in mass fraction). Turkish Ministry of Environment and Forestry integrated both Restriction of Hazardous Substance (RoHS) and Waste Electrical and Electronic Equipment (WEEE) Directives into a national legislation. Although analysis of the presence of such chemicals in various materials, including polymers is an important task and some methods have already been developed, for analytical chemists, extraction of such materials particularly from polymers is rather a challenging process. In recent years, along with the conventional Soxhlet extraction, ultrasonic, microwave and pressurized liquid extractions (PLE; Dionex trade name ASE for accelerated solvent extraction, Applied Separation trade name PSE for pressurized solvent extraction) have gained considerable interest as they are powerful techniques that reduce extraction time and solvent consumption, and provide automation [14–17].

Gas chromatography/negative chemical ionization mass spectrometry (GC/NCIMS), gas chromatography/high-resolution mass spectrometry (GC–HRMS) and gas chromatography/ion trap mass

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Table 1
ITMS–MS operating conditions.

Compound	Congener		Isolated parent ion (m/z)	Molecular formula	MW (g mol^{-1})	CID voltage (V)	Isolated product ions (m/z)
Tetra-BDE	47	^{12}C	486 $[M]^+$	$C_{12}H_6Br_4O$	485.80	0.98	324/326/328 377/379
	47	^{13}C	498 $[M]^+$	$^{13}C_{12}H_6Br_4O$	497.70	0.95	336/338/340
Hepta-BDE	183	^{12}C	564 $[M-2Br]^+$	$C_{12}H_3Br_7O$	722.48	3.5	402/404/406 453/455/457 481/483/485
	183	^{13}C	576 $[M-2Br]^+$	$^{13}C_{12}H_3Br_7O$	734.39	4	414/416–464/466/468 493/495/497
Nona-BDE	206	^{12}C	720 $[M-2Br]^+$	$C_{12}HBr_9O$	880.28	4	611/612/614/615 558/560/563/564
	206	^{13}C	732 $[M-2Br]^+$	$^{13}C_{12}HBr_9O$	892.18	3.45	623/624/626/628 571/572/573/575/576
Deca-BB	209	^{12}C	784 $[M-2Br]^+$	$C_{12}Br_{10}$	943.2	0.9	703/704/705/706 622/623/625
	209	^{13}C	796 $[M-2Br]^+$	$^{13}C_{12}Br_{10}$	955.08	1.5	714/715/717/718 635/638/639
Deca-BDE	209	^{12}C	800 $[M]^+$	$C_{12}Br_{10}O$	959.17	2	717/719/721/723 690/692/694 638/640/643
	209	^{13}C	812 $[M-2Br]^+$	$^{13}C_{12}Br_{10}O$	971.08	2.5	727/729/731/733/735 700/702/704/706 650/652/654/656

spectrometry (GC/ITMS) are the most commonly used MS techniques for the analyses of PBDE and PBB compounds. Although NCI-MS has higher sensitivity, it has lower selectivity compare with EI-MS, as the dominating bromine isotope ions (m/z 79 and 81), which are often the base peaks in full scan mass spectra, are selected for quantification. On the other hand, EI mode presents molecular ions and sequential loss of bromine atoms, which provides higher quality of structural information. GC coupled with HRMS is the most sensitive technique for organohalogen analysis, which is also used for PBDE determination. Disadvantages of this technique are high acquisition and maintenance costs that most laboratories involved in routine analyses cannot afford. In last the decade, GC/ITMS has been widely applied to the analyses of organic compounds as it eliminates matrix effects of the tandem MS. It is selective, sensitive and allows the use of isotope dilution mass spectrometry for quantification [18–22].

In isotope dilution mass spectrometry (IDMS), at the start of the analysis, an isotopically labeled analog (e.g., ^{13}C, ^{2}H for organic analytes) is added to the sample and allowed to reach equilibrium without any loss or isotopic fractionation. It compensates for any error at all stages of the analysis, i.e. from sample preparation to the final instrumental measurement, the response factor of which is calculated and used to determine the mass fraction of the analyte in the sample. Primary measurement methods, which are traceable to International System of Units like IDMS, provide a viable alternative to estimate "true value" in the absence of CRM [23–25].

In the method validation procedure, several parameters such as linearity, limits of detection and quantification (LOD/LOQ), trueness, repeatability, intermediate precision and uncertainty are assessed. Various laboratories are focused on validating their methods to improve the quality of their results and meet the requirements for ISO standard 17025. In this study, a bottom-up approach was applied to obtain the measurement uncertainty, which provides an opportunity for conducting detailed evaluation of uncertainty sources. It can guide the analytical chemist about the critical stages of the method, where uncertainty needs to be reduced [26–31].

The aim of this study is to develop a validated analytical method to determine the BDE-47, BDE-183, BDE-206, BDE-209 and BB-209 in polypropylene (PP), polyethylene (PE) and acrylonitrile butadiene styrene (ABS) polymeric matrix, using pressurized solvent extraction (PSE) system and gas chromatography, coupled to ion trap tandem mass spectrometry (GC–ITMS–MS). Quantification of the analytes was performed by isotope dilution mass spectrometry (IDMS). The method was applied to the selected consumer products.

2. Experimental

2.1. Sampling

Polypropylene, polyethylene and acrylonitrile butadiene styrene polymeric materials, which are the raw materials of hair dryer, computer monitor, toaster, microwave oven, carpet and electrical cables were obtained from the producers and distributors.

