

Rapid identification of RoHS-relevant flame retardants from polymer housings by ultrasonic extraction and RP-HPLC/UV

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Abstract

A rapid method was developed for the extraction and identification of RoHS-relevant organic flame retardants in polymer material. Extraction was carried out using ultrasonic supported solvent extraction (USSE) and isopropanol. HPLC separation was achieved using a reversed-phase phenylhexyl-modified column and methanol, containing 2-aminoethanol-buffered, alkaline water. Identification was carried out by scanning UV detection and comparison with a library assembled from spectra of reference substances. The method was used to extract and identify polymer additives in TV and PC monitor housings. The overall runtime required for extraction and chromatographic analysis is less than 10 min. The limits of detection comply with the recommendations set by the German draft law.

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1. Introduction

As a result of the directive 2002/96/EG (WEEE) by the European Parliament, recycling of polymers from electrical and electronic equipment (EEE) is expected to increase in the near future [1]. According to application recommendations, these polymers are filled with a large variety of chemical substances, where flame retardants form the main fraction [2,3]. Only polymers of the same polymer type and with a close match in additive content can be conjointly recycled [4]. For re-use, the accumulated materials have to be of uniform consistency. For this reason, a fast and reliable way to identify the contained substances is required.

In addition, the directive 2002/95/EG (RoHS) by the European Parliament prohibits the use of polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) [5]. These substances must not be present in recycled EEE materials. For brominated flame retardants as example, the Technical Application Committee (TAC) proposed an up-

per concentration limit of 0.1% (m/m). This value has been adopted in the draft law (ElektroG) of the Federal German Cabinet [6].

Earlier studies of our group have pointed out the problems that exist in analyzing the materials used in electrical and electronic equipment [7–10]. Methods were developed to cover common brominated flame retardants, including tetrabromobisphenol A, its derivatives and 1,2-bis(tribromophenoxy)ethane [5,11–17]. Recently, phosphorous based flame retardants like tricresylphosphate, resorcinol-bis(diphenylphosphate) or bisphenol A-bis(diphenylphosphate) (besides others) were introduced to replace brominated flame retardants [18–22]. For the operability of recycling procedures, the developed method must also be capable to identify these components.

The substances mentioned above, cover a wide range of molecular mass, polarity and acidity. Reversed phase high performance liquid chromatography (RP-HPLC), provides good opportunities for the necessary analytical separation. In addition, low limits of detection can be reached by ultraviolet (UV) detection [8]. In combination with organic solvents and ultrasonic supported solvent extraction (USSE), a fast,

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highly sensitive and reliable approach to leach polymers and to identify the extracted substances is possible [23]. When volatile organic solvents are used, ultrasonic cleavage is not expected to occur [24,25].

The purpose of this work was to develop a considerably faster method from an existing RP-HPLC/UV separation procedure developed by Riess et al. [8], with additional extension to phosphorous-based flame retardants (P-FR). An alternative sample extraction technique had to be found to further decrease the total time of the analysis. It is shown here that this is possible with a combination of a phenylhexyl-modified column and ultrasonic supported solvent extraction, while keeping a high degree of reliability.

2. Experimental

2.1. Instrumentation

The employed HPLC system was manufactured by Spectra-Physics, Darmstadt-Kranichstein, Germany. A model SP8800 pump and a model SP8780 auto sampler equipped with a 50 μl sample loop and variable injection volume from 10 to 50 μl were used. A spectra FOCUS scanning UV detection system was employed. The system is computer-controlled (OS/2 WARP operating system), using the Spectra-Physics PC1000 software package.

Polymer samples were pulverised in mills from Retsch, Germany. A Model SM 2000 (cutting mill) and Model ZM 100 (centrifugal mill) were used. Extraction was done in a Bioblock Scientific Ultrasonic Bath (2.01 bath volume, 46 kHz ultrasonic frequency, 80 W power) from Fisher Bioblock Scientific, Bd. Sébastien Brant, Illkirch, Cedex, France.

2.2. Chromatographic conditions

HPLC separations were carried out using a reversed phase column of phenylhexyl-modified, spherical silica gel (4.6 mm I.D., 150 mm length and 5 μm particle size, "Luna 5 μ Phenyl-Hexyl", from Phenomenex[®], Aschaffenburg, Germany). The pre-column was of the same modification (SecurityGuard[™] from Phenomenex[®], 4 mm I.D., 3 mm length).

