

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

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Abstract

An HPLC–UV/MS method has been developed to identify and quantify flame retardants in post-consumer plastics from waste of electric and electronic equipment (WEEE). Atmospheric pressure chemical ionisation spectra of 15 brominated and phosphate-based flame retardants were recorded and interpreted. The method was applied to detect flame retardant additives in polymer extracts obtained from pressurised liquid extraction of solid polymers. In addition, a screening method was developed for soluble styrene polymers to isolate a flame retardant fraction through the application of gel permeation chromatography (GPC). This fraction was transferred to an online-coupled HPLC column and detected by UV spectroscopy, which allowed a reliable qualitative and quantitative analysis of brominated flame retardants in the polymer solutions.

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1. Introduction

Flame retardants are unequivocally a great benefit to mankind since their application in polymers and textiles have led to a significant reduction of fire cases and resulting death casualties [1,2]. However, serious environmental and health concerns have been related to at least two groups of brominated flame retardants, viz. polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) [2–5]. Both groups have been shown to contain toxic congeners (mainly tetra–hexa-brominated congeners) and to form polybrominated dioxins and furans (PBDD/F) during thermal stress arising from normal applications that include production, compounding or mechanical recycling [6,7].

Other flame retardants, viz. 1,2-bis(tribromophenoxy)ethane (TBPE), hexabromocyclododecane (HBCD) and aryl phosphate, caused further concern. TBPE was accompanied by high PBDD/F values in flame retarded polymers [7], HBCD has been shown to accumulate in river sediments [8], and aryl phosphate fractions containing orthocresyl isomers were related to neurotoxic effects [9].

These aspects have led to regulatory actions against specific flame retardants such as the restricted use of PBB as well as penta- and octa-brominated diphenyl ethers (PentaBDE and OctaBDE) at an European level [10,11]. In addition, the German Chemikalienverbotsverordnung (ChemVV) defines strict maximum levels for PBDD/F, which have been shown to be exceeded by classical mechanical polymer recyclates produced from waste polymers containing PBB, PBDE and/or TBPE [7,12]. However, due to high recycling quotas demanded by the European waste of electric and electronic equipment (WEEE) directive [13], there are still ongoing efforts to realise the recycling of flame retarded polymers. For

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instance, the CreaSolv[®] process [14] is able to recycle polymers containing PBB and PBDE in accord with European and German regulations by an elimination of flame retardant additives and PBDD/Fs from the polymer matrix. Hence, there are regulatory and recycling approaches that favour efforts to optimise the analysis of flame retardants in polymer samples in order to certify flame retardant levels in both virgin and recycled materials.

The analysis of flame retardants in polymers has been realised by gas or liquid chromatographic techniques [15–17]. GC favourably coupled to MS detection allows both a high-resolution chromatographic separation and a high specific (and sensitive) detection. However, some flame retardants are characterised by high boiling points and require high injection and elution temperatures, which may lead to analytical artefacts due to thermal degradation [18]. In addition, GC analysis of phenol-based flame retardants require a derivatisation step [17]. Thus, most GC-based analytical methods are optimised and confined to single groups of flame retardants (mainly to PBDE or PBB).

LC often shows a lower chromatographic specificity and LC detectors are either non-specific (e.g. UV) or in the case of MS detection, confined to polar rather than non-polar samples. However, recent developments in LC–MS techniques based on atmospheric pressure chemical ionisation (APCI) enable mass-specific detection of hydrophobic compounds, including flame retardants [19].

A reliable analysis of flame retardants in polymer samples necessitates an efficient separation of additives from the polymer matrix. Solid–liquid extraction is the most common approach [20,21]. Gel permeation chromatography (GPC) provides an alternative separation approach, isolating flame retardants with molecular masses below 1000 μ from polymers with molecular masses larger than 10,000 μ [22]. However, this technique is confined to polymers soluble in organic solvents, as for example styrene-based thermoplastics. Considering that styrene based polymers cover approximately half of the plastics present in WEEE [23], and that these poly-

mers contain high quantities of brominated flame retardants [24], the restriction of GPC to soluble polymers is not a real deficit. Additionally, since GPC is an LC technique, an online coupling to HPLC systems appears to be promising.

Thus, there were two main targets for the present work. Firstly, a comprehensive LC–UV/MS method was to be developed for the identification and quantification of a wide range of flame retardants in polymers from WEEE covering both brominated and phosphate-based products. Secondly, a GPC separation of flame retardants and polymer matrix was tested in order to set up an online GPC–HPLC–UV instrument, equipped either with or without MS detection. This was intended to allow a direct detection of flame retardants from polymer solutions and to be applicable as quality control instrument in the production of electric and electronic equipment (EEE), as well as in recycling plants.

2. Experimental

2.1. Materials

2.1.1. Reagents and materials

Analytical grade dichloromethane, *iso*-octane, tetrahydrofuran (THF), acetone and ethanol, as well as HPLC-grade methanol and water, were purchased from Merck. An ammonium acetate/acetic acid buffer (pH 3.2) was prepared by dissolving 385 mg ammonium acetate and 10 ml acetic acid in 990 ml of HPLC-grade water (all reagents were purchased from Fluka). Silica gel (0.063–0.200 mm) was purchased from Merck. PTFE syringe filters (0.45 μ m) were purchased from Roth.

2.1.2. Flame retardant reference materials

Table 1 lists the flame retardants investigated in this study. 1000 ppm (w/w) standard solutions were prepared in THF. For HPLC–UV/MS they were further diluted with ethanol or an ethanol–acetone mixture (2:3, w/w). For GPC–HPLC–UV all standards were prepared in THF.

Table 1
Flame retardants investigated in this study

Abbreviation	Chemical name	CAS-No.	Source ^a
HBB	Hexabromobiphenyl, technical grade	059080-40-9	A
OBB	Octabromobiphenyl, technical grade	27858-07-7	A
PentaBDE	Pentabromodiphenyl ether, technical grade	32534-81-9	A
OctaBDE	Octabromodiphenyl ether, technical grade	32536-52-0	B
DecaBDE	Decabromodiphenyl ether, technical grade	1163-19-5	C
HBCD	Hexabromocyclododecane, technical grade	26447-49-4	A
TBBPA	Tetrabromobisphenol A, technical grade	000079-94-7	B
TBBPA-CO ₃	Tetrabromobisphenol A, Carbonate oligomer, phenoxy-terminated	094334-64-2	B
TBBPA-ae	Tetrabromobisphenol A bis (allylether), technical grade	025327-89-3	B
TBBPA-dbp	Tetrabromobisphenol A bis (2,3-dibromopropyl ether), technical grade	021850-44-2	B
TBPE	1,2-Bis(tribromophenoxy)ethane	037853-59-1	B
TPPi	Triarylphosphate, isopropylated	68937-41-7	B
CDP	Cresyl diphenyl phosphate	26444-49-5	B
RDP	Resorcinol-bis-diphenylphosphate	57583-54-7	B
BAPP	Bisphenol A, diphenylphosphate	181028-79-5	B

^a A: Promochem GmbH, Wesel, Germany; B: Great Lakes Chemical Corporation (Europe), Newton Aycliffe, UK; C: Sigma-Aldrich, Seelze, Germany.

Table 2
Samples investigated in this study

Sample name	Polymer type ^a	Flame retardants added	Description
A	ABS	None	Monitor housings
B	ABS	TBBPA, TBPE, OctaBDE, DecaBDE	Sample A, fortified
C	HIPS	None	Monitor housings
D	Mixed polymers, incl. styrene copolymers	TBBPA, TBPE, OctaBDE, DecaBDE	Shredded housing materials of monitors and TV sets
E	Mixed polymers, incl. styrene copolymers, PVC	TBBPA, TBPE, OctaBDE, DecaBDE	Shredded housing materials of monitors and TV sets
F	ABS, HIPS, ABS/PC, PPO/PS	TBBPA, TBPE, OctaBDE, DecaBDE	Artificially composed mixture of ABS, HIPS, ABS/PC, PPO/PC
G	See sample E	None	Sample E, not fortified
H	See sample E	None	Intermediate product of CreaSolv [®] process, derived from sample G

^a ABS: acrylonitrile–butadiene–styrene; HIPS: high impact polystyrene; PC: polycarbonate; PPO: polyphenylene oxide.