2.2. Calibrations standards

Native and isotopically labeled 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183), 2,2′,3,3′,4,4′,5,5′,6-nonabromodiphenyl ether (BDE-206), decabromodiphenyl ether (BDE-209) and decabromobiphenyl (BB-209) standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

A native stock solution was prepared gravimetrically, containing mass fraction of BDE-47 and BDE-183 in 6 mg kg^{-1} and 12 mg kg^{-1}, respectively, BDE-206, BDE-209 and BB-209 in 30 mg kg^{-1} in isooctane (Merck, Germany). An isotopically labeled stock solution was prepared gravimetrically, containing mass fraction of BDE-47 and BDE-183 in 2.5 mg kg^{-1} and 5 mg kg^{-1}, respectively, and BDE-206, BDE-209 and BB-209 in 12.5 mg kg^{-1} in isooctane. The calibration solutions were prepared at five concentration levels, using native and isotopically labeled stock solution. The concentration range of calibration solutions was presented in Table 5.

2.3. Sample treatment

Extraction of PBDEs and PBB from the polymeric matrix was performed by using pressurized solvent extraction (PSE) technique (Applied Separation, USA). Polymer granules were ground to 1 mm particle size by cryogenic grinder (pulverisette 14, Frisch,

Table 2
GC–MS/MS operating conditions.

Method number	1	2	3	4	5	6	7	8	9	10	11	12
Initial temp. (°C)	140	100	90	100	80	110	100	100	75	120	90	110
First holding time (min)	2	2	1	1	1	3	1	1	20	2	2	5
Rate-1 (°C/min)	10				10	30	20	2		15	30	40
Second temp. (°C)	180				200	200	180	140		230	145	200
Second holding time (min)	0				0	0	0	0		0	14	4.5
Rate-2 (°C/min)	3							4				
Third temp. (°C)	220							220				
Third holding time (min)	0							0				
Rate-3 (°C/min)	10	25	20	25	20	20	5	8	2	5	10	10
Last temp. (°C)	325	295	340	320	300	330	300	330	330	315	300	325
Last holding time (min)	5	14	2	5	15	1	20	1.2	8	1	1	15

Table 3
The applied sample preparation operating conditions.

Method number	Polymeric material	Temperature (°C)	Pressure (bar)	Static time (min)	Cycle	Solvent (%)
1	PP, PE	140	100	3	3	5% Cyclohexane 95% Toluene
2	PP, PE	150	110	3	3	5% Cyclohexane 95% Toluene
3	PP, PE	120	100	3	3	5% Cyclohexane 95% Isooctane
4	PE, ABS	50	100	5	3	100% Isooctane
5	PE, ABS	50	100	10	3	100% Isooctane
6	PE, ABS	60	100	5	3	100% Isooctane
7	PE, ABS	60	100	10	3	100% Isooctane
8	PP, PE, ABS	70	100	5	3	100% Isooctane
9	PP, PE, ABS	70	100	10	3	100% Isooctane
10	PP	80	100	5	3	100% Isooctane
11	PP	80	100	10	3	100% Isooctane
12	PP	90	100	5	3	100% Isooctane
13	PP	90	100	10	3	100% Isooctane

Table 4
Solving conditions of polymeric materials.

Method	Solvent	Amount of solvent (g)	Temperature (°C)	Mixing period (min)	Mixing speed (rpm)
1	Toluene	26	110	70	180
2	Toluene	17	110	70	180
3	Toluene	12	110	55	180
4	Isooctane	20	110	70	180
5	Isooctane	13	110	70	180
6	Isooctane	10	110	55	180

Germany). After a piece of glass wool (Hewlett Packard, USA) was placed to the bottom of a PSE cell (33 ml), 50 mg of sample was introduced into the cell. Then, isotopically labeled standard solution (175 μL) was carefully added, using a gas tight syringe (Hamilton, USA). The remaining part of the cell was filled with glass wool. *Iso*-octane (100%) was used as a solvent. Pressure and static time were kept as 100 bar and 10 min, respectively. The number of applied cycles was three, and flushing duration was 1 min. Temperatures were 80 °C for PP and 70 °C for PE and ABS. The extract was transferred into a round bottom flask (250 mL) and the mixture was concentrated under reduced pressure to 1–2 ml, which was then transferred into an amber glass vial (15 ml). The flask was washed with *iso*-octane (10 ml) and added to the extract. The solvent was evaporated under gentle stream of nitrogen until 2 g of sample was obtained. It was filtered through 0.45 and then 0.2 μm PTFE filters (Whatman, England) before injecting into a GC–MS/MS system.

ERM-EC591 and ERM-EC590, obtained from Institute for Reference Materials and Measurements (IRMM), were used as certified reference materials for the determination of BDE-47, BDE-183, BDE-209 and BB-209 in PP and PE matrixes. The mass fraction range of the target compounds was between 87 mg kg^{-1} and 780 mg kg^{-1} in CRMs.

As there was no CRM, while the dissolved ABS polymeric matrix was spiked with native standard stock solution to develop an extraction method for BDE-47, BDE-183, BDE-206, BDE-209 and BB-209, the dissolved PP and PE polymeric matrixes were spiked with native stock solution to develop an extraction method for BDE-206.