The chromatographic eluent consisted of aqueous buffered methanol (isocratic); the pH was 8.3 at 50 °C. To 1.01 of methanol, 1.5 cm^3 of buffer was added from a concentrated, aqueous solution consisting of 5.0 cm^3 2-aminoethanol (monoethanolamin, basic component; $\text{p}K_{\text{a}} = 9.5$, $\delta = 1.012 \text{ g cm}^{-3}$, $M = 61.08 \text{ g mol}^{-1}$) and 26.5 cm^3 of hydrochloric acid ($c = 1.0 \text{ mol l}^{-1}$). The measured pH was 9.3 at 23 °C. The mobile phase was degassed with Helium (99.999%, v/v) before and during operation.

For analysis, 10 μl of the sample were injected at a flow-rate of 2.5 $\text{cm}^3 \text{ min}^{-1}$ and 50 ± 2 °C column-oven temperature, which resulted in a pressure of approximately 9 MPa. The analysis run time was 4.5 min. The UV-spectra were recorded from 200 to 400 nm at a rate of 6.4 spectra per second.

2.3. Materials

Without exception, solvents of high quality grade ("Rotisolv[®] HPLC" or "Rotisolv[®] Pestilyse", Roth Company, Germany) were used. Reference solutions of the available, technical flame retardants (Table 1) were prepared in isopropanol.

2.3.1. Reference substances

Samples of the flame retardants diphenyl-cresyl-phosphate (DKP), resorcinol-bis(diphenylphosphate) (RDP)

Table 1
Flame retardant references

Acronym	Chemical name	Trade name	Formula	M (g mol^{-1})	CAS-RN	Applications ^e
TBP	2,4,6-Tribromophenol	PH-73 ^a	$\text{C}_6\text{H}_3\text{OBr}_3$	330.8	118-79-6	Polyphenols
TBBPA	Tetrabromobisphenol A	BA-59BP ^a	$\text{C}_{15}\text{H}_{12}\text{O}_2\text{Br}_4$	543.9	79-94-7	PC, ABS
TBPE	1,2-Bis(tribromophenoxy)ethane	FF-680 ^a	$\text{C}_{14}\text{H}_8\text{O}_2\text{Br}_6$	687.6	37853-59-1	ABS, PC, HIPS
OBB	Octabromodiphenyl	RBF-074 ^b	$\text{C}_{12}\text{H}_2\text{Br}_8$	785.4	27858-07-7	PS, HIPS
DBB	Decabromodiphenyl	RBF-102 ^b	$\text{C}_{12}\text{Br}_{10}$	943.2	13654-09-6	PS, HIPS, PUR
PENTA	Pentabromodiphenyl ether	DE-71 ^a	$\text{C}_{12}\text{H}_5\text{OBr}_5$	564.7	1163-19-5	ABS, PUR
OCTA	Octabromodiphenyl ether	DE-79 ^a	$\text{C}_{12}\text{H}_2\text{OBr}_8$	801.4	32530-52-0	ABS, HIPS, PS, PC
DECA	Decabromodiphenyl ether	DE-83 ^c	$\text{C}_{12}\text{OBr}_{10}$	959.2	1163-19-5	PS, HIPS, PUR
TPP	Triphenylphosphate	— ^c	$\text{C}_{18}\text{H}_{15}\text{PO}_4$	326.3	115-86-6	General purpose ^f
DPK	Diphenyl-cresyl-phosphate	— ^d	$\text{C}_{19}\text{H}_{17}\text{PO}_4$	340.3	26444-49-5	General purpose ^f
TKP	Tricresylphosphate	— ^c	$\text{C}_{21}\text{H}_{24}\text{PO}_4$	371.4	1330-78-5	General purpose ^f
RDP	Resorcinol-bis(diphenylphosphate)	— ^d	$\text{C}_{30}\text{H}_{24}\text{P}_2\text{O}_8$	574.5	57583-54-7	ABS, HIPS, PC, PUR
BDP	Bisphenol-A-bis(diphenylphosphate)	— ^d	$\text{C}_{39}\text{H}_{34}\text{P}_2\text{O}_8$	692.6	—	ABS, HIPS, PC, PUR

^a Substances were obtained from Great Lakes Europe, Frauenfeld, Switzerland.