2.1.3. Samples

This study focused on the investigation of flame retardants present in styrene housing materials sampled from WEEE dismantling plants. In contrast to mixed plastic waste from WEEE, these fractions exhibit a low material diversity and contain mainly styrene copolymers such as acrylonitrile–butadiene–styrene (ABS), high impact polystyrene (HIPS), blends of ABS and polycarbonate (PC), as well as of HIPS and polyphenylene oxides (PPO) [7].

Seven housing samples, denoted with the capital letters A to G, were analysed in this study. Nine hundred and eighty grams of each were dissolved in 3000 g THF to provide a homogenous sample solution. Samples B, D, E and F were fortified with 2 wt.% of four different brominated flame retardants, viz. tetrabromobisphenol A (TBBPA), TBPE, OctaBDE and DecaBDE, which was accomplished by addition of 20 g of the respective flame retardant to the sample solutions. As a further test material, an intermediate product of the CreaSolv[®] process [14] was chosen, derived from sample G as process input and denoted as sample H. Table 2 summarises sample names, description and fortification.

2.2. Methods

2.2.1. HPLC–UV/MS

2.2.1.1. Sample preparation. Dichloromethane was used to dilute sample solutions A–G, and to dissolve sample H. The resulting solutions were mixed with 20 g silica gel and dried at 30 °C. The procedure leads to silica particles covered with a thin film of the polymer and facilitates a complete extraction.

2.2.1.2. Extraction. Polymer covered silica particles were filled in ASE cartridges and extracted by pressurised liquid extraction (ASE 200, Dionex, Idstein, Germany) using *iso*-octane. The extractions were performed in three cycles (75% flush) at a pressure of 10 MPa and a temperature of 120 °C. Before the HPLC–UV/MS measurement, the extracts were diluted with ethanol or an ethanol–acetone mixture (2:3, w/w) by a factor of 10–100 and filtered with a 0.45 PTFE syringe filter.

2.2.1.3. Instrumental setup. Identification and quantification of flame retardants were performed on a HPLC–UV/MS coupling consisting of a LC system (Shimadzu, Duisburg, Germany), including a LCI OAT pump system, a SIL-10A auto injector, a SPD-10A UV detector, a SCL-10A controller, and a column oven (Mistral, Spark Holland, Emmen, NL) connected to a triple quadrupole mass spectrometer (ThermoQuest TSQ 7000). UV and MS data were processed with the Xcalibur[™] Data System (Thermo Electron, Dreieich, Germany). Flame retardant reference materials and sample extracts were separated on a reversed phase C₁₈ HPLC column (Hypersil ODS, 5 μm, 250 mm × 4.6 mm, Thermo Electron, Dreieich, Germany) thermostated at 40 °C. Ammonium acetate buffer–methanol (5:95, v/v) was used as an isocratic eluent at a flow rate of 1 ml/min. For detection, the mobile phase passed through an UV detector (set at 230 nm) before entering the atmospheric pressure chemical ionisation (APCI) source of the triple-quadrupole mass spectrometer operated in the negative full scan mode from 150 to 1000 μ. Negative APCI was chosen since initial trials with electrospray ionisation (ESI) did not produce valuable mass fragments.

2.2.1.4. Quantification. Quantitative information on the flame retardant level in the polymers was attained for TBBPA, TBPE, OctaBDE and DecaBDE. External five point calibration curves were obtained by injection of standard solutions containing 5–50 ppm (w/w) of the investigated technical reference materials. In the case of DecaBDE, only the areas obtained for the main component (i.e. decabromodiphenyl ether) were used for calibration and considered in the sample extracts. For quantification of technical OctaBDE, the relative area ratios determined for the reference material where compared with the respective area ratios for the sample. Since usually no significant differences were observed, a simple calibration approach was chosen, viz. areas determined for the main Octa-congener were related to the concentration of the technical mixture in the calibration standards. With these calibration curves and by means of regression analysis, extract concentrations were calculated. Actual concentrations in the

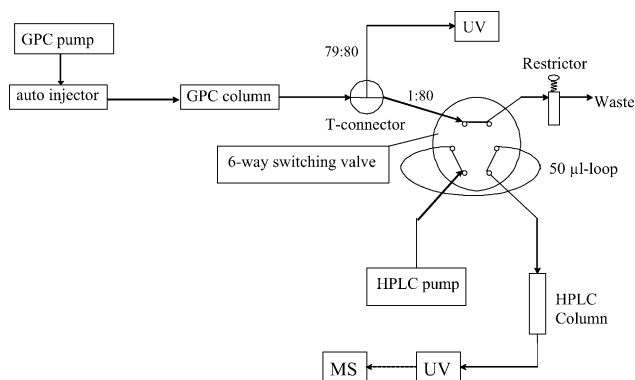


Fig. 1. GPC-HPLC-UV system.

polymer samples were calculated from the ratio of sample and extract weight.

2.2.2. Online GPC-HPLC-UV (occasionally coupled to MS)

2.2.2.1. Sample preparation. Polymer solutions A–F were diluted with THF to concentrations of 0.5% (w/w), samples G and H were dissolved and/or diluted to concentrations of 2% (w/w). All polymer solutions passed a 0.45 PTFE syringe filter prior to injection.

2.2.2.2. Instrumental setup. The above-described HPLC-UV/MS system was complemented with a second UV detector (SPD-10A, Shimadzu), a second pump device (ConstaMetric 4100, Thermo Separation Products) and an electronically controlled six-port valve (FCV-12AH, Shimadzu). Even with optimised GPC methods, the volume of the eluate containing the mass fraction below 1000μ is in the range of 1–3 ml, which by far exceeds the capacity of analytical HPLC columns. For this reason the GPC was coupled to the HPLC with a flow splitter and a six-port valve including a $50 \mu\text{l}$ sample loop (see Fig. 1). This construction is able to take a representative aliquot of the GPC eluate that accounts for approximately 1% of the eluate volume, to transfer this into the sample loop, and to flush it into the HPLC column, when all additives have been eluted from the GPC. The residual 99% of the GPC eluate passes a first UV detector in order to control the fraction sampling. The HPLC eluate was detected by the second UV detector and, occasionally by MS. An initial instrumental set-up of an online GPC-HPLC-UV-MS was applied to samples A–F, whereas samples G and H were subjected to an optimised instrumental set-up, improved in terms of lower detection limits, robustness and run without MS detection. Instrumental details are summarised in Table 3. For optimisation, the sample concentration in THF % and the GPC injection volume were raised to 2% and $40 \mu\text{l}$, respectively. In addition, a 50 \AA wide-bore GPC column was used and operated with an increased flow rate of 2 ml/min. HPLC separation was improved by application of an ODS 2 material and the variation in the composition of the mobile phase. In order to optimise the repro-

Table 3
Instrumental setup of an online GPC-HPLC-UV(MS)

	Initial setup	Optimised setup
GPC		
Column	Phenogel, $300 \text{ mm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$, 100 \AA (Phenomenex)	Phenogel, $300 \text{ mm} \times 7.8 \text{ mm}$, $5 \mu\text{m}$, 50 \AA (Phenomenex)
Mobile phase	THF	THF
Flow rate (ml/min)	0.35	2
Column temperature ($^{\circ}\text{C}$)	30	44
Injection volume (μl)	20	40
Polymer content of injected samples (%)	0.5	2
HPLC		
Column	Hypersil ODS, $5 \mu\text{m}$, $250 \text{ mm} \times 4 \text{ mm}$ (Thermo Electron)	SphereClone ODS 2, $5 \mu\text{m}$, $240 \text{ mm} \times 4.6 \text{ mm}$ (Phenomenex)
Mobile phase	isocratic mixture of ammonium acetate buffer/methanol/THF (32.5/25/42.5; v/v/v)	(1/5/1; v/v/v)
Flow rate (ml/min)	1	2
Column temperature ($^{\circ}\text{C}$)	30	44
Detection		
GPC detector	SPD-10A UV detector (Shimadzu, 254 nm)	SPD-10A UV detector (Shimadzu, 254 nm)
HPLC detector	SPD-10A UV detector (Shimadzu, 230 nm)	SPD-10A UV detector (Shimadzu, 230 nm)
	connected to a triple quadrupole mass spectrometer TSQ 7000 (ThermoQuest) in full scan mode	
Data processing	Xcalibur Data System (Thermo Electron)	Chromeleon software package (Dionex)

ducibility, analyte areas were reported in reference to the area of BHT (2,6-di-(1,1-dimethylethyl)-4-methylphenole) that is present in THF, p.a., as a stabiliser. BHT gives sensitive UV responses and is well separated from the most abundant brominated flame retardants. This approach allowed compensation for small deviations in the flow split ratio since the BHT areas detected in the HPLC eluate are directly related to the GPC fraction volume sampled by means of the six-port valve.

