Identification of brominated flame retardants in polymeric materials by reversed-phase liquid chromatography with ultraviolet detection

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Abstract

A fast and simple method for the qualitative identification of technical flame retardants in polymeric materials is described. The LC separation was achieved on a reversed-phase C_{18} column. The identification of a large variety of flame retardants in a single analytical LC run was achieved using a mixture of aqueous phosphate buffer and methanol with ultraviolet detection in the scanning mode. The method was used for the analysis of flame retardants in a number of polymeric waste materials from TV sets and personal computers, on the basis of a comparison with standards. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic polymer materials are widely used in various industries [1]. If flame retardancy is required, e.g. in electrotechnical applications such as TV cabinets or personal computer housings, flame retardant additives containing bromine, chlorine or phosphorus are often employed [2]. Each flame retardant has its own specific application in a number of polymers (see Table 1).

In waste plastics, especially in scrap from electronic applications, a large variety of polymers and flame retardants can be found. Due to the recent increase in recycling activities, fast universal methods for the identification of flame retardants, independent of the polymer matrix, are needed [3]. This is especially true for the polybrominated hydro-

carbons that were mostly used in recent years, such as tetrabromobisphenol A and its derivatives, tribromophenol, tetrabromophthalic anhydride, bistribromophenoxyethane, polybrominated biphenyls and biphenyloxides (see Table 1). Due to different structures and degrees of bromination, their physical and chemical properties are typical for environmentally critical substances [4,5]. Noticeable concentrations of some of these compounds were detected in various biotic samples [6,7]. Brominated dioxins and furans may be formed during synthesis, polymer compounding and combustion, as well as during the use of electrical appliances [8,9].

Various chromatographic techniques have been employed for the analysis of polymer additives [10–13]. As a result of the good separation performance, gas chromatography is often preferred [14]. However, for compounds with high molecular weight, high separation temperatures, that can induce thermal reactions, are required. High-performance liquid

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Table 1
Flame retardant reference samples

No.	Chemical name	Abbreviation	Trade name[a]	Molecular weight	Br content (%)	Main applications[c]
I	Tetrabromobisphenol A	(TBBPA)	BA-59 BP	543.9	59	EPR, PC, ABS
II	TBBPA-bis-2-(hydroxyethylether)	(TBBPA-EO)	BA-50	632.0	51	ABS
III	TBBPA-bis-(2,3-dibromopropylether)	(TBBPA-PE)	PE-68	943.6	68	PE, PP
IV	TBBPA-bisallylether	(TBBPA-AE)	BE-SI	624.0	51	PS foams
V	2,4,6-Tribromophenol	(TBP)	PH-73	330.8	73	EPR, Phenols
VI	1,2-Bis(tribromophenoxy)ethane	(TBPE)	FF-680	687.7	51	ABS. PC
VII	Tetrabromophthalic anhydride	(TBPSA)	PHT-4	463.7	68	UPE
VIII	Decabromodiphenyloxide	(DECA)	DE-83	959.2	83	general purpose
IX	Octabromodiphenyloxide	(OCTA)	DE-79	801.4	80	ABS. SB, PS, PC
X	Pentabromodiphenyloxide	(PENTA)	DE-71	564.7	71	PUR
XI	Decabromobiphenyl	(DBB)	-[b]	943.3	85	general purpose
XII	Octabromobiphenyl	(OBB)	FR250BA[b]	785.4	81	PS, SB
XIII	Hexabromobiphenyl	(HBB)	Firemaster BP-6[b]	627.6	76	SB

[a]Unless otherwise indicated all substances were obtained from Great Lakes Europe, Frauenfeld, Switzerland

[b]Substances were obtained from Mallinckrot–Baker Chemicals, Griesheim, Germany. FR250 BA is a product of Dow Chemical; Firemaster BP-6 was produced by Michigan Chemical.

[c]Abbreviations used: ABS Acrylonitrile butadiene styrene, EPR Epoxyresin, PC Polycarbonate, PE Polyethylene, PP Polypropylene, PS Polystyrene, UPE Unsaturated polyesters, SB Stryrene butadiene, PUR Polyurethane.

chromatography (HPLC) circumvents these problems. There are no thermally induced reactions, and molecules of high molecular weight and a wide range of polarity can be analysed. The time of analysis is relatively short and ultraviolet (UV) detection results in good detection limits. Reversed-phase [15] and normal-phase HPLC–UV methods [13,23] have already been applied in the analysis of polymer additives. However, the analysis of flame retardants by HPLC was confined to only a few specific compounds [1,16,17,23].