Polymeric material (50 mg) was grounded by cryogenic grinder to 1 mm particle size and then dissolved in toluene (20 ml) at 120 °C and 160 rpm for 1 h. After the polymer–solvent mixture was spiked with 550 mg of native stock solution, it was kept in an oven at 40 °C to evaporate the solvent, which took 56 h to reach a constant mass.

2.4. Instrumental analysis

The analyses were conducted using a GC 2000 series gas chromatography coupled to a Polaris-Q ion trap mass spectrometer (Thermo Electron Corporation, Bremen, Germany). GC–ITMS–MS was in EI mode. Separation of the compounds was performed through a 10 m HT-5 fused silica capillary column (0.25 mm i.d., 0.1 μm film thicknesses). The injection volume was 1 μL. Purified helium was used as a carrier gas with a constant flow rate of 1 mL min^{-1}. The temperature of the ion source was 230 °C. The oven temperature was programmed from 120 °C (held for 2 min) to 230 °C at an increasing rate of 15 °C min^{-1} and from 230 °C to 315 °C (held for 1 min) at an increasing rate of 5 °C min^{-1}. The temperatures of the injection port and interface were kept at 280 °C. The chromatographic separation of the analytes and the examples for the chromatographic separation of native and isotopically labeled compounds are shown in Figs. 1 and 2, respectively.

Detection was based on the patterns of fragmentation of the congeners by MS/MS. The optimized ITMS–MS operating conditions for the analyses of the analytes are summarized in Table 1. IDMS was used to quantify the analytes.

2.5. Experimental setup of the method validation

The analytical method was validated by evaluating the linearity and working range, limit of detection (LOD), limit of quantification (LOQ), trueness, repeatability and intermediate precision parameters.

Table 5
Calibration parameters.

Compounds	Mass fraction range of native compound (mg kg^{-1})	Mass fraction of labeled compound (mg kg^{-1})	R^2	RF	RSD (%)	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
BDE-47	1–5	0.2	0.9979	1.20	5	0.079–0.093	0.26–0.31
BDE-183	2–10	0.4	0.9990	0.92	5.6	0.112–0.156	0.37–0.52
BDE-206	5–25	1	0.9988	0.82	8	0.423–0.440	1.41–147
BDE-209	5–25	1	0.9974	0.95	7.6	0.482–0.493	1.61–1.64
BB-209	5–25	1	0.9971	1.11	8.2	0.463–0.477	1.54–1.59

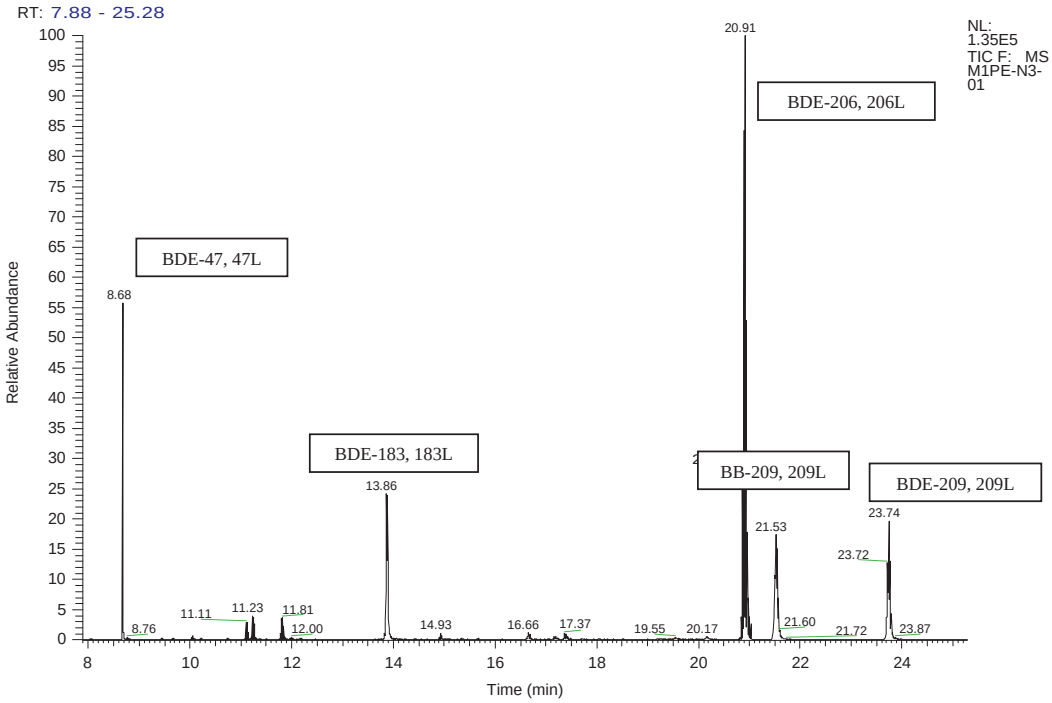

Fig. 1. Chromatographic separation of the PBDE and PBB compounds in sample extract.

3. Results and discussion

3.1. Optimization

3.1.1. GC/MS–MS optimization

Before obtaining suitable GC–MS/MS operating conditions described in Section 2.4, various oven temperature programs (Table 2) were evaluated to have an accurate chromatographic peak separation and proper symmetry on peak shapes.