2.2.2.3. System adjustment, calibration and quantification. Both setups were adjusted by injecting 1000 ppm THF solutions of four brominated flame retardants (TBPA, TBPE, OctaBDE and DecaBDE) into the GPC, which allowed the identification of a flame retardant retention time window. The flow splitter was adjusted to a split ratio of approximately 1:80, resulting in a fixed HPLC injection volume below $20 \mu\text{l}$. The system was calibrated for the four brominated flame retardants mentioned above using mixed standard solutions from 250 to 1000 ppm. Calibration curves were obtained and

Table 4

HPLC retention time sequences and typical mass fragments obtained by atmospheric pressure chemical ionisation followed by negative full scan mass spectrometry (150–1000 μ) detected for polybrominated biphenyls and polybrominated biphenyl ethers

Flame retardant	Retention time (min) (%) ^a	Characteristic masses ^b	Fragment interpretation	Proposed structure ^{c,d}
HBB	6.8 (2.0)	–	–	PentaBB
	7.5 (9.2)	–	–	PentaBB
	8.3 (5.7)	–	–	HexaBB
	8.9 (61.7)	–	–	HexaBB (2,2',4,4',5,5')
	10.2 (17.7)	–	–	HeptaBB
	11.0 (3.6)	–	–	HeptaBB
OBB	9.1 (1.7)	–	–	HeptaBB
	10.3 (2.4)	720/722	[C ₁₂ H ₂ OBr ₇] [–]	OctaBB
	11.3 (71.9)	800	[C ₁₂ HOBBr ₈] [–]	NonaBB
PentaBDE	5.6 (28.7)	–	–	TetraBDE (2,2',4,4')
	6.1 (4.3)	–	–	PentaBDE (2,2',3,4,4')
	6.6 (12.5)	–	–	PentaBDE (2,2',4,4',6)
	7.2 (46.8)	–	–	PentaBDE (2,2',4,4',5)
	8.8 (3.1)	–	–	HexaBDE
	9.7 (4.6)	–	–	HexaBDE
OctaBDE ^e	9.7 (8.1)	329/331, 563/565	[C ₆ H ₂ Br ₃ O] [–] , [C ₁₂ H ₄ Br ₅ O] [–]	HexaBDE
	10.5 (39.9)	329/331, 409, 643	[C ₆ H ₂ Br ₃ O] [–] , [C ₆ HBr ₄ O] [–] , [C ₁₂ H ₃ Br ₆ O] [–]	HeptaBDE (2,2',3,4,4',5',6)
	11.3 (21.2)	329/331, 409, 720/722	[C ₆ H ₂ Br ₃ O] [–] , [C ₆ HBr ₄ O] [–] , [C ₁₂ H ₂ Br ₇ O] [–]	OctaBDE
	12.8 (6.8)	409, 720/722	[C ₆ HBr ₄ O] [–] , [C ₁₂ H ₂ Br ₇ O] [–]	OctaBDE
	13.4 (6.4)	487/489, 720/722	[C ₆ Br ₅ O] [–] , [C ₁₂ H ₂ Br ₇ O] [–]	OctaBDE
	14.0 (15.7)	409, 487/489, 800	[C ₆ HBr ₄ O] [–] , [C ₆ Br ₅ O] [–] , [C ₁₂ H ₁ Br ₈ O] [–]	NonaBDE
DecaBDE	16.3 (1.4)	487/489, 800	[C ₆ Br ₅ O] [–] , [C ₁₂ H ₁ Br ₈ O] [–]	NonaBDE
	17.9 (98.6)	487/489	[C ₆ Br ₅ O] [–]	DecaBDE

^a Area percentages of single peaks are indicated in brackets.

^b The most abundant or, with uneven numbers of bromine, the two most abundant isotopes were listed.

^c BB refers to bromobiphenyl, BDE to bromodiphenyl ether.

^d Assignment supported by refs. [2,4,24,26,27], most abundant isomers in brackets.

^e Six main peaks and four further congeners were separated.

applied to the external quantification of brominated flame retardants in the injected sample solutions. Concentrations in reference to solid polymers were computed by considering the polymer content of the sample solutions.

3. Results and discussion

The results of the present work are discussed in two subsections. Section 3.1 presents an in-depth characterisation of 15 brominated and phosphate-based flame retardant reference materials by means of HPLC–UV/MS and online GPC–HPLC–UV. Section 3.2 refers to the analysis of flame retardants in polymers from WEEE by means of both methods.

3.1. Characterisation of flame retardant reference materials

3.1.1. HPLC–UV/MS

A variety of flame retardants frequently employed in styrene-based polymers [7,25] were analysed with the HPLC–UV/MS method and resulted in an UV chromatogram and a total ion chromatogram for each additive tested. Retention times of the most abundant UV signals and the corre-

sponding characteristic mass fragments detected by APCI mass spectrometry are summarised in Tables 4 and 5.

In agreement with the work of Riess and van Eldik [16], reversed phase HPLC–UV turned out to be a capable method to identify the investigated brominated flame retardants which exhibit characteristic retention times or, as far as HBB, OBB, PeBDE, OctaBDE, DecaBDE, HBCD, and TBBPA–CO₃ are concerned, a characteristic sequence of retention times.

In contrast, absolute and relative retention times of phosphate-based flame retardants are rather small. Thus, the significance of the identification of phosphate-based flame retardants on the basis of retention time only is considerably smaller. In the case of small system fluctuations, TBBPA, RDP and CDP are not sufficiently separated to allow their unequivocal identification by UV detection only.

The capability of the identification method increased considerably on including information obtained by mass spectrometry. Whereas the application of an ESI source produced only weak MS responses, negative APCI of the brominated and phosphate-based flame retardants led to characteristic mass fragments in most cases (see Tables 4 and 5). The fragmentation patterns observed include proton abstraction that result in quasi-molecular ions [M – H][–] and the cleavage of ether bridges. The latter fragmentation pattern dominates for

Table 5

HPLC retention times and typical mass fragments obtained by atmospheric pressure chemical ionisation followed by negative full scan mass spectrometry detected for brominated and phosphate-based flame retardants

Flame retardant	Retention times (min) ^a	Characteristic masses ^b	Fragment interpretation
HBCD	4.5, <u>4.8</u>	641	[HBCD-H ⁺] ⁻
TBBPA	3.4	543	[TBBPA-H ⁺] ⁻
TBBPA-CO ₃	<u>3.6</u> (UV), 4.8 (UV + MS)	663	[Ph-(CO ₃)-TBBPA]-H ⁺] ⁻
TBPE	11.8	329/331	[C ₆ H ₂ Br ₃ O] ⁻
TBBPA-ae	7.2	583, 543	[TBBPA-allyl] ⁻ , [TBBPA] ⁻
TBBPA-dbp	11.6	743, 543	[TBBPA-DBP] ⁻ , [TBBPA] ^{-c}
TPPi	<u>3.3</u>	249	[DPP(<i>i</i> -Pr) ₀] ^{-d}
	3.6	291	[DPP(<i>i</i> -Pr) ₁] ⁻
	4.4	333	[DPP(<i>i</i> -Pr) ₂] ⁻
	5.3	375	[DPP(<i>i</i> -Pr) ₃] ⁻
CDP	3.6	263 and 249	[CDP-phenyl] ⁻ or [CDP-cresyl] ⁻
RDP	3.4	497 and 249	[RDP-phenyl] ⁻
BAPP	4.0	615 and 249	[BAPP-phenyl] ⁻

^a Main peak, in reference to UV response, is underlined.

