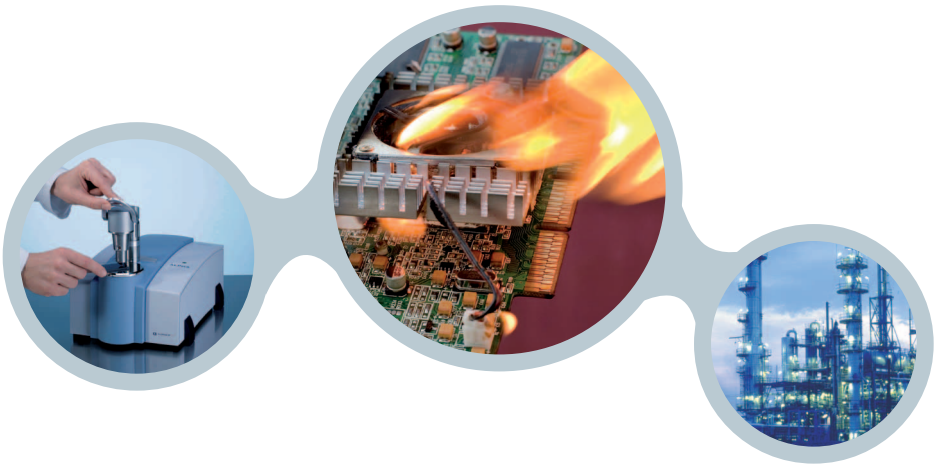


Application Note AN # 59

Identification of brominated flame retardants in polymers

International Regulations

The WEEE (Regulation of waste disposal for electronic and electrical equipment) and RoHS (Restriction of the use of certain hazardous substances in electrical and electronic equipment) directives, adopted by the European Union since July 2006, are aimed to reduce the amount of electronic waste and to limit the use of certain hazardous substances such as brominated flame retardants. The purpose is to protect the environment, to alleviate personal health issues and to reduce contamination through brominated materials which may be used in recycling processes. RoHS bans six harmful substances: Lead (Pb), Mercury (Hg), Cadmium (Cd), Chromium-VI (Cr-VI) as well as polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE). The retardants PBB and PBDE are only allowed if they are below the limit of 0.1% by weight. PBB and PBDE are compounds, which have been added in the past to polymers with a minimum 5 to 10 percent by weight to achieve an effective property. RoHS bans chemicals like Tetrabromobisphenol A (TBBPA), brominated aromatic Triazines, Pentabromodiphenylether (PentaBDPE) and Octabromodiphenylether (OctaBDPE). An additional and widely-used flame retardant of the PBDE class is Decabromodiphenylether (DeBDPE), which is as yet an exception in RoHS.

Bruker Optics, as a manufacturer of high performance FT-IR spectrometers, offers a very suitable measurement method for detecting these flame retardants in thermoplastic polymers.

Polymer	**Flame retardant**		
	Decabromo-diphenylether	Tetrabromo-bisphenol A	Brominated polystyrene
PBT	•		•
ABS	•	•	•
PC/ABS	•	•	
SB	•		
PS	•	•	•
PE	•		
PP	•		•
PA	•		•
PVC	•		

List of possible polymer flame retardant- combinations.

FT-IR spectroscopy as a fast and easy method

The principle of FT-IR (Fourier-Transform Infrared) spectroscopy is based on the excitation of molecular vibrations. Molecules with a changeable dipole moment are called infrared

active, because the IR radiation will only be absorbed, if the dipole moment of the corresponding functional group changes during vibration. Each functional group absorbs IR radiation at a characteristic wavelength. Therefore an unknown substance can be identified by comparing it with spectra of known substances. In addition quantitative analysis is possible using calibration spectra of known concentrations.

For quantification of the total Bromine amount (and Pb, Hg, Cd, Cr-VI), X-ray fluorescence analysis (XRF) is used. However the type of brominated flame retardant cannot be determined by X-ray alone. Fortunately the FT-IR technique, which is sensitive to molecular structure, makes this determination possible and molecular Br-contents of more than 5 % can be rapidly and non-destructively analysed.