The identification of brominated flame retardants present in real samples, is based on a comparison of the peak retention times t_R, and the corresponding UV absorption spectra with those of known standards. A characteristic sequence of peaks (peak pattern recognition) is also useful for the identification of certain technical flame retardants. The purpose of this work was to develop a fast RP-HPLC/UV method, suitable for the analysis of extractable flame retardants from polymers. With the aid of the optimized HPLC parameters, UV spectral and retention time data for the reference substances were determined and collected in an analytical data base. The feasibility of this method for the identification of brominated flame retardants in polymer samples is demonstrated.

2. Experimental

2.1. Materials

2.1.1. Reference sample preparation

All solvents used were of HPLC-grade (Aldrich). Samples of flame retardants were obtained as a gift from Great Lakes Europe, Frauenfeld, Switzerland. Some of them are also commercially available (No. I and IX Aldrich, No. V and VII Lancaster). Samples No. XII, XIII and XIV were obtained from Mallinckrodt–Baker Chemicals. The investigated substances are listed in Table 1. All reference samples were homogenized before use. Reference sample solutions were prepared in *n*-propanol. In order to prevent photodegradation processes, samples in the solid state were stored in the dark. Dissolved samples and polymer extracts were stored in brown glass bottles at 5°C.

2.1.2. Polymer sample preparation and extraction

Seventy-eight used TV and 34 personal computer housings were collected from a local recycling company. Polymer samples were grinded to a size of 1000 μm by the combination of cutting and centrifugal mills (Model SM 2000 and ZM 100, Retsch, Germany) under cooling with liquid nitrogen prior to

extraction. 0.50 g of the plastic shavings were mixed with 0.20 g fibrous cellulose in a soxhlet thimble to avoid agglomeration. The samples were extracted with 50 ml methanol and *n*-propanol in a soxhlet apparatus for three h. After cooling to room temperatures, the extraction solutions were filtered through a membrane disk filter (0.45 μm).

2.2. Instrumentation

Liquid chromatographic separations were performed with a Spectra Physics HPLC model SP8800 LC-Pump system. Sample injections were performed with a Spectra Physics SP8780 Autosampler, equipped with a 50 μl sample loop, allowing the variation of the injection volume. Usually 10 μl of the sample were injected after an equilibration time of one minute. The ultraviolet detection was done with the aid of a Thermo Separation Products Spectra FOCUS Detector in the scanning mode. Control over the pump and autosampler, as well as data acquisition and handling, were performed with a Spectra-Physics PC1000 software package. The analysis was carried out at a temperature of $23\pm2°C$. Chemical separations were achieved on a 4 mm ID, 250 mm long column (Nucleosil ET 250/4/8, Macherey–Nagel, Germany). C18 (ODS) reversed-phase and a particle size of 7 μm was used as stationary phase. 97% methanol and 3% buffered water of pH=7 were used as mobile phase at a flow-rate of 1.0 ml min^{-1}. The water was buffered by dissolving 0.1509 g (M=136.09 g mol^{-1}) KH$_2$PO$_4$ and 0.2477 g (M=141.96 g mol^{-1}) Na$_2$HPO$_4$ of p.a. quality in 100 ml water [18].

3. Results and Discussion

3.1. Preliminary studies

The first objective of our work was to find suitable conditions for the RPLC separation of the flame retardants listed in Table 1. These separation conditions could then be used for the identification of the flame retardants following extraction from the waste polymers. The flame retardants investigated, show a large difference in polarity. Preliminary experiments showed that only alcohols such as

methanol, ethanol or n-propanol are able to dissolve a relatively polar phenol such as tetrabromobisphenol A (No. I), as well as the rather non-polar decabromodiphenyloxide (No. VIII). Due to the relative low viscosity of methanol, it was chosen as the main component of the mobile phase. *n*-propanol turned out to be the best sample solvent.