^b The most abundant or, with uneven numbers of bromine, the two most abundant isotopes were listed.

^c DBP: refers to a dibromopropyl group.

^d DPP refers to diphenylphosphate anions with the indicated number of *iso*-propyl groups.

all investigated aromatic flame retardants. This is strong evidence for the assumption that negative APCI produces stable phenolate anions.

3.1.1.1. Polybrominated biphenyls. The analysis of HBB and OBB by means of HPLC–UV/MS results in sequences of UV peaks, whereas no noteworthy MS signals are detected for HBB and only weak responses were observed for OBB. According to Hardy [2], technical HBB consists of penta-, hexa- and hepta-brominated congeners representing 4, 63 and 33% of the mixture, respectively. In order to assign the six UV signals detected for technical HxBB to this congener distribution, the minor peaks at 6.8 and 7.5 min seem to present pentabromobiphenyls, well separated from two hexabromobiphenyls (RT 8.3 and 8.9 min) including the major component at 8.9 min and two less intense heptabromobiphenyls (RT 10.2 and 11.0 min) (see Table 4). Due to lacking MS responses this proposed assignment could not be confirmed.

Technical OBB consists of at least four main components: one hexabromobiphenyl, two octabromobiphenyl isomers, and a nonabromobiphenyl congener as major components [2]. In the HPLC chromatogram, only three signals were detected of which the last one to elute dominated considerably. It was characterised by the mass fragment $m/z = 800$, which correlates with the sum formula C₁₂HOBBr₈. The second component shows a weak mass fragment $m/z = 720/722$ that correlates with the sum formula C₁₂H₂OBr₇, whereas for the first eluting peak no MS response was detected. In reference to the results obtained for HBB, it becomes evident that the main peak represents a nonabromobiphenyl, whereas the earlier eluting peak (RT 10.3 min) belongs to octabromobiphenyl congeners since penta- to heptabromobiphenyls were shown to give no detectable responses by negative APCI–MS (see Table 4). However, this allows us to interpret the detected anion as C₁₂HOBBr₈ with proton abstraction from an octa-

brominated hydroxyl biphenyl, which was produced in the reaction of nonabromobiphenyl with water that leads to the substitution of bromine by an OH group. Consequently, the weak C₁₂H₂OBr₇ anion represents a hepta-brominated hydroxyl biphenyl.

3.1.1.2. 1,2-Bis(tribromophenoxy)ethane. TBPE causes a single peak in the UV and the MS chromatogram (Table 5). The main identified mass fragments, $m/z = 329$ and 331, refer to bromine isotopes of a tribromophenolate anion caused by an ether cleavage.

3.1.1.3. Polybrominated diphenyl ethers. HPLC–UV/MS analysis of PentaBDE shows six noteworthy UV signals, whereas no signals were detected by APCI–MS. In terms of the UV data, the first, third and fourth eluting peaks contribute 29, 13 and 47% to the total peak area, respectively. As outlined by Sjödin et al. [26] and Huber and Ballschmiter [27], technical PentaBDE contains tri- to hexa-brominated diphenyl ether isomers. Sjödin et al. [26] identified 2,2',4,4'-tetraBDE (37 wt.%), 2,2',4,4',5-pentaBDE (35 wt.%) and 2,2',4,4',6-pentaBDE (6.8 wt.%) as the main components in the technical product, as well as two hexa-brominated isomers, viz. 2,2',4,4',5,5'-hexaBDE (3.9 wt.%) and 2,2',4,4',5,6-hexaBDE (2.5 wt.%), and one penta-brominated isomer, viz. 2,2',3,4,4'-pentaBDE (1.6 wt.%) as minor components. On the basis of a consecutive elution of PBDE homologues and similar UV responses for the separated peaks at 230 nm, both supported by findings of Riess and van Eldik [16], we propose to assign the 6 UV signals to the six main isomers identified by Sjödin et al. (see Table 4) according to their relative peak areas.

For OctaBDE six main peaks were identified by UV (see Table 4), accompanied by four less intense signals. MS detection revealed clear responses for all detected UV signals, but UV and MS chromatograms exhibit significantly different

relative area ratios for the single peaks. From a comparison of the results obtained for technical OctaBDE with those for PentaBDE, it becomes evident that the last peak for technical PentaBDE equals the first peak for OctaBDE. This would suggest the signal to result from a hexabromobiphenyl ether, since this is the only homologous group present in both PentaBDE and OctaBDE [4]. The presence of tri-brominated phenolate ions detected by MS further supports this assignment, since all three hexa-brominated isomers, identified in technical PentaBDE [26], possess three bromine atoms in each phenyl ring. However, the second set of mass fragments around $m/z = 563$ and 565 identified for this peak, correlates with a negatively charged penta-brominated diphenyl ether. On assigning this structure to hexa-brominated diphenyl ether reveals that fragmentation operates via a bromine rather than a proton abstraction process.

This result allows an in-depth interpretation of the mass fragments determined for the residual five main components of technical OctaBDE and enables us to assign the separated peaks to groups of homologues (see Table 4). The second OctaBDE signal is characterised by tri- and tetra-brominated phenolates, as well as a negatively charged hexabromodiphenyl ether. Since the latter fragmentation is due to bromine abstraction, this peak can be interpreted as

HeptaBDE. This component is responsible for the dominant UV signal and can be attributed to mainly 2,2',3,4,4',5',6-HeptaBDE, which is the predominant hepta-brominated congener present in currently produced OctaBDE [26]. The third and the fourth peaks of the OctaBDE mixture represent tetra- and penta-brominated phenolate ions, respectively, and show a negatively charged hepta-brominated diphenyl ether fragment. Based on the discussed principles, both peaks can be assigned to octa-brominated diphenyl ethers. The remaining congener of technical OctaBDE is characterized by a negatively charged octa-brominated diphenyl fragment as well as tetra- and penta-brominated phenolate ions, thus supporting the assignment as nona-brominated diphenyl ether.

Both identified fragmentation mechanisms, viz. ether cleavage producing bromophenolate anions and bromine abstraction, are included in Fig. 2 where a typical APCI mass spectrum is presented for the last eluting main congener assigned to nona-brominated diphenyl ether (RT 14.0 min). The quintet of mass fragments between $m/z = 404.6$ and 412.7 refers to a tetra-brominated phenolate ion, whereas the sextet between $m/z = 482.6$ and 492.5 points to a penta-brominated phenolate. Mass fragment $m/z = 800$ corresponds to a negatively charged octabromodiphenyl ether. Since the identified penta- and tetra-brominated phenolates result from ether