^b Substances were obtained from ULTRA Scientific, 250 Smith Street, North Kingstontown, RI, USA 02852.

^c Substances were obtained from Aldrich Chemical Company.

^d Substances were the courtesy of the Federal Institute for Materials Research and Testing, Berlin, Germany.

^e Selected Applications. Abbreviations used: ABS (acrylonitrile-co-butadiene-co-styrene), HIPS (high impact polystyrene), PC (polycarbonate), PS (polystyrene), PUR (polyurethane).

^f Also used as plasticizer.

and bisphenol A-bis(diphenylphosphate) (BDP) were a courtesy of the Federal Institute for Materials Research and Testing (Table 1). Decabromodiphenyl ether (DECA), triphenylphosphate (TPP) and tricresylphosphate (TKP), as well as the polymers acrylonitrile-butadiene-styrene-copolymer (ABS) and high-impact polystyrene (HIPS) were purchased from Sigma-Aldrich Chemie GmbH, Munich, Germany. Tetrabromobisphenol A (TBBPA), tribromophenol (TBP), 1,2-bis(tribromophenoxy)ethane (TBPE), octabromodiphenyl ether (OCTA) and pentabromodiphenyl ether (PENTA) were a courtesy of Great Lakes Europe. Octabromobiphenyl (OBB) and decabromobiphenyl (DBB) were obtained from ULTRA Scientific Europe GmbH, Wesel, Germany.

Reference samples were stored under exclusion of light to prevent photolysis. A special mixture of reference substances was prepared to develop a feasible chromatographic separation. The mixture consisted of DBB, DECA, TBBPA, TBP, TBPE and TPP, dissolved together in isopropanol, each with a concentration of approx. 50 ppm (m/m). Solutions of low concentration were prepared directly before use.

2.3.2. Industrial polymer references

To determine the reliability and performance of the developed method for industrial material from electrical and electronic equipment, 45 samples of miscellaneous housings (e.g. from TVs, PC monitors, mobile phones etc.) were analysed. These samples were already scrutinised by TDS- or "Soxhlet"-GC/MS and by FT-IR methods [11,12]. The polymers contained BDP, DBB, DECA, OBB, OCTA, TBBPA, TBP, TBPE or TPP, respectively. The concentrations of the flame retardants ranged from approx. 1 to approx. 15% (m/m).

2.3.3. Special polymer references

Polymer references to determine the limits of detection (LOD) were specially prepared. Polymer material was dissolved in dichloromethane (for HIPS) or acetone (for ABS) and mixed with the particular flame retardant. The solid material was obtained by co-precipitation of the polymer and the flame retardant while letting the solvent evaporate under continuous stirring at room temperature. Afterwards, the samples were dried thoroughly at 65 °C, embrittled with liquid nitrogen and ground to a powder with a maximum grain size of 1000 µm. Concentrations of flame retardants from 0.05 to 2.0% (m/m) were prepared.

2.4. Extraction

Besides using solid pieces of the industrial polymers for ultrasonic extraction, a fraction of 5 ± 1 g was taken, embrittled with liquid nitrogen and ground to a particle size less than 1000 µm. Three portions from the industrial material of 0.5 g each were then extracted separately, in order to exclude faulty measurements due to the possible inhomogeneity of the samples. From special polymer references, only one por-

tion of 0.5 g was taken for extraction from the special polymer references. The material was considered to be homogeneous as a result of the selected preparation procedure.

The granulate material was transferred into 20 cm³ test tubes (Fiolax, Schott, Germany) and extracted at room temperature with 5 cm³ of isopropanol. The tubes were immersed halfway into the water of an ultrasonic bath and left there for 5 min under the influence of ultrasound. The extractives were filtered through a membrane disk filter of 0.2 µm pore size prior to chromatographic analysis.

If necessary, the inner glass surface of the tube was conditioned twice with 7.5 cm³ of isopropanol or acetone, treating it with ultrasound for 5 min.

