

Analysis of brominated and phosphate-based flame retardants in polymer samples by HPLC-UV/MS and online-GPC-HPLC-UV

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Introduction

Serious environmental and health concerns have been related to polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)¹. Both groups of brominated flame retardants have been proven to contain toxic congeners (mainly tetra-, penta- and hexabrominated congeners) and to form polybrominated dioxins and furans (PBDD/F) under thermal stress arising from normal applications including production, compounding or mechanical recycling².

Additionally, three further flame retardants, TBPE, HBCD as well as arylphosphates, are under discussion: TBPE is accompanied with high PBDD/F levels in flame retarded polymers³, HBCD has been shown to accumulate in river sediments⁴, and aryl phosphate qualities containing orthocresyl isomers were related to neurotoxic effects⁵.

These aspects have led to industrial product optimisations and regulatory actions against specific flame retardants as the restriction of use of PBB, PentaBDE and OctaBDE on an European level^{6,7}. In Germany, there is an additional indirect regulation regarding the end-of-life management of flame retarded polymers, since polymers containing PBB, PBDE and TBPE have practically to be excluded from classical mechanical recycling approaches, since a re-extrusion of these material have been shown to increase levels of PBDD/F above the threshold levels according to German Chemikalienverbotsverordnung (ChemVV)^{3,8}. As a reaction, the European industry phased out the application of PBB in the last decade and currently starts to replace PBDE with phosphate-based flame retardants.

Hence, there are two main applications for the analysis of flame retardants in polymeric samples. Firstly, the quality control during production of electric and electronic equipment in order to certify the absence of PBB, OctaBDE and PeBDE and, thus, the compliance with the RoHS directive⁶. Secondly, the characterisation of waste polymers in order to qualify them for material recycling or recovery processes.

Here we present two analytical approaches for the identification and quantification of brominated and phosphate-based flame retardants. The first is an HPLC-UV/MS approach, which allows the separation and unequivocal identification and quantification of at least 15 different technical flame retardants. The second approach was set-up as a screening tool, consisting of a GPC separation coupled to an HPLC-UV device.

Methods and Material

Reference materials

Technical grade reference materials of 11 brominated and 4 phosphate-based flame retardants were investigated in this study (Table 1). Reference materials were purchased from Promochem (Wesel, Germany), Sigma-Aldrich (Seelze, Germany) or donated by Great Lakes Chemical Corporation (Europe) (Newton Aycliffe, UK).

Samples

Polymer samples from waste electric and electronic equipment were analysed, mainly consisting of polystyrene co-polymers. For HPLC-UV/MS samples were extracted with iso-octane by accelerated solvent extraction (ASE, Dionex, Germany), for GPC extraction online coupled to HPLC-UV, they were dissolved in tetrahydrofuran (THF). Extracts and polymer solutions passed 0.45 µm syringe filters before injection.

Table 1: Flame retardant reference materials investigated in this study.

Brominated flame retardants	
Tetrabromobisphenol A, TBBPA	1,2-bis(tribromophenoxy)ethane, TBPE
TBBPA-Carbonate oligomer, TBBPA-CO3	TBBPA bis(2,3-dibromopropyl ether), TBBPA-dbp
Pentabromodiphenylether, PentaBDE	TBBPA bis (allylether), TBBPA-ae
Octabromodiphenylether, OctaBDE	Phosphate based flame retardants
Decabromodiphenylether, DecaBDE	Triarylphosphate, isopropylated, TPPi
Hexabromobiphenyl, HBB	Cresyl Diphenyl Phosphate, CDP
Octabromobiphenyl, OBB	Resorcinol-bis-diphenylphosphate, RDP
Hexabromocyclododecane, HBCD	Bisphenol A, diphenylphosphate, BAPP