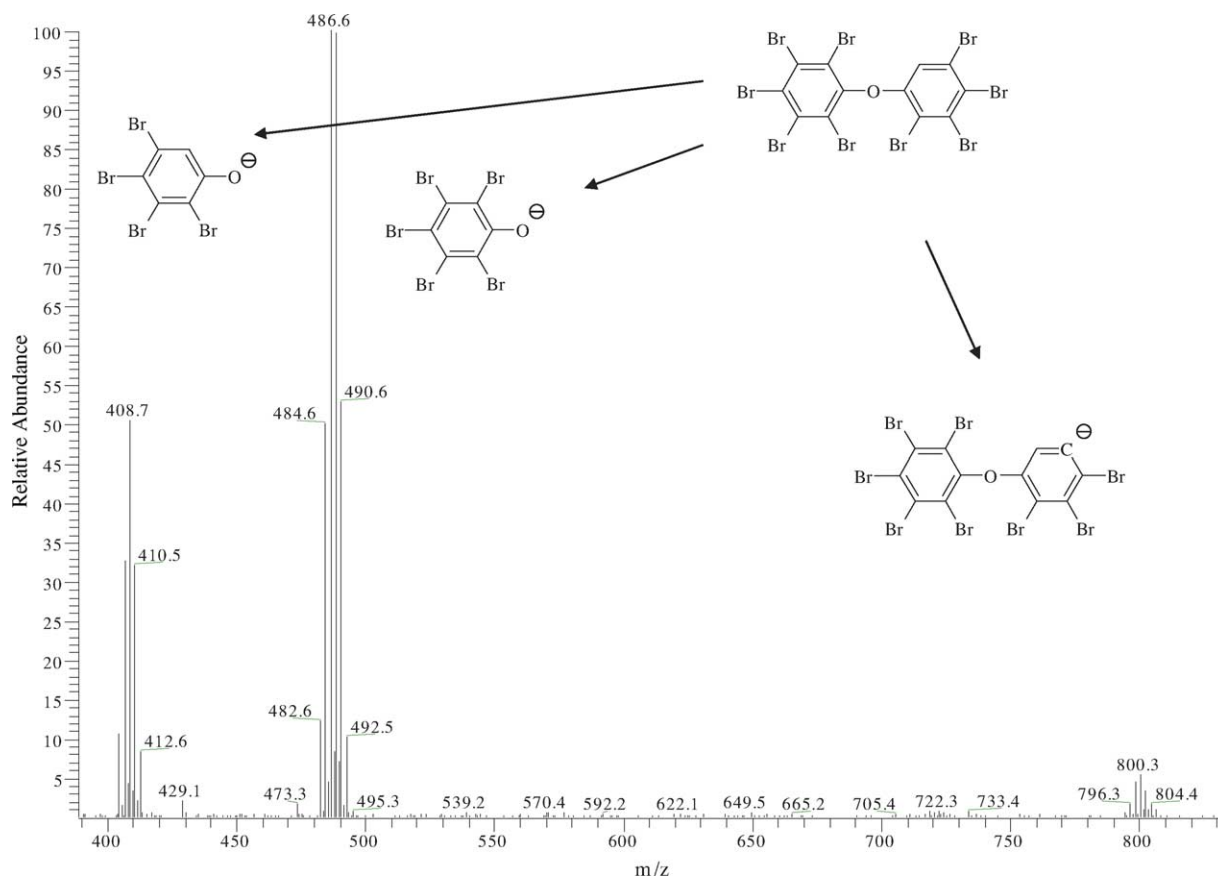


Fig. 2. APCI spectrum of an OctaBDE congener (RT 14.0 min).

cleavage of a nona-brominated diphenyl ether, the higher abundance of penta-brominated fragments is remarkable. In comparison, the intensity of tri-brominated phenolates produced through the ether cleavage of TBPE is significantly lower. Furthermore, di- and tri-brominated phenolates expected from the cleavage of PentaBDE could not be detected at all. These findings reveal that the MS response of brominated phenolate anions increases with increasing number of bromine substituents, which results from the increased stabilisation of the negative charge.

Technical grade DecaBDE provides two signals in both the UV spectra and MS chromatogram, which can easily be attributed to a small amount of nonabromodiphenyl ether eluting at 16.3 min and the main decabromodiphenylether component that elutes at 17.9 min (Table 4). Whereas the mass spectrum of the latter substance contains six bromine isotopes of pentabromophenolate only, the spectrum of nonabromobiphenyl, exhibits typical mass fragments of tetra- and pentabromophenolate, as well as a negatively charged octabrominated diphenylether. As discussed for OctaBDE congeners, we suggest a fragmentation mechanism via bromine abstraction from nona-brominated biphenyl ether. Fig. 3 summarises the proposed assignment of peaks detected for both OctaBDE and DecaBDE.

3.1.1.4. Hexabromocyclododecane. Technical HBCD consists of three isomers (α , β , γ) with γ -HBCD being the predominant product [24]. Using HPLC–UV/MS we detected only a weak UV response, but the MS chromatogram revealed two significant peaks of which the second dominated. For both peaks the quasimolecular anion $[M - H]^-$ was identified as the dominant mass fragment.

3.1.1.5. Tetrabromobisphenol A and related compounds. TBBPA, TBBPA-ae and TBBPA-dbp were detected with single peaks by UV and MS detection. Increasing retention times were obtained with increasing ether group ($H < \text{allyl} < \text{dibromopropyl}$, see Table 5). MS fragmentation can easily be interpreted by a proton abstraction from TBBPA or cleavage of one or both ether groups in the substituted TBBPA compounds. For the phenyl terminated carbonate oligomer of TBBPA, two signals were identified with UV, whereas only the second eluting one produced a MS response. The fragments detected correspond to five bromine isotopes which were identified as the monophenylcarbonate-substituted TBBPA anion.

3.1.1.6. Phosphate-based flame retardants. Since all investigated phosphate-based flame retardants consist of aryl

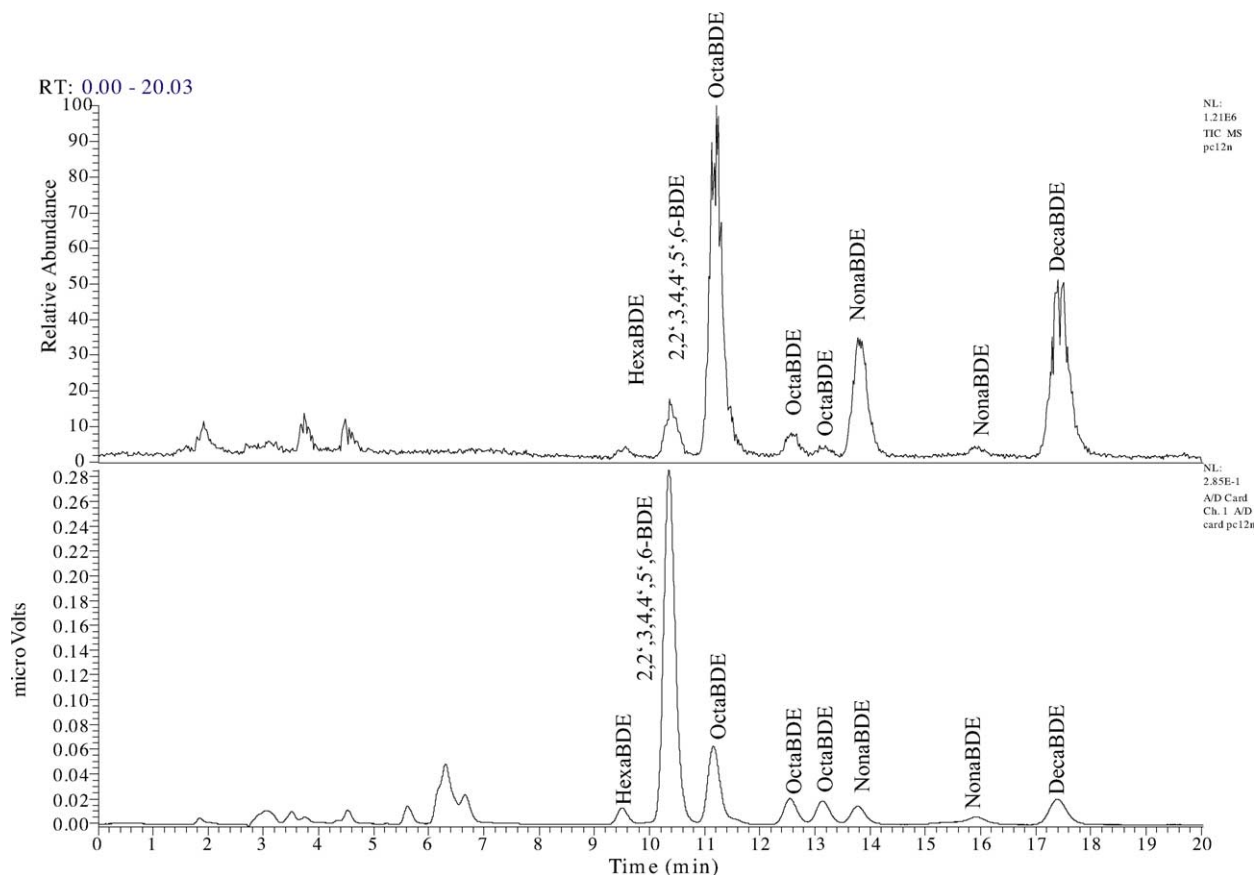


Fig. 3. UV-chromatogram (bottom) and MS-chromatogram (top) of sample C (shredded monitor housings) obtained with HPLC–UV–MS. Isomers of technical OctaBDE and DecaBDE are assigned according to Table 4. UV signals between 3.5 and 8 min could not be identified as one of the flame retardants investigated in this study.