At first several stationary phases were tested. A reversed-phase (RP)-C18, a RP-CN and a RP-phenyl were compared. Some components were absorbed on the CN-phase whereas for the phenyl phase an insufficient separation into two groups (one and two aromatic systems) was observed. The separation experiments were therefore started with a 10 μm particle size C-18 RP-column and 100% methanol as the mobile phase. The retention time of tetrabromobisphenol A itself was not reproducible under these conditions. Modification of the mobile phase with 3% of buffered water changed the retention time from 1.60 to 1.45 min, although an extension of the retention time was expected on the basis of the weaker solvent strength. The degree of hydration at the phenolic function, which depends on the pH value of the mobile phase, seems to be responsible for the change in retention times. All other substances showed the expected behaviour: their retention times increased on using a weaker eluent. In order to increase the separation performance, several solvent gradients (e.g. start: A 95%, B 5%, gradient (t=5 mm) to A 100%; A=75% methanol/20% *n*-propanol/5% buffered water; B=buffered water) and a change in particle size to 7 μm were also tested. The gradient method enhances the selectivity but not the resolution. Due to polymer wax in the extracts [19], 7 μm is the smallest particle size suitable for a moderate pressure in the system. Under these conditions (C18 (ODS) stationary phase, 7 μm particle size and a mobile phase of 97% methanol and 3% buffered water (pH=7), at a complete run time of 18 min) all the components of the flame retardants are sufficiently resolved. The retention times as well as the UV absorption maxima and detection limits for the latter chromatographic conditions are given in Table 2.

According to Table 2, substances I to VIII can be identified by one characteristic peak, with reproducible retention times, if buffered water (pH=7) is used in the mobile phase. The other substances IX to

Table 2
Chromatographic data obtained for reference substances

No.[a]	Retention time t_{Ret} (min)[c]	Detection limit ($S/N=3$) (ppm)	UV maxima (nm)
I	1.45	14	206, 291
II	2.80	80	203, 280
III	10.32	47	206, 280
IV	6.16	31	206, 280
V	1.55	24	214, 252, 319
VI	10.67	34	209
VII	1.52	23	222
VIII	16.56	48	226
IX[b]	9.56	40	218
X[b]	6.26	28	204
XI[b]	9.18	47	226
XII[b]	9.31	39	223
XIII[b]	7.51	20	215

[a]See Table 1.
[b]Data are given for the main component of these technical mixtures.
[c]R.S.D.: 0.05 to 0.81% (n=5).

XIII show sequences of peaks (see Table 3) under these chromatographic conditions, which can be accounted for in the following way.

From the literature [16,22,23] it is well known that commercial flame retardants, based on polybrominated biphenyls (PBBs) or biphenylethers (PBDEs), consist of several components of varying degree of bromination, although the product itself shows consistent quality and physicochemical properties. This is a result of different production methods or conditions, depending on the producer [16,22,23]. In contrast to the decabrominated compounds, penta- and octabromodiphenyloxides, as well as hexabromo- and octabromodiphenyl, show characteristic sequences of peaks that are also useful for the identification of the substances. The retention times, area percentage at 220 nm and ultraviolet maxima of these samples are reported in Table 3.

For instance, in the case of the main band of the biphenyls, a barthochromic shift of ca. 5 to 13 nm

Table 3
Characteristic sequence of peaks for technical flame retardants

No.	Abbreviation	Retention time t_R [min]	Area % at $\lambda=220$ nm	UV-maxima [nm]
IX	OCTA	7.28	1.1	212
		7.86	0.6	218
		8.59	6.6	211
		9.56	44	219
		9.94	16	220
		10.62	1.8	219
		11.80	9.9	223
		12.37	15	226
		15.00	1.0	226
		15.83	1.4	228
X	PENTA	4.91	30	201
		5.42	2.3	204
		5.72	11	204
		6.26	47	205
		7.75	4.6	202
		8.44	3.9	207
XII	OBB	7.61	2.0	219
		8.51	3.2	225
		9.31	63	225
		9.60	31	222
XIII	HBB	5.90	3.1	214
		6.49	9.3	214
		7.51	64	216
		8.52	17	221
		9.58	5.2	224

occurs for the more highly substituted compounds. The shift in the ultraviolet maxima is observed [21], but it is not linearly correlated with the retention times. This was already found and reported by de Kok [23]. In a normal-phase HPLC system, retention times decrease with an increasing number of bromine atoms in the molecules. Ortho substituted compounds show promoted retention [23]. In our case of a reversed-phase system, retention times behave vice versa. The retention time tends to increase for the higher substituted compounds due to their more non-polar character, although this rule is not strictly adhered to in all cases.

