Identification of brominated flame-

FTIR-Spectroscopy – Method for compliance with the RoHS directive

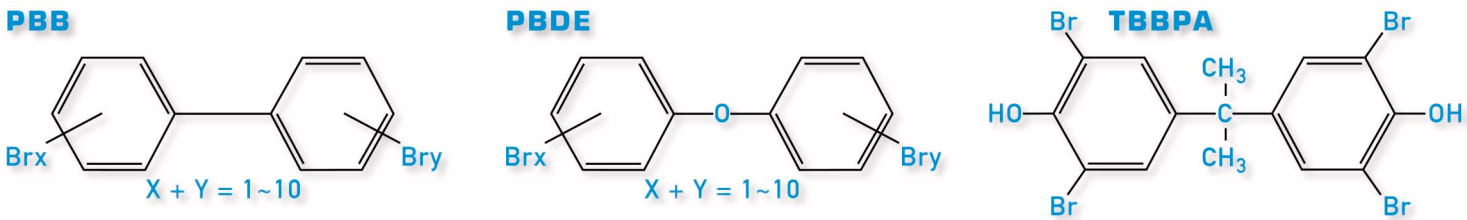

Figure 1: Structural formulae of brominated biphenyls

The RoHS* directive (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) regulates the restriction of the use of brominated flame-retardants in electrical and electronic devices as of July 2006. Consequently, polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) can no longer be used as flame-retardants in polymers unless their concentrations are lower than 1,000 ppm. The objective of the RoHS directive is the protection of human health and the environment from hazardous effects. During recycling of electronics waste, contamination by brominated compounds should therefore be reduced.

Polybrominated biphenyls are classified as health hazards. PBB and PBDE are chemicals that have, in the past, been used as flame-retardants in polymers in concentrations of 5 % up to 10 %. RoHS restricts the use of compounds such as tetrabrominated biphenyl A (TBBA), brominated polystyrene and brominated aromatic triazine.

Figure 1 presents the structural formulae of brominated biphenyls.

According to RoHS, the following compounds are considered hazardous: pentabrominated diphenyl ether (PentaBDE) and octabrominated diphenyl ether (OctaBDE). OctaBDE has been used in polymers such as ABS and PS. Currently, decaBDE is largely being used as a flame retardant in PS, PE, ABS and polyester. DecaBDE has not yet been included in the RoHS directive. Commercial decaBDE however consists of a mixture of approximately 97 % - 98 % decaBDE and 0.3 % up to 3 % of other BDE's. Therefore, when a polymer contains 10 % decaBDE (containing 1 % contamination of other brominated BDE's), the PBDE content will exceed the RoHS threshold value of 1,000 ppm.

FTIR spectroscopy – fast, non-destructive, simple

In order to comply with the requirements of the RoHS directive, first the total bromine content of a sample is determined. If this exceeds 5 % after the preliminary examination using the EDX systems, infrared spectroscopy is recommended as this will enable identification of compounds. This simple and non-destructive method quickly leads to useful results. Compound identification is possible as the flame-retardants, were present up to now in polymers in concentrations of higher than 5 %. This level is still detectable in polymer mixtures using FTIR. Concentrations that approach the detection limit, however, must be measured using other analytical methods. In this case, GCMS is highly suitable as all brominated compounds can be separated and detected down to the trace level. GCMS, on the other hand, is more time consuming with respect to sample preparation and data analysis.

In general, it is recommended to carry out an overall pre-screening via energy-dispersive X-ray fluorescence (EDX). Using this analytical method the total concentration of elemental bromine in the sample is detected, although it is not possible to distinguish which compound actually contains bromine. When more than 5 % of total bromine is detected, FTIR can be used for further identification of bromine compounds. When less than 5 % bromine is detected, GCMS analysis can be implemented for separation and identification.

Fast and straightforward IR-analysis of polymers is possible since

Brominated Flame Retardants	Thermoplastic Polymers										
	ABS	PS	PP	PE	PC	PC/ABS	Poly amide	Polyester	PVC	S-PS	S-PU
Tetrabromobisphenol A	●	●			●						
Decabromodiphenyl Ether	●	●	●	●	●	●	●	●	●	●	●
Octabromodiphenyl Ether	●	●	●	●							
Brominated Aromatic Triazine	●	●	●	●	●	●		●			
Brominated Polystyrene	●	●	●	●	●	●	●	●			

Brominated Flame Retardants	Thermoplastic Polymers			Others			
	Epoxy	Unsaturated Polyester	Phenol	Elastomer	Adhesive · Paint	Fiber	Woody
Tetrabromobisphenol A	●	●	●		●		
Decabromodiphenyl Ether	●	●	●	●	●	●	
Octabromodiphenyl Ether				●	●		
Brominated Aromatic Triazine							
Brominated Polystyrene							

Table 1**: Typical polymers and their flame-retardants. Listing of brominated flame-retardants and their use in polymers. (ABS = acrylonitrile-butadiene-styrene, PS = polystyrene, PP = polypropylene, PE = polyethylene, PC = polycarbonate, PVC = polyvinylchloride, PU = polyurethane)

retardants in polymers

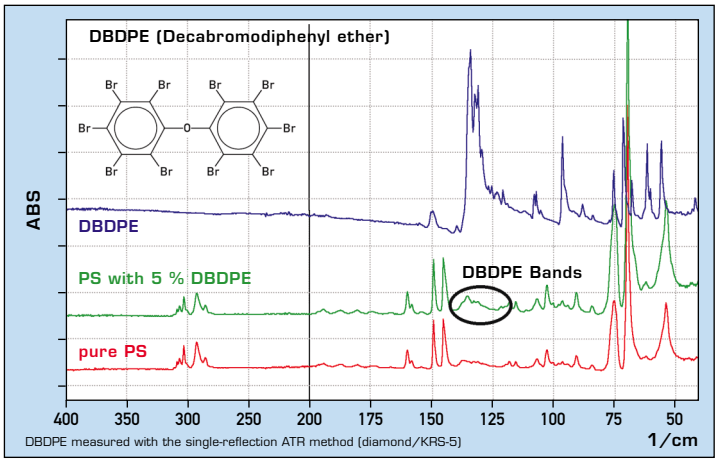

Figure 2: Polystyrene spectra with and without flame-retardant as well as the IR spectrum of the flame-retardant decabrominated diphenyl ether.