3. Results and discussion

The aim of our work was to find a fast, reliable and law compliant method to identify flame retardants (FRs) in styrene-based housing polymers from WEEE. This was done by a combination of fast extraction and rapid identification of the various polymer additives listed in Table 1.

3.1. Chromatographic method development

The basis for this chromatographic method was provided by Riess et al. [8]. The 250 mm, octadecyl-modified column was replaced by a 150 mm, phenyl-hexyl-modified column and a pre-column of the same modification was added. Increasing the flow rates up to 1.5 cm³/min did not significantly shorten the time of analysis. Increasing the flow to a higher rate than 1.5 cm³/min produced unfavourably high pressures of above 20 MPa. This still was observed changing to different solvents such as acetonitrile, THF or aqueous dilutions of these, containing various buffer systems at acidic or basic pH values. Only an increase in the column oven temperature to 50 °C produced workable pressures of 5 to 7 MPa. Significant shortening of the analysis time was then achieved by increasing the flow rate to 2.5 cm³/min, which generated a feasible pressure of 9 MPa.

To obtain a better separation of TBP and TBBPA, their phenolic character was utilised. Increasing the pH to 9.3 at room temperature (8.3 at 50 °C), by changing the buffer to 2-aminoethanol/HCl, diminished the retention time. The eluent consisted of 1.5 cm³ concentrated, aqueous buffer per 1 litre of methanol; the pressure was stable at 9 MPa. Application of this change resulted in shorter retention times also for the biphenyls and diphenyl ethers. As a result, t_R for DECA was below 4 min. On assuming DECA to have the longest t_R and assuring that no substances, e.g. polymer fragments, are carried on to the next run, the total time for one measurement was set to 4.5 min.

To assess the feasibility and quality of the new analytical procedure, the testing of results with known references is indispensable for verification. To accelerate quantification, to detect the limits of the system used, and to reduce costs,

solutions of the mentioned flame retardants were prepared instead of using the (few) commercially available standard reference solutions.

First, the limits of detection (LOD) for dissolved flame retardants were determined (Table 2, columns 1–5). To visualize the suitability of the separation, a chromatogram of a mixture of several flame retardants in different concentrations is shown in Fig. 1. Due to the high load of the analytic column, the retention times are slightly shifted. Since this

special mixture of substances was made for verification purposes, it is not likely that this combination will be found in waste polymers from electrical and electronic equipment. However, the separation of the components is satisfactory and each contained flame retardant can be identified from its particular UV-spectrum.

Six of the 13 analysed substances generated more than one peak in the chromatogram. Technical flame retardants like polybrominated biphenyls or polybrominated diphenyl ethers

Table 2
Investigated parameters of the examined flame retardants

Component	t_R (min)	UV-max (nm)	Relative height ^a (%)	Limits of detection from reference solution ^b ($\mu\text{g}/\text{cm}^3$)	Limits of detection from reference polymer ^{b,c} ($\mu\text{g}/\text{g}$) (%(m/m))
TBP	0.66	210	100.0	0.6	Not determined
TBBPA	0.77	205	100.0	1.1	790 (0.079)
TPP	0.90	<200	100.0	2.3	1450 (0.145)
TKP	0.91	<200	100.0	2.4	Not determined
DKP	0.95	<200	100.0	2.8	Not determined
	1.13	<200	4.6		
RDP	0.88	<200	9.7	3.1	1380 (0.138)
	0.98	<200	100.0		
	1.09	<200	33.9		
	1.23	<200	7.9		
BDP	1.13	<200	100.0	2.9	1290 (0.129)
	1.31	<200	4.0		
	1.55	<200	12.1		
	2.27	<200	1.5		
PENTA	1.31	<200	74.5	1.7	780 (0.078)
	1.45	203	40.0		
	1.50	203	100.0		
	1.59	204	25.5		
	1.73	206	10.0		
OCTA	1.09	212	0.4	1.4	880 (0.088)
	1.20	209	1.1		
	1.33	209	0.4		
	1.42	211	0.4		
	1.53	210	1.8		
	1.65	212	16.2		
	1.79	214	100.0		
	1.95	214	9.6		
	2.08	216	25.9		
	2.19	219	43.9		
	2.56	220	3.9		
	2.82	223	14.0		
	3.16	223	0.4		
	3.66	224	0.9		
TBPE	2.09	206	100.0	0.9	700 (0.070)
DBB	2.21	223	100.0	3.4	830 (0.083)
OBB	1.76	221	2.9	4.4	870 (0.087)
	1.90	216	4.0		
	1.98	217	3.0		
	2.10	220	13.6		
	2.38	220	100.0		
	2.71	223	4.2		
DECA	3.78	224	100.0	4.5	860 (0.086)