The initial temperature related to the retention time of first peak in the chromatogram was determined to be 120 °C. As the number of ramps and temperature rates effected the peak separation, after a series of experiments, two ramps and 15 °C/min and 5 °C/min temperature rates were found to be suitable. GC column was selected carefully, considering that the highly brominated congeners have the degradation problems in column. A short column prevents the degradation of the highly brominated PBDEs and PBBs, and due to the high boiling points of PBDEs, a high final temperature is required, which means the column must be resistant to high temperature. Thus, the use of 10 m HT-5 fused silica capillary column (0.25 mm i.d., 0.1 μm film thicknesses) capable of a temperature up to 380–400 °C was preferred.

The ion trap tandem mass spectrometry (IT–MS–MS) technique can eliminate the complexity coming from the sample matrix since tandem mass spectrometry minimizes the chance of isobaric interferences and significantly reduces the noise. It provides perfect selectivity and sensitivity. Additionally, the use of isotope dilution mass spectrometry can overcome the problems associated with the degradation and matrix effect and gives unambiguous quantification of all target analytes and precisions. Uncertainty of the measurement consists of various steps like weighing of initial and final sample, volume of added isotopically labeled standard stock solution, calibration graph, recovery and repeatability. The repeatability parameter has the highest relative uncertainty value in the uncertainty budget. In order to obtain low uncertainty values, method must provide high repeatability, which means high precision. IDMS technique, which is traceable to International System of Units, is the primary measurement method, providing high accuracy and precision compare with internal standard addition or external calibration techniques [32]. The use of IT–MS/MS and IDMS techniques in this study gave high accuracy and precision (Table 6–9).

Initial step for the MS–MS optimization was the selection of most abundant ion from each PBDE and PBB full scan spectrum as the precursor ion acquired on EI mode. Then, PBDE and PBB standard solutions were analyzed in full scan mode in 50–1000 m/z range. The parameters affecting isolation and fragmentation of precursor ions in the ion trap were optimized to achieve the best robustness and sensitivity for the PBDE and PBB analyses. As the $[M]^+$ ion of BDE-47 and BDE-209, and $[M\text{-}2Br]^+$ ions of native and isotopically labeled BDE-183, BDE-206, BB-209 and isotopically labeled BDE-209 were found to be the most intense peaks, they were selected as the precursor ions for the subsequent MS–MS analyses (Table 1). The precursor ion produced parent and product ions which were used for the quantification of PBDE and PBB under application of voltage. The right voltage value was determined, for which, the criteria was

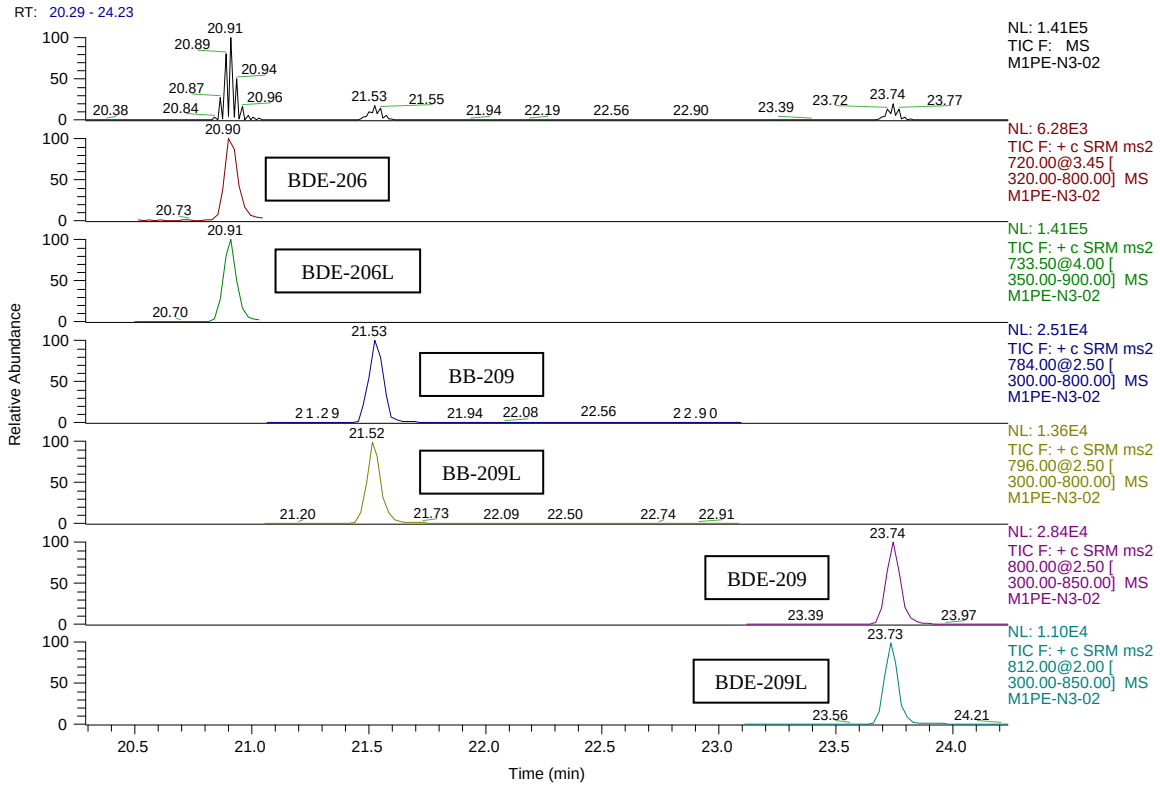

Fig. 2. Chromatographic separation of the native and isotopically labeled PBDE and PBB compounds in sample extract.