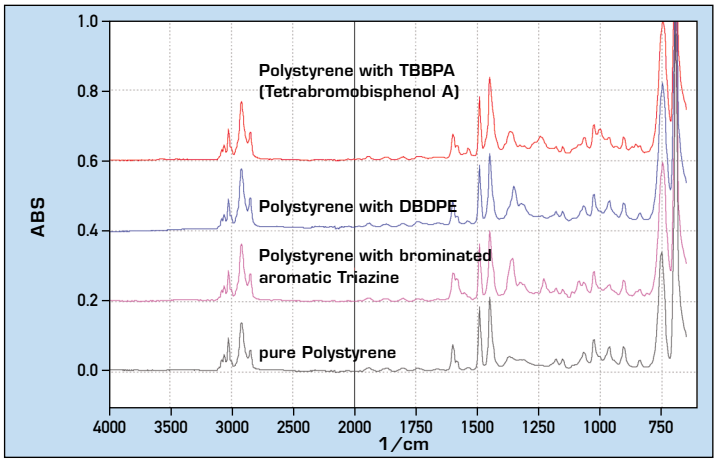

Figure 3: IR spectra of polystyrene with several flame-retardants

brominated biphenyls exhibit their own very characteristic infrared spectra. The polystyrene example exhibits three spectra: DBDPE, PS with DBDPE and pure PS. The range in the IR fingerprint, where DBDPE in PS identification is possible, is clearly discernible (Figure 2). Figure 3 shows polystyrene with other brominated flame-retardant additives.

Fast identification of brominated flame-retardants

The fingerprint region of 1500 cm^{-1} - 1000 cm^{-1} is important for the identification of brominated flame-retardants, where clear differences between the spectra can be seen. Based on this information, an analytical method for fast identification of brominated flame-retardants and polymers has been developed using Shimadzu's FTIR-8400S in combination with a single-reflection accessory.

In the present example, a diamond ATR unit with KRS-5 crystal was used as single-reflection accessory. A diamond as sample surface is recommended as the polymer can be present in a flexible or solid state. The diamond sample surface enables the application of high pressures to ensure that the sample is positioned tightly on the crystal so that optimum penetration of the sample by the IR beam is guaranteed. The beam penetrates the sample surface to a depth of approximately 2 µm.

As RoHS specifies a homogeneous sample material, this depth of penetration is sufficient in order to completely characterise the sample. Using this measuring configuration, the spectrum is acquired within a very short time interval (approximately 1 min.) and is evaluated automatically according to RoHS guidelines.

To validate analysis results, the spectrum is compared subsequently with a library of polymer spectra. For polymer identification, a database already containing 41 polymers (see table 2) is used. This database contains logical associations and the Distinction Software tests for plausibility, for instance by evaluation of signal ratios.

The decision criterion includes warning messages that range from "Identification of the polymer not possible" to "Applied pressure not sufficient" and finally to the conclusion "O.K." or "Not O.K.". These FTIR analysis results can be considered as unambiguous when combined with the pre-analysis from the EDX System.

Infrared spectrometry can therefore be regarded as a fast and simple alternative solution to the preselection of polymers. Minimal sample pretreatment is necessary and fast results are obtained via predefined methods.

Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene	PI	Polyimide
ABS+PBDE	ABS containing PBDE	PMMA	Polymethyl methacrylate
EVA	Ethylene-vinylacetate copolymer	PMMA+PBDE	PMMA containing PBDE
NYLON	Nylon	POM	Polyoxymethylene (acetal)
NYLON+PBDE	Nylon containing PBDE	POM+PBDE	POM containing PBDE
PBT	Poly(butylene terephthalate)	PP	Polypropylene
PBT+PBDE	PBT containing PBDE	PP+PBDE	PP containing PBDE
PC	Polycarbonate	PPS	Poly(phenylen sulfide)
PC+PBDE	PC containing PBDF	PPS+PBDE	PPS containing PBDE
PC+TBBPA	PC containing TBBPA (Tetrabromobisphenol A)	PS	Polystyrene
PCTFE	Polychlorotrifluoroethylene	PS+PBDE	PS containing PBDE
PCTFE+PBDE	PCTFE containing PBDE	PS+TBBPA	PSPS containing TBBPA
PE	Polyethylene	PS+Triazine	PS (containing brominated aromatic triazine)
PE+PBDE	Polyethylene containing PBDE	PU	Polyurethane
PEEK	Polyether-ether-ketone	PVA	Poly(vinyl alcohol)
PEEK+PBDE	PEEK containing PBDE	PVC	Poly(vinyl chloride)
PEI	Polyetherimide	PVDF	Poly(vinylidene fluoride)
PES	Polyester	PVDF+PBDE	PVDF containing PBDE
PES+PBDE	PES containing PBDE	SBS	Styrene-butadiene-styrene copolymer
PET	Poly(ethylene terephthalate)	SBS+PBDE	SBS containing PBDE
PET+PBDE	PET containing PBDE		

Table 2: Overview of 41 polymers and polymer mixtures in an expandable database

* Directive 2002/95/EC of the European Parliament and of the council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment

** Flame retardants chemicals association of Japan (FRCJ)