HPLC-UV/MS

Identification and quantification of flame retardants reference materials was realised on a HPLC-UV/MS coupling comprising of an LC system (Shimadzu, Duisburg, Germany), including an LC10AT pumping system, SIL-10A auto injector, a SPD-10A UV detector, and a SCL-10A controller, 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, 250 x 4mm, Thermo Finnigan, Dreieich, Germany) thermostated to 40°C. We used isocratic ammonium acetate buffer/methanol (5/95, v/v) as eluent at a flow rate of 1 mL/min. For detection, the mobile phase passed an UV detector (set at 230 nm) before entering the atmospheric pressure chemical ionisation (APCI) source of the triple-quadrupole mass spectrometer. The mass spectrometer operated in the negative full scan modus from 150-1000u.

Quantification was realised by external calibration standards, prepared with the reference materials listed above.

Online GPC-HPLC-UV

The intention of this approach was the GPC-based separation of brominated flame retardants from the polymer matrix, which allows an online-coupling to the existing HPLC-UV/MS method. Such a system requires filtrated polymer solutions as samples as well as a column coupling between GPC

and HPLC column. Therefore, 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). A 50Å wide-bore GPC column (Phenogel, 300 x 7.8 mm, 5µm, Phenomenex, Torrance, CA, USA) was applied, operated with THF at a flow rate of 2 ml/min. HPLC separation was achieved on a SpereClone™ column (ODS(2), 5µm, Phenomenex, Torrance, CA, USA) using methanol/THF/water (450/90/90) as mobile phase at a flow rate of 2 ml/min. GPC and HPLC column were thermostated to 44°C.

The GPC was coupled to the HPLC via a flow splitter and a six port valve including a 50 µl sample loop (see fig. 1). The online analysis starts with the valve in the inject position directing the GPC eluate into the waste. When the flame retardants begin to elute from the GPC column, the 6 port valve switches to the load position and transferred roughly 1% of the additive fraction into the sample loop; the residual 99% of the GPC eluate passed the first UV detector in order to monitor the online-extraction. At the end of the flame retardant retention time window the valve switched back into the inject position, the GPC eluate trapped in the sample loop was flushed into the HPLC column and the HPLC eluate was detected by the second UV detector and by MS.

For quantification, an internal standard, BHT (2,6-di-(1,1-dimethylethyl)-4-methylphenole), was added to samples and external standards and analyte areas were related to the BHT area.

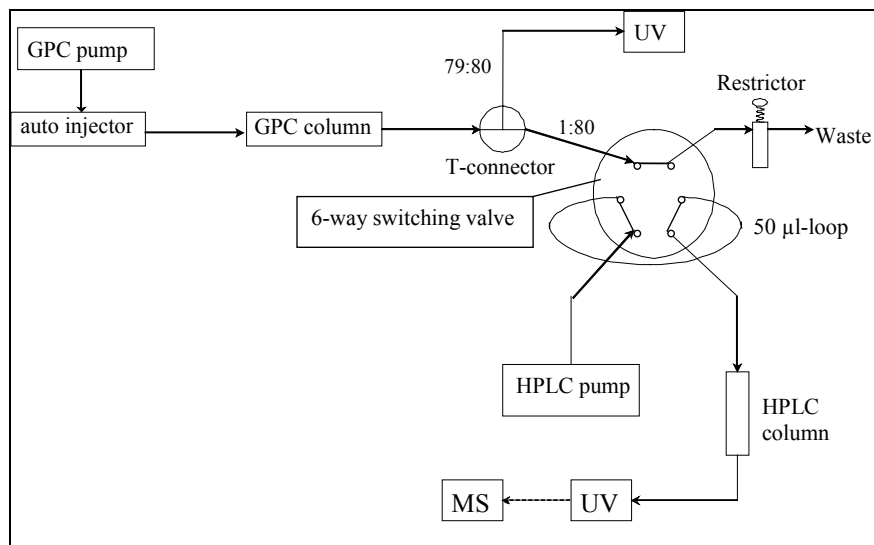


Fig 1: GPC-HPLC-UV/MS system

Results and Discussion

HPLC-UV/MS results

15 different flame retardant reference materials were analysed with the HPLC-UV-MS approach. HPLC retention times as well as APCI mass spectra were recorded and interpreted for all reference materials. This enabled us to identify and quantify these flame retardants in sample extracts as well. In most cases, negative APCI mass spectrometry resulted in specific mass fragments, which were identified as:

- a) proton abstracted quasimolecule anions $[M-H^+]$,
- b) substituted phosphate or phenolate anions resulting from the cleavage of an ether bridge or
- c) anions resulting from a bromine abstraction $[M-Br]$.

Figure 2 illustrates the second and the third fragmentation mechanism for a nonabrominated biphenyl ether detected in technical OctaBDE.

The combination of unspecific UV- and specific MS detection proved to be a powerful means to identify and quantify all investigated flame retardants, since drawbacks of the single devices were eliminated:

- a) HPLC separation is sufficient for the unspecific UV identification of brominated flame retardants due to specific retention times or specific retention time sequences⁹. However, the separation of phosphate-based flame retardants is limited due to small differences in absolute and relative retention times. Here specific MS detection allows an unequivocal identification.
- b) Pentabrominated biphenyl ether and hexabromobiphenyl gave no sensitive MS responses. Here, HPLC separation and UV detection are sufficient for an unequivocal identification.

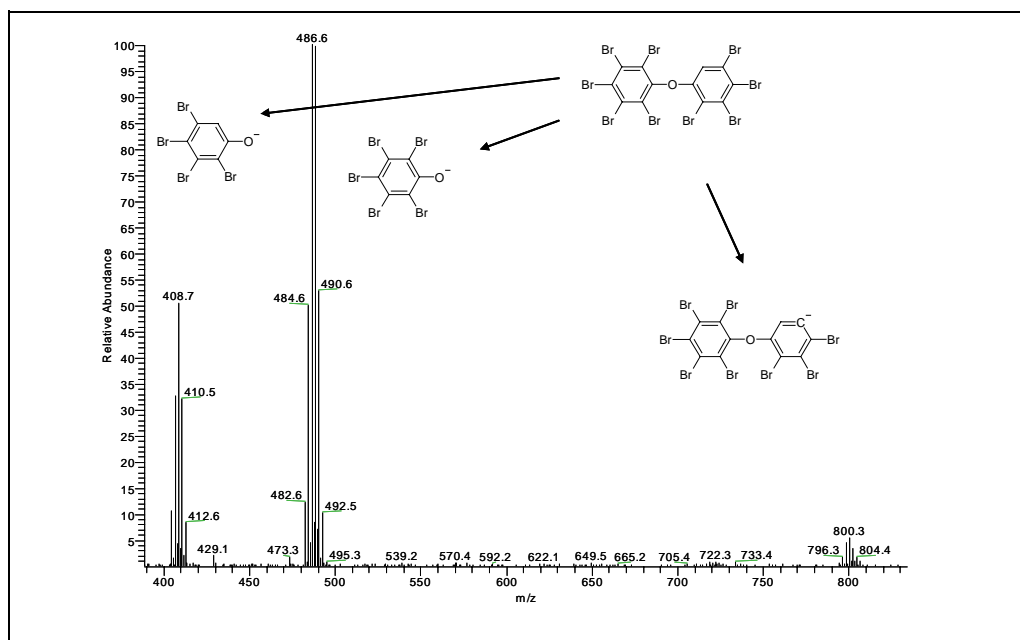


Fig. 2: APCI spectrum of a NonaBDE congener

Online GPC-HPLC-UV

Separation of brominated flame retardants from the polymeric matrix by GPC proved to be a fast and complete extraction step for soluble polymers. Furthermore, the coupling depicted in figure 1 is able to transfer the flame retardants into the HPLC-UV/MS device allowing a sensitive identification and quantification of brominated flame retardants. Since most brominated flame retardants can easily be identified by peak retention times or elution sequences, MS detection supports the identification but is not necessary. Only for HBCD MS detection is obligatory.