Table 6
Recovery results of ERM-EC591 and ERM-EC590.

Compound	ERM-EC591 (PP)		ERM-EC590 (PE)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
BDE-47	90.0	2.5	92.6	2
BDE-183	90.1	2.3	93.9	2.3
BDE-209	88.7	3.5	93.7	3.4
BB-209	85.5	3.1	89.5	3.2

assigned as the relative abundance of product ion to be ≥10% and ≤40% of parent ion. The voltage values are given in Table 1, following the criteria.

3.1.2. *Optimization of sample preparation step*

In the sample preparation part, except the method defined in Section 2.3, different sample preparation conditions were applied to obtain the recovery value of the method between 80% and 100% (Table 3).

The efficiency of the extraction method depends on the type of solvent, temperature, static time and cycle number. The selection of the extraction solvent is the one of the critical step for performing PSE on polymeric matrixes. As the solvents should have high swelling ability and should not dissolve the sample. Then, 100% *iso*-octane gave the satisfactory result.

Temperature is another important parameter, having synergistic effect on both polymer structure and extraction kinetics. In order to increase polymer and analyte mobility during extraction, i.e. extraction efficiency, glass transition (transition from the glassy to the rubbery state in amorphous polymers) temperature (T_g) of a polymer matrix should be below the extraction temperature. Although, diffusion and mass transfer kinetics of an analyte from a polymer matrix into a solvent are generally increased by increase of temperature, stability of the analyte need to be considered as some analytes like highly brominated congeners could have degradation problems. Extraction using *iso*-octane caused dissolution of the polymer at the boiling point of the solvent, even at 90 °C. On the other hand, 70–80 °C was found to be the best extraction temperatures. Then, the best static time, which is the time of transfer of analyte from polymer to solvent, was optimized to be 10 min.

After obtaining the suitable chromatographic and sample preparation conditions, method validation was studied, using either CRM or spiked polymeric material to assess trueness and recovery. After a long study of all the methods with different amounts of polypropylene, 50 mg of polypropylene and the method 2 was found to be the best one (Table 4), which was then applied to all the polymers.

3.2. *Method validation*

An in-house validation procedure was accomplished on the basis of the EURACHEM and IUPAC guidelines [33,34].

3.2.1. *Linearity and working range*

In order to evaluate linearity and working range, calibration solutions were prepared gravimetrically, using native and labeled PBDEs and PBB standard solutions in *iso*-octane at five concentrations and analyzed with three replicates. Concentrations of the labeled standards were kept constant at each level. The calibration graph was established by plotting the peak area ratios for native/labeled compounds versus their mass fraction ratios. Linearity was assessed on the basis of the linear regression and squared correlation coefficient, R^2, which is required to be >0.9950, and RSD of the average response factor. The response factor was calculated by Eq. (1). As the PBDE and PBB are sensitive to light and temperature, RSD was set at 10%. Working range, R^2 and

Table 7
The recovery data of spiking experiments for each polymeric matrix and at each fortification level.

Compounds	Mass fraction (mg kg^{-1})	Recovery	RSD (%)	Mass fraction (mg kg^{-1})	Recovery	RSD (%)	Mass fraction (mg kg^{-1})	Recovery	RSD (%)
ABS									
BDE-47	1	90.5	4.0	2.5	91.1	3.4	5	88.1	3.2
BDE-183	2	92.5	3.0	5	92.0	3.5	10	86.4	3.1
BDE-206	5	88.5	3.8	12.5	90.2	3.9	25	91.5	3.2
BDE-209	5	80.3	4.8	12.5	79.6	3.8	25	85.9	4.1
BB-209	5	79.8	4.6	12.5	85.1	4.1	25	90.7	3.5
PP									
BDE-206	5	81.3	3.5	12.5	88.2	4.1	25	88.6	3.3
PE									
BDE-206	5	86.5	4.6	12.5	84.3	4.1	25	90.1	3.9

Table 8
Repeatability and intermediate precision results (RSD %).

Compound	**PP**		**PE**		**ABS**	
	Within a day	Between days	Within a day	Between days	Within a day	Between days
BDE-47	3.0	4.4	3.9	4.2	3.5	3.8
BDE-183	3.9	3.4	3.6	3.3	3.9	3.6
BDE-206	4.1	3.7	4.2	4.0	3.2	2.9
BDE-209	5.4	4.6	5.7	3.5	5.1	4.5
BB-209	4.9	3.5	4.6	4.4	4.7	3.9

response factor values are given in Table 5. The response factors were also used to determine the mass fraction of the analytes.

$$RF = \frac{A_{ABx} x C_{ISx}}{A_{ISx} x C_{ABx}} \quad (1)$$

RF	Response factor
C_{ABx}	Concentration of native compound (ng/g)
A_{ABx}	Peak area of native compound
A_{ISx}	Peak area of labeled compound
C_{ISx}	Concentration of labeled compound (ng/g)

3.2.2. LOD and LOQ

Certified reference materials were used to develop an analytical method for determination of the analytes in PP and PE matrixes. The mass fractions of the analytes in the CRMs were between 87 mg kg^{-1} and 780 mg kg^{-1} and the working range was constituted according to this mass fraction range. LOD and LOQ studies were carried out by spiking the starting material at lower mass fraction values such as 0.1 mg kg^{-1} for BDE-47, 0.2 mg kg^{-1} for BDE-183 and 0.5 mg kg^{-1} for BDE-206, BDE-209 and BB-209. The analytical method was applied to the 10 spiked samples. The LOD and LOQ values were calculated by multiplying the standard deviation (SD) by 3 and 10, respectively. LOD and LOQ values were presented in a range as they were determined for each matrix.