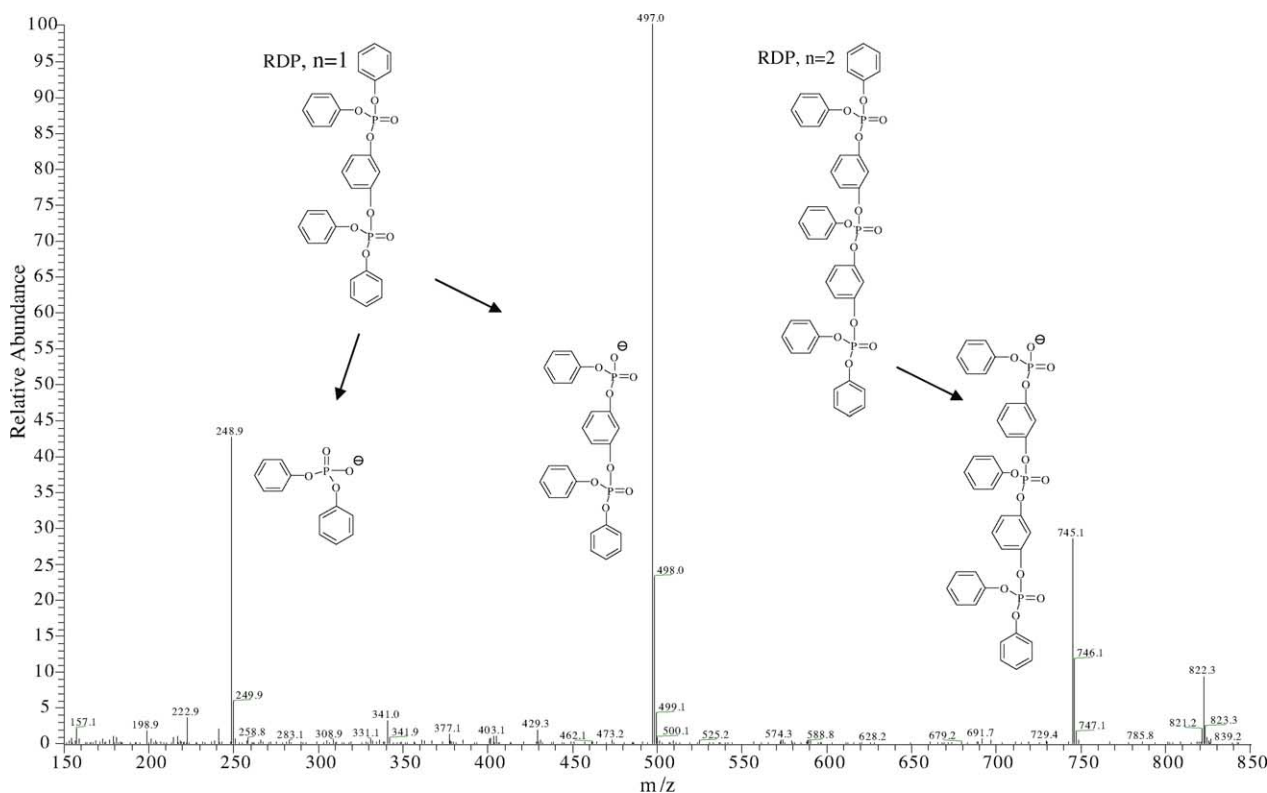


Fig. 4. APCI spectrum of resorcinol-bis-diphenylphosphate (RDP).

substituted (poly)phosphates, the fragmentation is the same for all these substances. It proceeds via cleavage of the phosphate aryl bond, forming stable substituted phosphate ions. By way of illustration, Fig. 4 shows the APCI spectrum of RDP with three dominant fragments at $m/z = 249$, 497 and 745. Mass fragment $m/z = 497$ indicates a phenyl abstraction ($m/z = 77$) from the molecule ion ($m/z = 574$, referring to the smallest congener), fragment $m/z = 745$ is formed by phenyl abstraction from the second largest congener. Fragment $m/z = 249$ results from cleavage of the phosphate–resorcinol bond forming a diphenylphosphate anion.

3.1.1.7. Detection limits of HPLC–UV/MS. Rough estimates of detection limits were defined with signal-to-noise ratios (S/N) of 10 and calculated on the base of S/N values, which were obtained by injections of 10 ppm standard solutions of the 15 flame retardant reference materials. For UV detection, the computed detection limits of the 15 reference materials were in the range between 0.5 and 100 ppm. These detection limits obtained at 230 nm are significantly lower than those reported by Riess and van Eldik [16], who employed an UV detector in the scan mode. Significantly reduced detection limits were found with MS detection. They were in the range between 0.01 and 1 ppm for most of the tested substances. Only for PeBDE, HBB and OBB they were larger than 100 ppm. Thus, MS validation or interpretation of

UV chromatograms is not available for these three flame retardants.

However, the materials, which are to be characterised by this method, contain flame retardants additives in the range between 0.1 and 24%, and the threshold values defined in European regulations [10,11] were established at 0.1%. Thus, for the scope of this work the calculated detection limits are sufficient.

3.1.2. Online GPC–HPLC–UV

Fig. 5 displays analytical results obtained for a mixture of flame retardant reference materials by means of the optimised instrumental setup for the GPC–HPLC–UV system. The mixture contained 400 ppm of TBBPA, OctaBDE, DecaBDE, and TBPE, respectively. The figure illustrates the GPC separation and highlights the additive fraction sampled and transferred to the HPLC column in a grey shade. The second chromatogram displays the UV responses obtained for this additive fraction. It follows that congeners of the four flame retardants can be identified, even when the altered HPLC separation, due to the modification of the mobile phase for online GPC–HPLC coupling, changes absolute and relative retention times. Nevertheless, although the internal standards BHT, TBBPA and DecaBDE are well separated, TBPE elutes within the OctaBDE elution window. The optimised HPLC conditions were shown to avoid co-elution of TBPE