Limits of detection obtained with this set-up were below 0.05% (referred to the solid polymer). Thus, the device is predestinated for quality assurance in production plants in order to state the compliance of polymers and products with European regulations, which allow a maximum of 0.1% for OctaBDE and PentaBDE.

A second application of the GPC-HPLC-UV device might be usage as a process control tool in a polymer recycling plant, treating flame retardant polymers like the CreaSolv™ process¹⁰. This process aims to eliminate flame retardants and PBDD/F from waste polymers and to recover polymer recyclates with substantially reduced flame retardant levels.

Here we present data obtained for an input polymer material subjected to the CreaSolv™ process in a pilot experiment and its referring recyclate. The inserted chromatogram in figure 3 shows the GPC separation, with a polymer peak at 2.8 min well separated from the additive fraction, indicated by the grey area. (The excluded peak shoulder at 4.7 min is due to the solvent peak). Figure 3 displays also the UV chromatograms obtained for the input (dotted line) and the recyclate sample (drawn line). The overlay reveals substantial lower levels for all three brominated flame retardants detected: TBBP A, TBPE and DecaBDE.

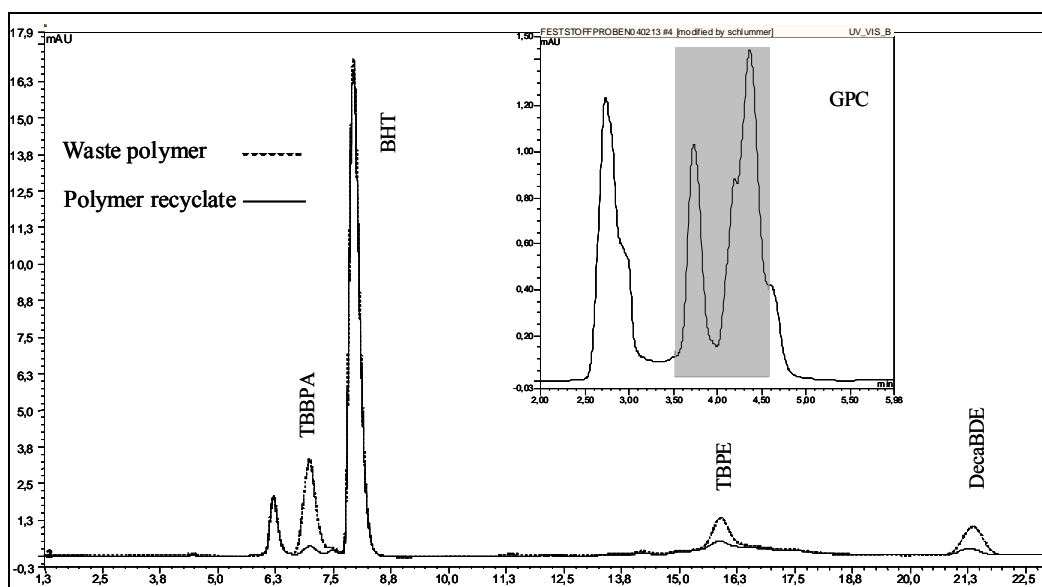


Fig. 3: Application of the GPC-HPLC-UV method as process control tool

Thus, the analytical screening method presented here turns out to be a powerful tool for a recycling plant treating flame retarded polymers, since it reliably identifies flame retardants present in the input and it quantifies regulated flame retardants in the products. It allows to control the flame retardant elimination rate as well as the compliance of the recyclates with European directives mentioned above^{6,7}.

Using GPC-HPLC-UV, the CreaSolv™ process could be identified as an effective process to eliminate brominated flame retardants from the polymer matrix.

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