^a Per cent of highest peak at its UV maximum. The italic numbers mark the peak with 100% relative height. If the UV maximum is below 200 nm, peak height is determined at 200 nm.

^b At a signal to noise ratio of 3 or better for the main peak.

^c In filtered extractives from polymer references.

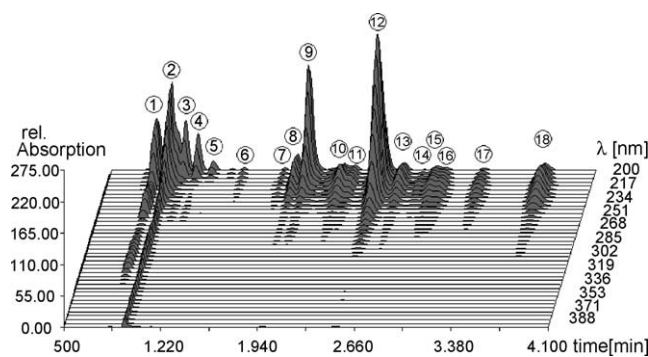


Fig. 1. Chromatogram of selected flame-retardants. (1): Tribromophenol (TBP), $15 \mu\text{g}/\text{cm}^3$; (2): tetrabromobisphenol A (TBBPA), $20 \mu\text{g}/\text{cm}^3$; (3): triphenylphosphate (TPP), $20 \mu\text{g}/\text{cm}^3$; (4) and (5): congeners of Resorcinol-bis(diphenylphosphate) (RDP), $25 \mu\text{g}/\text{cm}^3$; (6)–(8) and (13)–(17): congeners of octabromodiphenyl ether (OCTA), $20 \mu\text{g}/\text{cm}^3$; (9): bis(tribromophenoxy)ethane (TBPE), $20 \mu\text{g}/\text{cm}^3$; (10): decabromobiphenyl (DBB), $20 \mu\text{g}/\text{cm}^3$; (11) and (12): congeners of octabromobiphenyl (OBB), $50 \mu\text{g}/\text{cm}^3$; (18): decabromobiphenyl ether (DECA), $30 \mu\text{g}/\text{cm}^3$.

(e.g. PENTA, Fig. 2) and also the phosphorous based flame retardants, often consist of several components, so called congeners. These congeners are by-products of the chemical synthesis and are not removed from the technical product. The absorption maxima of the congeners from one technical flame retardant can vary, e.g., depending on the grade of bromination (Table 2). To reduce the complexity of the semi-automated identification and quantification procedure by the software, all peak ratios resulting from one product were calculated at the wavelength of the UV-maximum of the main component.

The insufficient separation of the congeners from several multi-congener components was a concession to the brevity of the method. As a result, the determination of one single peak area from such flame retardants could not always be done correctly by the software. For this reason, the peak heights were used to calculate the peak ratios.

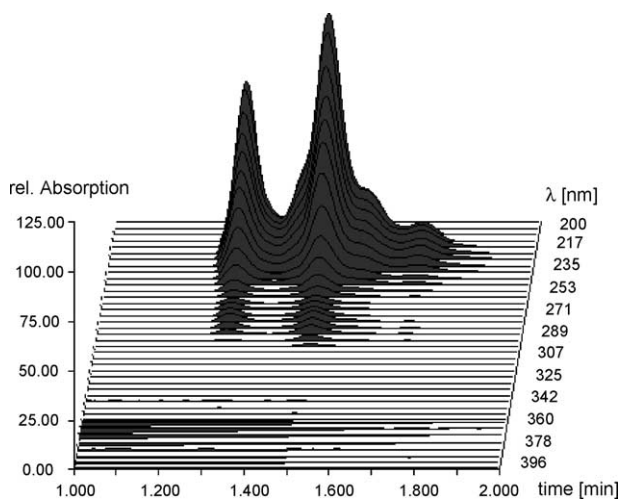


Fig. 2. Chromatogram of technical PENTA.