For the identification of the flame retardants,

characteristic fingerprints or sequence of peaks together with the ultraviolet spectra were used (for examples see Fig. 1). All these data were collected in an analytical database. Qualitative detection limits between 13 and 47 ppm at a signal to noise ratio of 3, referring to the identification of the flame retardants in polymer samples, are also included in Table 2.

3.2. Identification of flame retardants in polymer samples from polymer waste materials

In order to demonstrate the feasibility of the developed analytical method for the identification of
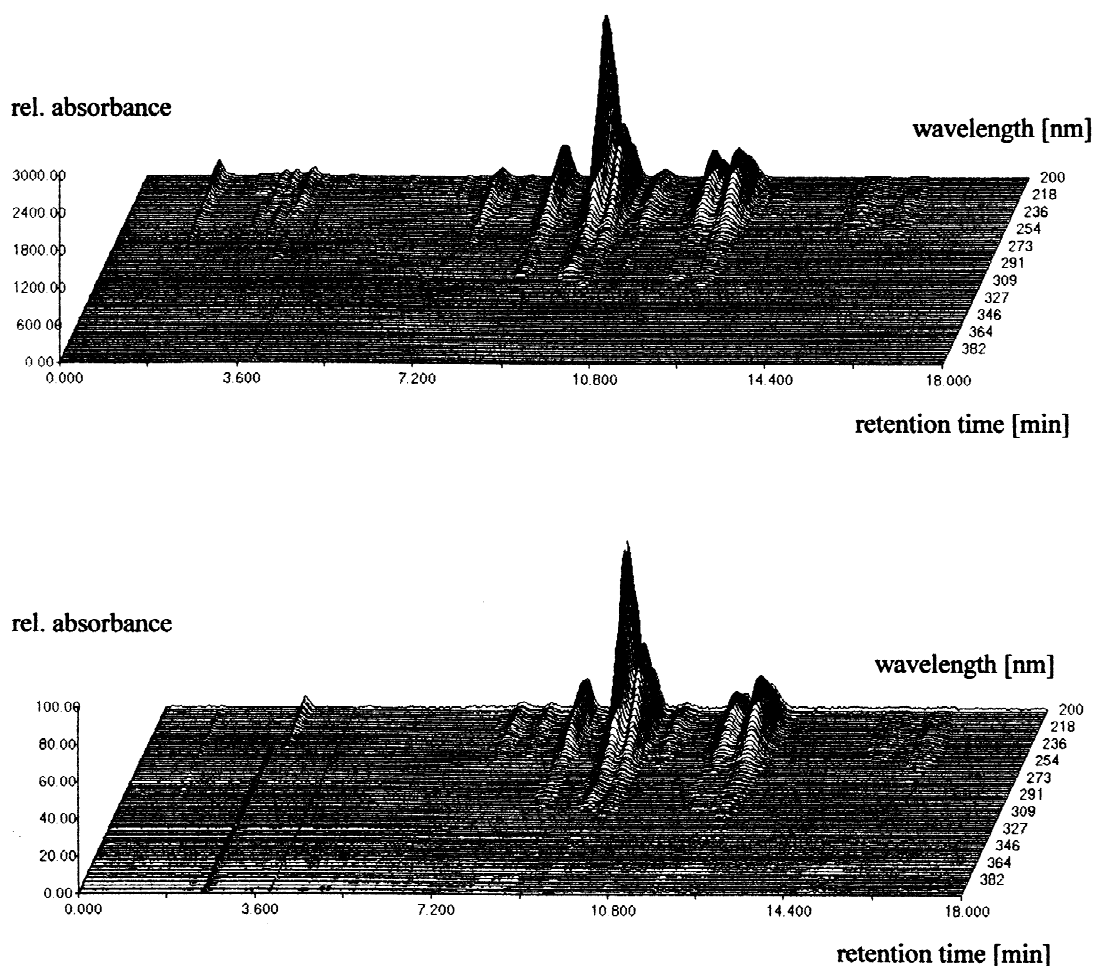

Fig. 1. Chromatogram of an extract (top) of a flame retarded computer housing and the corresponding standard as three dimensional chromatogram (bottom).

