

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 (SecurityGuardTM 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; $\text{p}K_a = 9.5$, $\delta = 1.012 \text{ g cm}^{-3}$, $M = 61.08 \text{ g mol}^{-1}$) 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 ("Rotisol[®] HPLC" or "Rotisol[®] 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.

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