3.2.3. Trueness

For the assessment of the trueness of BDE-47, BDE-183, BDE-209 and BB-209 in PP and PE matrixes, ERM-EC591 and ERM-EC590 certified reference materials, obtained from Institute for Reference Materials and Measurements (IRMM), were used. The trueness was assessed by means of six replicates of the CRM in a day (Table 6).

Table 9
Expanded relative uncertainty (%) values for all target compounds in each matrix.

Compound	PP	PE	ABS
BDE-47	6.5	7.5	7.1
BDE-183	8	6.7	8.5
BDE-206	9.4	9.8	8.1
BDE-209	10	13	9.7
BB-209	11	9.6	10

As there was no CRM for BDE-206 in PP and PE, and BDE-47, BDE-183, BDE- 206, BDE-209 and BB-209 in ABS, the trueness was investigated as recovery of the analytes in spiked samples. In order to obtain the concentrations indicated on the calibration graph, the spiking was conducted for three uncontaminated polymeric materials at three fortification levels, such as lower, middle and higher parts of the linear range. The recovery was assessed by means of three replicates for each fortification level in a day. The average recovery data and relative standard deviations (RSD) are given in Table 7.

3.2.4. Repeatability and intermediate precision

Repeatability and intermediate precision were assessed, applying the method to the CRM, and spiking the polymeric matrixes at the middle concentration of linear range with three replicates in a day for five days. The results are given as relative standard deviation in Table 8.

3.3. Uncertainty estimation

Uncertainty of the measurement was obtained by bottom-up approach. Uncertainty sources were sample weighing, adjusting the final amount of sample by weighing, preparation of native and labeled standard stock solutions, which were used to prepare calibration solutions, calibration graph, spiking of labeled standard solution at the beginning of the extraction, recovery and repeatability.

3.3.1. Uncertainty of weighing of the starting and final sample

Combined standard measurement uncertainty of weighing the first and last samples was calculated using Eq. (2) where u_{cal} was obtained from the manufacturer's certificate of the balance. This value was used for both sample and tare.

$$u(W) = \sqrt{(u_{Calsample})^2 + (u_{Caltare})^2} \quad (2)$$

where,

$u(W)$	Combined standard measurement uncertainty of weighing the starting or final samples
$u_{Calsample}$	Standard measurement uncertainty from calibration of balance while measuring sample

$u_{Caltare}$ Standard measurement uncertainty from calibration of balance while measuring tare

3.3.2. Uncertainty of native and labeled standard stock solution

Combined standard measurement uncertainty of both native and labeled standard stock solutions, which were prepared gravimetrically, was calculated using Eq. (3), where $u(P)$ was obtained from manufacturer's certificate of the standard solution.

$$\frac{u(C_{SS})}{C_{SS}} = \sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(W)}{W}\right)^2} \quad (3)$$

where,

$u(C_{SS})$ Combined standard measurement uncertainty of standard stock solution
$u(P)$ Standard measurement uncertainty from purity of standard solution
$u(W)$ Standard measurement uncertainty from weighing the standard solution (Eq. (4))
C_{SS} Concentration of standard stock solution
P Purity of standard stock solution
W Weight of standard stock solution

$$u(W) = \sqrt{(u_{Calsample})^2 + (u_{Calsolvent})^2 + (u_{Caltare})^2} \quad (4)$$

where,

$u(W)$ Combined standard measurement uncertainty of weighing
$u_{Calsample}$ Standard measurement uncertainty from calibration of balance while measuring sample
$u_{Calsolvent}$ Standard measurement uncertainty from calibration of balance while measuring solvent
$u_{Caltare}$ Standard measurement uncertainty from calibration of balance while measuring tare

3.3.3. Uncertainty of calibration graph

The combined standard measurement uncertainty from calibration graph was calculated using Eq. (5).

$$u(c_0) = \frac{S}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S_{xx}}} \quad Sxx = \sum_{i=1}^{n} (c_i - \bar{c})^2 \quad (5)$$

where,

$u(c_0)$ Combined standard measurement uncertainty of calibration curve
S Residual standard deviation
B_1 Slope
p Number of measurement to determine c_0
n Number of measurement for calibration
c_0 Determined concentration of the sample by using calibration curve
c Average value of the different calibration solution concentrations

3.3.4. Uncertainty of spiking of isotopically labeled standard solution

Combined standard measurement uncertainty from spiking the isotopically labeled standard stock solution was calculated using Eq. (6). The amount of isotopically labeled standard stock solution was measured volumetrically.

$$u(V) = \sqrt{(u_{Cal})^2 + (u_{Temp})^2} \quad (6)$$

where,

$u(V)$ Combined standard measurement uncertainty of the volume of the spiked isotopically labeled standard stock solution
u_{Cal} Standard measurement uncertainty of the calibration of syringe
u_{Temp} Standard measurement uncertainty of the temperature effect

The volumetric calibration standard uncertainty, u_{cal}, was obtained from the manufacturer's certificate of syringe.

$$u(temp) = \frac{\Delta T V Q}{\sqrt{3}} \quad (7)$$

where,

$u(temp)$ Standard measurement uncertainty of the temperature effect
V Measured volume (mL)
Q Average coefficient of volume expansion of the solvents (*iso*-octane)
ΔT Laboratory temperature variation
$\sqrt{3}$ Rectangular distribution coefficient

3.3.5. Uncertainty of recovery

For the assessment of the recovery for BDE-47, BDE-183, BDE-209 and BB-209 in PP and PE matrixes, ERM-EC591 and ERM-EC590 certified reference materials, obtained from Institute for Reference Materials and Measurements (IRMM), were used. The recovery was assessed by means of six replicates of the CRM in a day.