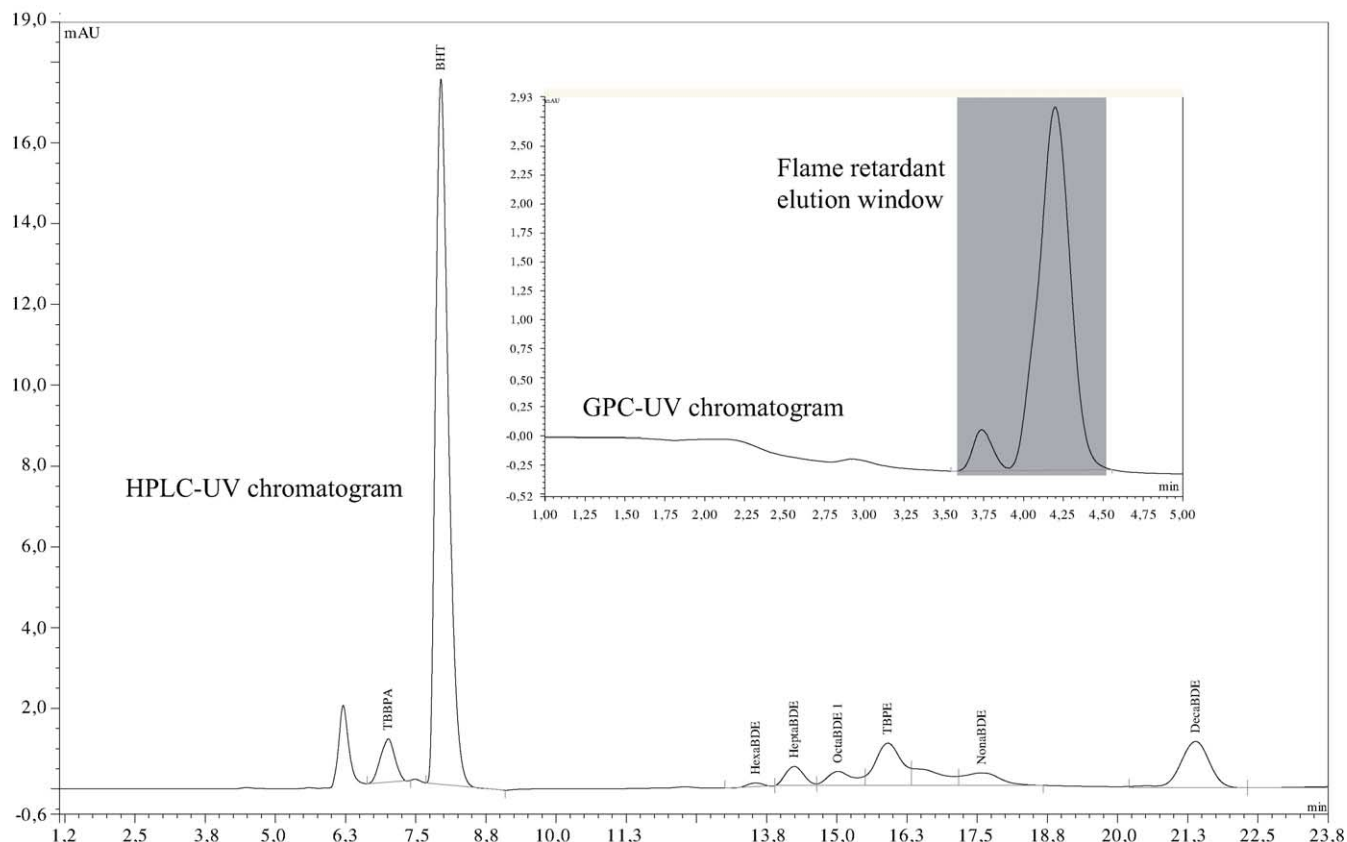


Fig. 5. GPC–UV and HPLC–UV chromatograms of a standard mixture obtained by online GPC–HPLC–UV. The mixture contained 400 ppm of TBPE, OctaBDE, TBPE, and DEC A, respectively. The grey area in the GPC chromatogram indicates the additive fraction, sampled and transferred into the HPLC.

with one of the six main congeners of OctaBDE, thus allowing a sufficient isolation and quantification even when both flame retardants are present in the same sample.

As shown in Fig. 1, the online GPC–HPLC–UV system can be coupled directly to APCI–MS, to enable online validation of the UV data. This provides precious information especially for early eluting compounds such as TBBPA, since a co-elution of RDP, CDP, TBBPA–CO₃ or other sample components cannot be excluded by UV only. For the late eluting flame retardant congeners, OctaBDE, DecaBDE and TBPE, no co-elutions were identified with MS so far. Thus, UV detection appears to be sufficient for identification and quantification of these components.

3.2. Analysis of polymer samples derived from WEEE

Two approaches were chosen to identify and quantify flame retardants in styrene housing polymer samples derived from WEEE dismantling plants: HPLC–UV–MS analysis of samples extracts and online GPC–HPLC–UV, occasionally coupled to MS. Whereas the first method is based on solid–liquid extraction, the second is restricted to polymer solutions and thus to soluble polymer samples.

Styrene housing polymers are exposed to elevated temperatures and thus frequently contain brominated and phosphate-based flame retardants at concentrations up to 24 wt.% [1,25].

Therefore, these samples are expected to provide a variety of flame retardants and thus allow a detailed testing of the developed identification and quantification method.

3.2.1. HPLC–UV/MS

Fig. 3 reports the UV and total ion chromatograms obtained for a pressurised liquid extract of sample C. Both chromatograms depict a complex mixture of compounds present in the extract. Based on the comprehensive characterisation of flame retardant reference materials summarised in Tables 4 and 5, all typical isomers of technical OctaBDE and DecaBDE were identified in this sample.

The presence of both DecaBDE and OctaBDE in HIPS is remarkable, since for HIPS in general the application of DecaBDE is reported [24,25]. This may lead to the assumption that the identified OctaBDE congeners result from degradation of DecaBDE owing to polymer aging or to the shredder process. However, the determined fingerprint of OctaBDE congeners perfectly resembles that obtained for technical reference material, which is unlikely for a degradation process and, thus indicates the application of a mixture of both flame retardants. At least seven peaks were identified in the UV chromatogram eluting between 3 and 7 min, which could not be assigned to one of the flame retardant reference materials investigated in this study. Even when for some signals the retention times were close to single peaks of technical flame

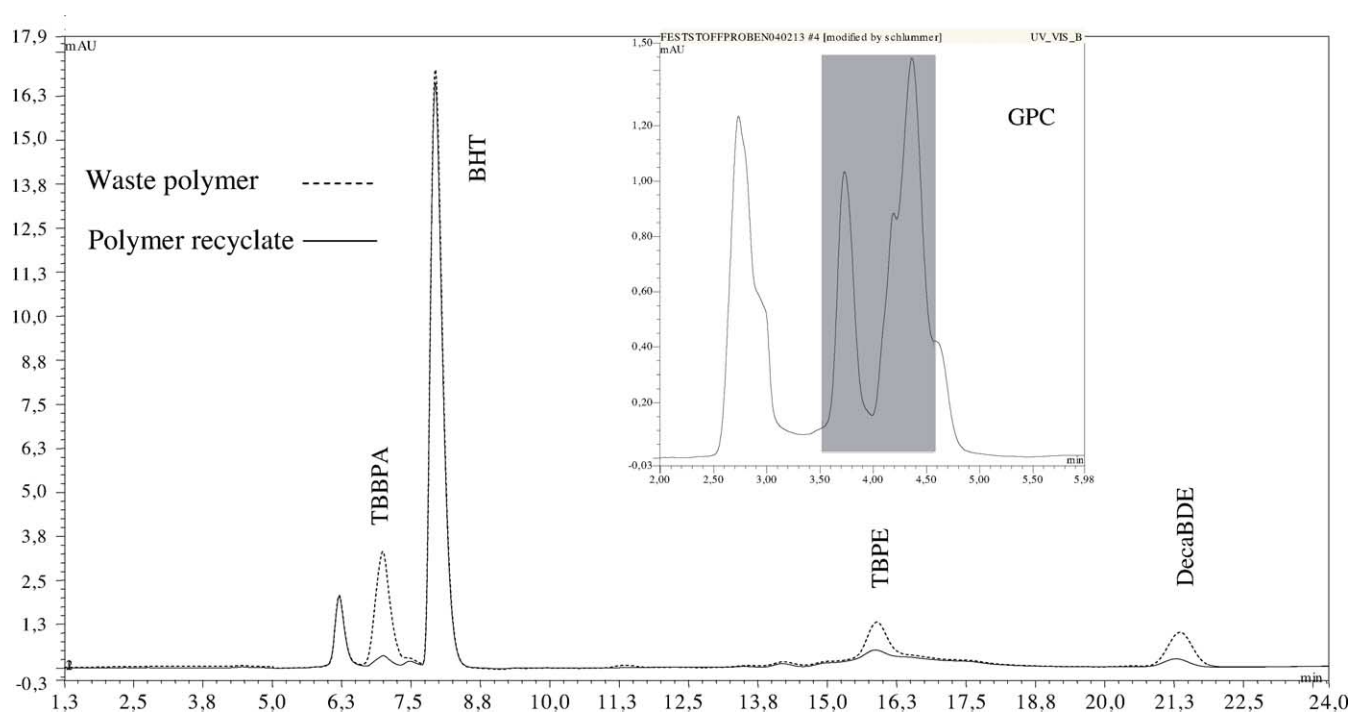


Fig. 6. Application of the GPC–HPLC–UV method as process control tool: an overlay of two chromatograms is displayed reflecting samples of a pilot recycling experiment with the CreaSolv[®] process. The dotted chromatogram displays the WEEE polymers used as process input (sample G), the drawn line shows the results for the reference recycled polymer (sample H) indicating substantial lower levels for TBBPA, TBPE and DecaBDE. The inserted chromatogram shows the improved GPC separation, the grey area indicates the GPC fraction, sampled and transferred to the HPLC.

retardant mixtures, neither typical peak sequences nor characteristic mass fragments were recognised. Therefore, these signals have to be attributed to polymer oligomers or other additives as impact modifiers or stabilisers.