The compounds of interest show significant absorption bands in the so-called IR fingerprint region (2000 cm^{-1} - 600 cm^{-1}), which allows a rapid and reliable discrimination. Even though a few bands of the flame retardant can overlap with those of the polymer, differentiation can be achieved using the OPUS IDENT-software package.

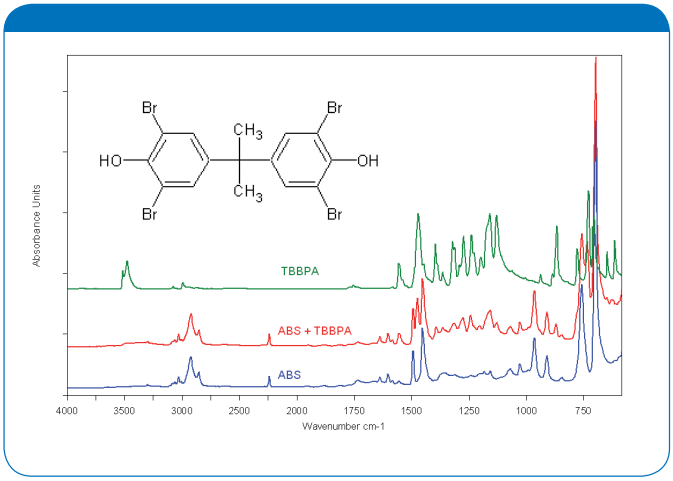
Measurement technique

The well-established ATR-technique (Attenuated Total Reflection) is used to provide a fast and easy sample screening by simply pressing the sample with the pressure clamp onto the surface of the ATR crystal. Hereby the IR radiation penetrates slightly (a few microns) into the sample surface. The IR detector of the FT-IR spectrometer can then measure the absorbance due to the sample. A Diamond ATR crystal is recommended due to its robustness and hardness, because the materials for identification can often scratch other ATR crystal types. Additionally this diamond crystal type allows a relatively high pressure to ensure a sufficient optical contact between sample and crystal and therefore gives optimised FT-IR spectra.

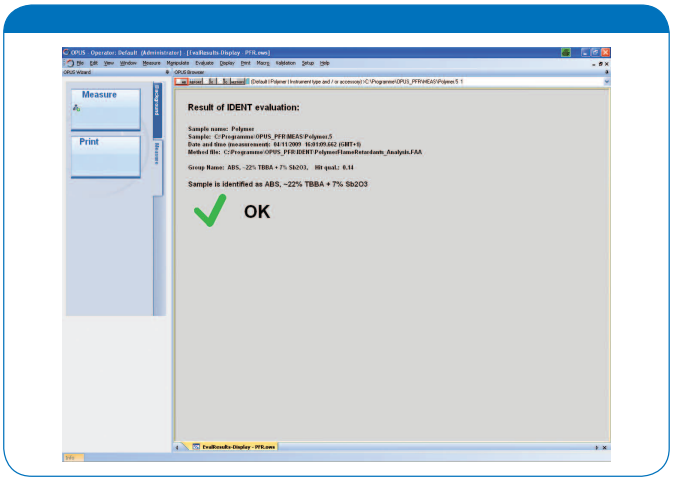
Identification

A defined database in combination with a specially developed program identifies the polymer and flame retardant that is used. After a measurement, the identification software "IDENT" automatically checks a measured spectrum with spectra of the IDENT-library in terms of compliance. The analysis result, identified polymer and flame retardant, is displayed in a report window within the software workspace and can be printed out automatically if desired. The library includes most common polymer/flame retardant (FR)-combinations, which are on the market now. A reliable FR determination is possible with greater than 5 percent by weight of flame retardant; in the case of certain polymers even an amount of 3 percent by weight is detectable. For lower concentrations typically GC-MS analysis is used.

FT-IR analysis in combination with the ATR technique offers the tremendous advantage of obtaining a significant result in a short time with nearly no sample preparation.



FT-IR spectra of ABS (blue), ABS with TBBPA (red) and pure TBBPA (green) measured with an Diamond ATR-unit.



Result of an identification, ABS with TBBPA

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