As there was no CRM for BDE-206 in PP and PE, and BDE-47, BDE-183, BDE-206, BDE-209 and BB-209 in ABS, the recovery was investigated in spiked samples. In order to obtain the concentrations indicated on the calibration graph, the spiking was performed on three uncontaminated polymeric materials at three fortification levels, such as lower, middle and higher parts of the linear range. The recovery was assessed by means of three replicates for each fortification level in a day.

$$u(R_m) = R_m\sqrt{\left(\frac{\overline{u(C_{obs})}}{\overline{C_{obs}}}\right)^2 + \left(\frac{u(C_{cert})}{C_{cert}}\right)^2} \quad (8)$$

$$R_m = \frac{\overline{C_{obs}}}{C_{cert}} \quad (9)$$

Where,

$u(R_m)$ Combined standard measurement uncertainty of recovery
$u(C_{obs})$ Standard measurement uncertainty of observation of CRM or fortified material
$u(C_{cert})$ Standard measurement uncertainty of certification of CRM or fortified material
R_m Mean recovery
C_{obs} Obtained concentration in recovery experiments
C_{cert} Spiked or certified concentration

When the study was performed with CRM, $u(C_{cert})$ was obtained from the certificate of the CRM, but if the study was performed with spiked sample, $u(C_{cert})$ was calculated by using Eq. (10).

$$u(C_{cert}) = \sqrt{u^2_{CalWsample} + u^2_{CalWstandard} + u^2_{CalWtare} + u^2_{Css}} \quad (10)$$

where,

$u(C_{cert})$ Standard measurement uncertainty of certification of CRM or fortified material
$u(C_{SS})$ Standard measurement uncertainty of native stock solution
$u_{CalWsample}$ Standard measurement uncertainty from calibration of balance while measuring sample
$u_{CalWstandard}$ Standard measurement uncertainty from calibration of balance while measuring native standard stock solution
$u_{CalWtare}$ Standard measurement uncertainty from calibration of balance while measuring tare
$C_{obs}$was obtained by analyzing the samples, and calculated by Eq. (11).

$$u(C_{obs}) = \frac{SD}{\sqrt{n}} \tag{11}$$

where,

$u(C_{obs})$ Standard measurement uncertainty of obtained concentrations in the recovery experiments
SD Standard deviation
n Number of sample

3.3.6. Uncertainty of repeatability

The standard measurement uncertainty from repeatability of the method was calculated, by using Eq. (12).

$$u(r) = \frac{RSD}{\sqrt{n}} \tag{12}$$

where,

$u(r)$ Standard measurement uncertainty of repeatability
RSD Relative standard deviation
n Number of sample

Consequently, the combined standard measurement uncertainty of the analyte in the matrixes was calculated by Eq. (13). In order to obtain expanded uncertainty, combined standard measurement uncertainty has to be multiplied by 2 (coverage factor) at 95% confidence level. The expanded relative uncertainties for all the compounds in each matrix are given in Table 9.

$$\frac{u_c(A)}{C_A} = \sqrt{\left(\frac{u(W_{SS})}{W_{SS}}\right)^2 + \left(\frac{u(W_{FS})}{W_{FS}}\right)^2 + \left(\frac{u(C_{NS})}{C_{NS}}\right)^2 + \left(\frac{u(C_{LS})}{C_{LS}}\right)^2 + \left(\frac{u(V_{LS})}{V_{LS}}\right)^2 + \left(\frac{u(c_0)}{c_0}\right)^2 + u(R_m)^2 + u(r)^2} \tag{13}$$

where,

$u_c(A)$ Combined standard measurement uncertainty of analyte
C_A Concentration of analyte
$u(W_{SS})$ Combined standard measurement uncertainty of weighing the starting sample
W_{SS} Weight of starting sample
$u(W_{FS})$ Combined standard measurement uncertainty of weighing the final sample
W_{FS} Weight of final sample
$u(C_{NS})$ Combined standard measurement uncertainty of native stock solution
C_{NS} Concentration of native stock solution
$u(C_{LS})$ Combined standard measurement uncertainty of labeled stock solution
C_{LS} Concentration of labeled stock solution
$u(V_{LS})$ Combined standard measurement uncertainty of added volume of labeled stock solution
V_{LS} Added volume of labeled stock solution
$u(c_0)$ Combined standard measurement uncertainty of calibration curve
c_0 Determined concentration of the sample by using calibration curve
$u(R_m)$ Combined standard measurement uncertainty of recovery
$u(r)$ Standard measurement uncertainty of repeatability

3.4. Application on real samples

The proposed method was applied to eight polypropylene, six polyethylene and four acrylonitrile butadiene styrene raw materials that are used in the production of hair dryer, computer monitor, toaster, microwave oven, carpet and electrical cables. When consumers start to use these appliances, there is a possibility of losing PBDE and PBB contents because of the presence of these analytes as additive in polymeric matrix. In order to have a realistic result, this study provided determination of the concentrations of these compounds in various home appliances before they were on market. The mass fractions of PBDE and PBB in polymeric materials are given in Table 10.