Quantification can be performed with the UV or MS data. The UV signals proved to be more reproducible as compared to the MS results, which is probably due to co-extraction of polymer components that accumulate in the APCI source. These residues may suppress the ionisation and lower the absolute responses during longer sample processing. Hence, we suggest using UV detection for quantification and MS detection for identification and validation purposes.

3.2.2. Online GPC–HPLC–UV

On applying the optimised online GPC–HPLC–UV system to analysis of flame retarded polymer solutions, GPC separates the additive fraction clearly from the bulk polymer within 5 min (see inserted chromatogram in Fig. 6). After sampling of this fraction and transfer to the HPLC, a persuasive and sensitive separation of TBBPA, BHT, TBPE and DecaBDE is obtained (Fig. 6). In comparison with the separation attained by HPLC–MS, the chromatographic resolution was reduced due to the modification of the mobile phase. This was necessary since separation based on ammonium acetate buffer and methanol only is significantly disturbed when THF solutions are injected.

By double injection of different samples, the reproducibility of the system was tested and convincing deviations below 10% were found. In addition, the system gave linear responses for the four investigated brominated flame retardants, allowing a quantification from 20 to 1000 ppm, in reference to the sample solution.

For polymer solutions with 3 wt.% dry mass as sample matrix, the sensitivity is sufficient to quantify levels below 0.1% for TBBPA, OctaBDE, DecaBDE and TBPE. PentaBDE is expected to have comparable limits of quantification, but has not been tested yet since it is not applied in polymeric housing materials.

Fig. 6 presents two UV chromatograms as an overlay obtained for a waste polymer (sample G) and its recyclate produced by a lab-scale CreaSolv[®] process (sample H). The example indicates that besides TBBPA, which might be over-estimated due to phosphate-based additives, TBPE and DecaBDE were unequivocally identified in both samples. However, the levels of all three brominated flame retardants are considerably lower in the recycled polymer.

In this application, GPC–HPLC–UV functions as process control and output control unit at the same time: Two analytic runs with analysing times lower than 25 min are able to monitor (a) the elimination rate obtained for brominated flame retardant additives and (b) the absolute concentration of the recycling product. Since OctaBDE, PeBDE and PBB were below the limit of detection in both samples, the recyclate

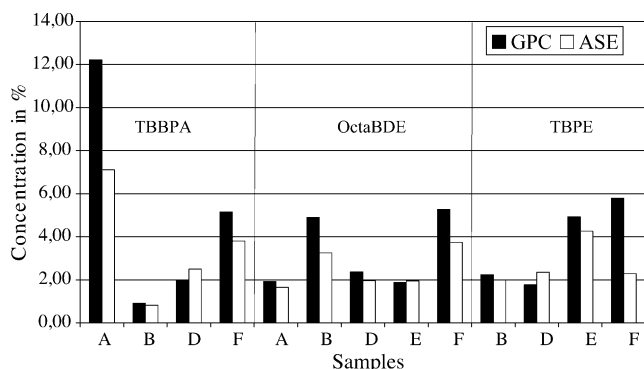


Fig. 7. Levels of brominated flame retardants detected in polymer samples derived from WEEE by means of pressurised liquid extraction (referred to as ASE) followed by HPLC–UV/MS compared to results obtained by GPC–HPLC–UV/MS (referred to as GPC).

is expected to comply with European regulations [10,11]. In addition, a reduced potential to form PBDD/F during thermal stress is anticipated due to the observed elimination of TBPE and DecaBDE in the process.

3.2.3. Method comparison in terms of conformity and accuracy

Both methods were used for the quantification of brominated flame retardants in the same set of samples (samples A, B, D, E and F, see Table 2), whereas the initial instrumental setup was used for online GPC–HPLC–UV. Both systems were calibrated with TBBPA, TBPE, and OctaBDE.

The results are presented in Fig. 7, where pressurised liquid extraction followed by HPLC–UV/MS is referred to as ASE, and GPC denotes results obtained by GPC–HPLC–UV. In most cases, ASE and GPC values deviate less than 20% from the arithmetic mean and demonstrate an adequate comparability of both methods. Conversely, with TBBPA in sample A and TBPE in sample F, significant differences were observed in two cases where GPC extracts exceeded the ASE results by a factor of 1.7 or 2.5, respectively.

Samples B, D, E and F were fortified with known amounts of flame retardants, which were proved not to be present in the original samples. This allowed the estimation of analytical recoveries for these additives, defined as the percent ratio of the concentration detected divided by the concentration expected. The calculated recoveries are displayed in Fig. 8 and vary in general in the range between 80 and 125%. Thus, the accuracy of both methods is also satisfactory. Again two results fall out of this range. Recoveries obtained for TBBPA in the ASE extract of sample B and TBPE in the ASE extract of sample F are remarkably high (135%) or low (47%), respectively.

Positive and negative deviations in the range of 20% can be due to several reasons. First, the distribution of brominated flame retardants in the sample matrices may not be homogeneous. With regard to solid liquid extraction, incomplete ASE extractions have to be considered, as reported by Riess et al. [21]. In reference to GPC–HPLC–UV, the flow split

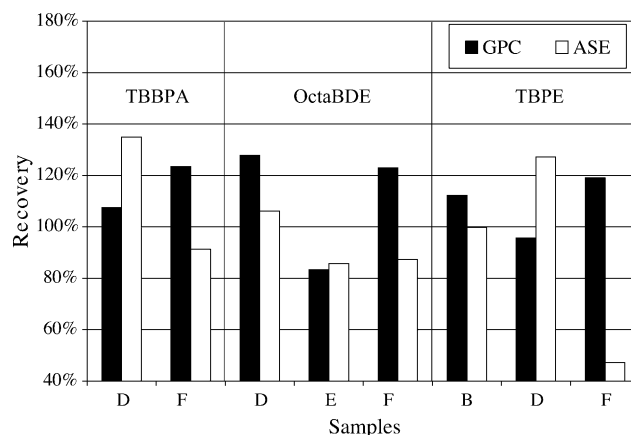


Fig. 8. Recoveries of brominated flame retardants, which were added to the polymer samples prior to analysis.

used in the initial instrumental set-up may have caused deviations in the transfer of the GPC eluate. However, this could be improved in the optimised set-up by the use of BHT as an internal standard.

More significant deviations, identified for TBBPA in samples A and B, as well as for TBPE in sample F, point at drawbacks in both methods. Pressurised liquid extracts (ASE) were diluted with ethanol or a mixture of acetone/ethanol. Polymers or oligomers, which were co-extracted, precipitated during this step, serving as an adsorption surface. As seen for sample F, this might lead to lower results for TBPE, which has a limited solubility in alcohols [28]. TBBPA might be over-estimated with both methods when a co-elution with phosphate-based flame retardants (RDP, CDP) or other additives not investigated here, is not perceived in the UV chromatogram.

4. Conclusions

The European directive 2002/95/EC [10] bans the use of OctaBDE and PentaBDE, and restricts the use of polybrominated biphenyls (including HBB and OBB) in EEE. European directive 2003/11/EC [11] prohibits the distribution of products that contain OctaBDE or PentaBDE levels above 0.1%. Therefore, producers of EEE are forced to cover these polymer additives with their quality control measures, in order to guarantee compliance with the mentioned standards.

For this application, pressurised liquid extraction followed by HPLC–UV/MS proved to be a powerful technique, and covers at least 15 brominated and phosphate-based flame retardants in a single-shot method. However, operating and maintaining a MS system might be out of the scope of an EEE producer. In contrast, the screening GPC–HPLC–UV tool presented in this study could be part of a routine quality control, since reproducibility and limits of quantification are sufficient to obtain reliable results at levels around 0.1% dry mass. Along with validation measurements for positive

tested samples in an external specialised laboratory running a MS system, this might be a feasible approach.

Furthermore, the applicability of online GPC–HPLC–UV was demonstrated for the monitoring of recycle qualities, since marketing of material recycles requires information on the kind and amount of flame retardants present in the recycling products in order to guarantee compliance with the European directives mentioned above [10,11]. With regard to the solvent-based polymer recycling process mentioned above [14], the presented screening tool is recommended as a process control device.

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