Further identifications of extracted flame retardants were performed by using an internal library of chromatograms for the specific flame retardants and their associated UV-spectra, assembled from the results obtained up to this point.

3.2. Extraction method advances

The usual methods for the extraction of additives from polymers, such as Soxhlet extraction and accelerated solvent extraction (ASE), require a relatively long time to be accomplished properly. Except for the indispensable shredding and grinding of the sample, the extraction process, including cleaning and preparation of the extraction apparatus, necessitates disproportionately more time than the chromatographic method described above. For example, a Soxhlet extraction of previously ground polymer material requires 6–8 h. Therefore, we developed an extraction method suiting the brevity of the analytical method and simultaneously including all associated procedures.

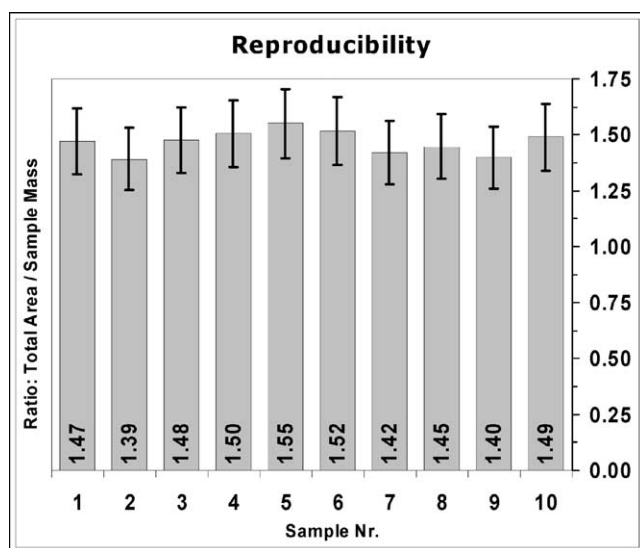
The ideal method should permit a non-demanding, rapid and fail proof sampling procedure that allows the operator to perform the measurement on the first sample while already preparing the next one. During the course of our experiments, we considered ultrasonic supported solvent extraction (USSE) to be a technique capable of combining short operation time with rapid cleaning and conditioning. Enhancing this technique allowed us to reduce the total time necessary for taking, extracting and preparing samples and extractives to less than 10 min. Cleaning is not necessary due to the use of standard size and thus inexpensive test tubes, which are fully disposable. Furthermore, no conditioning is necessary for the purpose of this extraction. Tests clearly showed that the tubes do not contain any chemicals that can be dissolved under these circumstances.

First, the extraction of solid samples was tested on the flame retardants contained in the 45 industrial references from miscellaneous housings. A solid polymer probe was cut to fit the dimensions of the test tube, and underwent USSE. Verification of correct results for the detected flame retardants was done by comparing the analytical results with those obtained before by GC/MS and FT-IR. No cleavage products were detected as a result of the exposure to ultrasound.

All flame retardants from the industrial materials could be extracted, unless their concentration in the polymer was lower than approx. 3% (m/m). This is appropriate for the identification of flame retardants from commercially available polymers, but it is insufficient to suit the 0.1% (m/m) limits set by the Technical Application Committee (TAC).

An advance in the LOD was expected on repeating the extractions using ground polymer material instead of solid pieces. For that reason, the polymers were pulverised and examined again. Due to this modification, all flame retardants from the industrial references could be detected, regardless of their concentration. As a result, all further extractions related to the analytical investigations were done on previously ground material.

Table 3
10-fold reproducibility of extraction



To determine the LOD for this extraction technique, reference polymers with flame retardant concentrations lower than those available from the industrial references were necessary. These materials are not available commercially. Hence, they were prepared from the particular polymers and flame retardants by combined dissolution and subsequent precipitation. The investigated LODs from polymer material (Table 2, column 6) correspond to the limits of 0.1% (m/m) claimed by the TAC.