Brominated flame retardants are a group of organic compounds containing bromine, which are capable of preventing combustion of organic materials such as textiles and plastics by producing an inhibitory effect. On the other hand, as BFRs are not strongly bounded to the polymeric structure, they could easily be released to the environment, causing contamination. Therefore, application of PBDE and PBB has been restricted by the European Union and Turkish Republic. The European Commission Directive 2002/95/EC prohibits the use of deca-BDE (BDE-209) in polymeric parts of electrical and electronic devices. Moreover, the European Regulation 850/2004, implementing the Stockholm Convention on persistent organic pollutants (POPs) (Commission Decision 2005/618/EC), sets the “maximum limits” for the total sum of polybrominated diphenyl ethers (PBDE) as 0.1 g/100 g (expressed in mass fraction). Turkish Ministry of Environment and Forestry integrated both Restriction of Hazardous Substance (RoHS) and Waste Electrical and Electronic Equipment (WEEE) Directives into a national legislation. Although the usage of deca-BDE has been prohibited by the governments, we determined it in most of the polymeric raw materials, except PE-2, PE-5 and PP-5, used in the production of computer, carpet, hair dryer, toaster and microwave oven. The mass fraction value of deca-BDE was obtained as close to the mass fraction of other compounds. However, the sum of PBDE and BB-209 mass fractions was achieved below the maximum limits permitted by directives. For instance, BDE-47 was detected in all polymeric raw materials except PP-7 used in production of computer. BDE-183 was determined in all polymeric raw materials except PE-3, PP-1 and PE-4 used in the production of computer and toaster, hair dryer and cables In case of BDE-206, only PP-1, 4, PE-5 and ABS-1, 2, 3 did not contain the compound. BB-209 was not found in PP-1, PE-1, 5 and ABS-1, 2, 3 raw materials.

Table 10
The mass fraction (mg/kg) ± expanded measurement uncertainty values of PBDEs and BB-209 in the raw materials.

	BDE-47	BDE-183	BDE-206	BDE-209	BB-209
Computer					
PP-3	104+/−7	76+/−6	101+/−9	96+/−10	99+/−11
PP-4	108+/−7	90+/−7	–	81+/−8	90+/−10
PP-7	–	90+/−7	81+/−8	92+/−9	92+/−10
PE-2	96+/−7	90+/−6	96+/−9	–	86+/−8
PE-3	83+/−6	–	102+/−10	98+/−13	97+/−9
ABS-4	123+/−9	95+/−8	109+/−9	90+/−9	97+/−10
Hair dryer					
PP-1	86+/−6	–	–	75+/−8	–
PP-2	96+/−6	102+/−8	91+/−9	191+/−19	83+/−9
PP-8	91+/−6	76+/−6	93+/−9	81+/−8	97+/−11
PE-5	76+/−6	68+/−5	–	–	–
PE-6	89+/−7	90+/−6	102+/−10	93+/−12	189+/−18
Toaster					
PP-5	91+/−6	87+/−7	101+/−9	–	82+/−9
PP-6	96+/−6	72+/−6	102+/−10	91+/−9	83+/−9
PE-3	83+/−6	–	102+/−10	98+/−13	98+/−9
Microwave oven					
PP-5	91+/−6	87+/−7	101+/−9	–	82+/−9
PP-6	95+/−6	72+/−6	102+/−10	91+/−9	83+/−9
PE-1	94+/−7	81+/−6	99+/−10	72+/−9	–
Carpet					
PE-2	96+/−7	90+/−6	95+/−9	–	86+/−8
ABS-4	123+/−9	95+/−8	110+/−9	90+/−9	97+/−10
ABS-2	90+/−6	101+/−9	–	79+/−8	–
Cable					
PP-3	105+/−7	76+/−6	101+/−10	96+/−10	99+/−11
PP-4	108+/−7	90+/−7	–	81+/−8	90+/−10
PE-4	92+/−7	–	98+/−9	91+/−12	91+/−9
ABS-1	88+/−6	101+/−8	–	85+/−8	–
ABS-2	90+/−6	101+/−9	–	79+/−8	–
ABS-3	93+/−7	98+/−8	–	82+/−8	–

4. Conclusion

In this study, a new analytical method, based on pressurized solvent extraction and GC–MS/MS techniques, for determination of BDE-47, BDE-183, BDE-206, BDE-209 and BB-209 in polypropylene, polyethylene and acrylonitrile butadiene styrene polymeric matrixes, has been reported. It is a fast method as PSE system provides extraction of six samples in a run. Thus, when one needs to analyze a single sample the method requires one and a half hours. However, when one needs to analyze multiple samples (up to 6), the time spent per sample is reduced. For example, six samples take 5 h to analyze, which represents a 45% time-saving. It is an inexpensive method as PSE system requires less solvent than the other extraction systems such as ultrasonic and microwave assisted extractions and soxhlet extraction. The reliability and performance of the method was demonstrated by applying uncertainty calculation and method validation, remarkable part of which was to use isotope dilution mass spectrometry (IDMS) for quantification and certified reference material (CRM) for trueness assessment.

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