flame retardants in single polymer samples, a total of 78 TV housings and 34 personal computer housings were analysed as received from the recycling company. The average age of the housings was between 17 and 22 years for the TV sets and between two and ten years for the personal computers. All polymers were styrene-based polymers. Following the described analytical procedure, the leachable additives in the polymer samples were analysed. From a comparison of the data in the database with those of the samples, the flame retardants could be identified. Octabromobiphenyl (No. XII) was identified in 17%, decabromobiphenyl (No. XI) in 4% and 1,2-bis(tribromophenoxy)ethane (No. VI) in 4% of the TV housings. Decabromodiphenyloxide (No. XI) (51%) and octabromodiphenyloxide (No. IX) (26%) often occur together in the TV housing samples. The same is observed for the personal computer housings where decabromodiphenyloxide (No. XI) was identified in 55% and octabromodiphenyloxide (No. IX) in 18% of the samples. Moreover tetrabromobisphenol A (No. I) was identified in 18% and 1,2-bis(tribromophenoxy)ethane (No. VI) in 9% of these samples.

Fig. 1 shows a typical three dimensional chromatogram for an extract of a flame retarded ABS-polymer, as well as the three dimensional chromatogram of the corresponding standard. Octabromodiphenyloxide can be identified, as indicated by the characteristic sequence of peaks and by comparing UV spectra with those in the database.

The identification of the UV spectra can be improved by comparing differentiated UV spectra ($dI/d\lambda$ or $d^2I/(d\lambda)^2$). Fig. 2 presents an example for the differentiation of the UV spectrum obtained for the main component of octabromodiphenyloxide at 9.56 min.

For all investigated samples containing octabromodiphenyloxide, the sequence of peaks is the same as far as retention times and the UV spectra are concerned. They are also the same as for the reference samples (see Fig. 1). However, there are slight differences in the composition of the flame retardants depending on the manufacturer as already pointed out, such that the relative peak areas of the peaks at a certain wavelength do vary. But this does not reduce the value of the described identification method. For all other flame retardants listed in Table
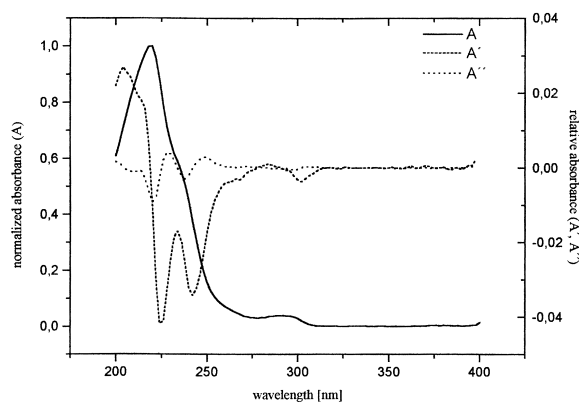

Fig. 2. Differentiation of UV-spectra, UV-absorption of octabromodiphenyl oxide at 9.56 min 'A'; first order differentiation with respect to λ 'A''' second order differentiation with respect to λ 'A'''.

3, the same effect as described was observed. The of the retention time for these samples is influenced by matrix effects and a R.S.D., e.g. for a sequence of five extracts containing polybrominated biphenyloxides, of 1.04% ($n=5$) is found. This is due to the large variety and high amount of additives in the polymer extracts.

In a specific class of main polymer only certain flame retardants occur (see Table 1). For recycling purposes, samples are usually sorted by polymer and flame retardant prior to the material recycling step. This circumvents the limitation that flame retardant I, V and VII are not sufficiently resolved by the described method.

4. Conclusions

A simple and reliable method for the identification of flame retardant species in polymer samples in a single liquid chromatographic step has been developed. This method makes it possible to identify polybrominated flame retardants in styrene based polymer samples. The application to other sample matrices has to be investigated in future work. The method is characterized by a short analysis time, which is only influenced by the sample preparation procedures. Modern extraction techniques [20] will assist in shortening this time. In future, attention will be focused on the identification of other leachable

substances of lower molecular weight in the extracts. For this purpose the analytical database has to be extended by including more reference substances for this method. The use of the described method for quantitative analysis in comparison to other methods will be the scope of future work.

Acknowledgements

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