The high LOD for the phosphorous-based flame retardants is the result of low UV-activity of the plain hydrocarbon-substituted phosphoric acid derivatives investigated. As a result of TPP often being contained in polymers as a plasticizer, this component is not always an indicator for flame retardancy. However, it also can be contained as a congener in TKP and related phosphorous-based flame retardants.

The reproducibility of USSE is shown in Table 3. Ten different samples of the same reference polymer were extracted and subsequently analysed. The reference contained 0.13% (m/m) OCTA, which is close to the LOD. Each column represents the total peak area for one injection (summed up for all congeners of OCTA) divided by the respective sample mass. It is shown that the fluctuations are in the range of approximately 10% of the peak area (represented by the error bar), which is the average background noise at this concentration. Different concentrations as well as different flame retardants show equal or better results. These tests also prove that the special reference material is homogeneous.

For reliable results on DECA, it is indispensable to prepare the extractive shortly before the chromatographic measurement. DECA soon starts to decompose into various components when dissolved in alcohol. This significantly lowers the limits of detection. The decomposition is detectable within 2–4 days of storage, depending on the storage temperature and, if not stored in brown glass vials, also on the influence of

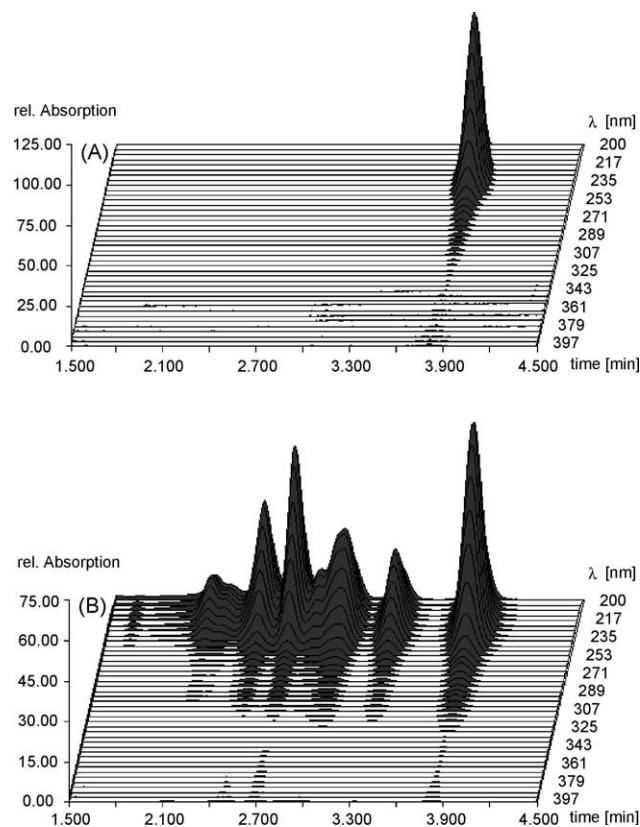


Fig. 3. Fresh and decomposed DECA.

light. Fig. 3 clearly shows the single peak of freshly extracted DECA (A) and the multiple peaks evoked by the products of decomposition after 4 days of storage (B). The deterioration of LOD is caused by the decreasing peak of DECA due to decomposition. For best results, the extractives have to be analysed directly after extraction and filtering.

Decomposition of any flame retardant due to the influence of ultrasound could not be detected. However, cleavage caused by ultrasound was not expected because of the volatility of isopropanol. The solvent is quasi cushioning the collapse of the bubbles by evaporating into the cavity, preventing destructive action to polymers and substances.

4. Conclusions

We developed a rapid, reliable and law compliant procedure to investigate flame retardants in polymer housings from electrical and electronic equipment. Extraction and chromatographic analysis can be done within only 10 min. The extraction technique allows the operator to run the measurement and to prepare the samples simultaneously. The limits of detection for PBB and PBDE (including 1,2-bis(tribromophenoxy)ethane) comply with the limits of 0.1% (m/m) recommended by the TAC and are thus in accordance with the ElektroG draft law. In addition, the spectrum of substances includes various phosphorous-based flame retardants.

The overall cost of this analytical method was significantly reduced by omission of time and cost intensive extraction methods. The preparation of the method itself is rather extensive. Though, once set up, it provides a fast, reliable and law compliant procedure for analysing flame retardants in styrene-based polymers from WEEE.

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