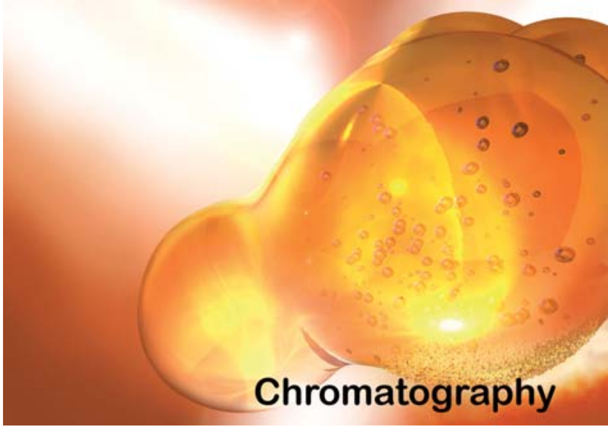


Application Note

Qualitative and quantitative Analysis of Brominated Flame Retardants (PBB und PBDE)

Introduction

On the 13th of February 2003 the European Union published the new regulation on electric and electronic waste (WEEE, **W**aste **E**lectrical and **E**lectronic **E**quipment) as well as the restriction of the use of certain hazardous substances in electric and electronic equipment (RoHS). Thus both regulations became effective, and in January 2005 they were transferred into national law. According to RoHS, lead, mercury, cadmium, Chromium (VI), polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) are forbidden from July 2006. Shimadzu, one of the worldwide leading manufacturers of analytical instrumentation offers the complete hardware and software for the secure identification of hazardous substances as well the know-how and competence.

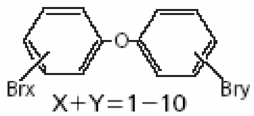
Brominated Flame Retardants

Brominated Flame Retardants are used since decades in various consumer products. Due of their risk for health and the suspected cancerogenity of some of the congeners these compounds are forbidden to be used in new electric and electronic parts or shall not exceed the limit of 1000 ppm. Particularly, Pentabromdiphenylether (PentaBDE) and Octabromodiphenylether (OctaBDE) are mentioned, the latter is used in the polymers ABS and PS. Currently, mainly DecaBDE is used as flame retardant in the polymers PS, PE, ABS and polyester.

Analysis of Brominated Flame retardants

For the analysis of brominated flame retardants (PBB, polybrominated biphenyls; PBDE, polybrominated diphenylether, Fig. 1) in concentrations < 5% to the ppm-range the method of GCMS is used. With GCMS, it is possible to identify and quantify also small amounts of contaminants by comparison with standard samples and their specific retention times and mass spectra.

PBDEs



X+Y=1−10

Number of bromine atoms		Molecular formula	Molecular weight	Number of isomers
1	nomo	$C_{12}H_9BrO$	248	3
2	di	$C_{12}H_8Br_2O$	326	12
3	tri	$C_{12}H_7Br_3O$	404	24
4	tetra	$C_{12}H_6Br_4O$	482	42
5	penta	$C_{12}H_5Br_5O$	560	46
6	hexa	$C_{12}H_4Br_6O$	638	42
7	hepta	$C_{12}H_3Br_7O$	716	24
8	octa	$C_{12}H_2Br_8O$	794	12
9	nona	$C_{12}HBr_9O$	872	3
10	deca	$C_{12}Br_{10}O$	950	1
1~10				209

Fig.1: structures of PBDE´s

Pyrolysis GCMS of Brominated Flame retardants

For GCMS analysis, there are two possibilities. For screening of the samples, the method of pyrolysis GCMS can be used. This method has the advantage that the samples are measured directly without tedious sample preparation. In a pyrolysis oven, the samples are heated and the polybrominated substances are evaporated from the polymer. This evaporation takes place at relatively low temperatures of 300-400°C. At these temperatures the polymers are not decomposed.

Double-shot Pyrolysis

The Pyrolyser Py-2020iD from Shimadzu uses the so-called double-shot method. In a first step, the PBBs and PBDEs are evaporated from the polymer (Thermodesorption). In a second step, the polymers are decomposed at high temperatures (>550°C). After evaporation from the polymer, the PBB´s and PBDE´s are separated by gas chromatography and detected in the mass spectrometer. Figure 2 shows such a pyrolysis chromatogram. The PBDEs can be identified unambiguously by their mass spectra (Fig. 3).

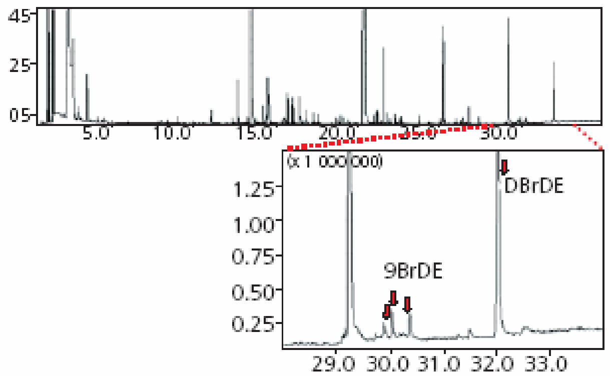


Fig.2: identification of PBDE´s by pyrolysis GCMS

Identification of polymers by F-Search software and data base

The polymer itself can be identified by using the unique F-Search library. The F-Search library contains the GCMS TIC´s of polymers. By using the mass spectra of the polymer fragments the polymer itself is identified automatically. With the double-shot method information on the use of brominated flame retardants as well as on the polymer itself can be obtained using the same sample.

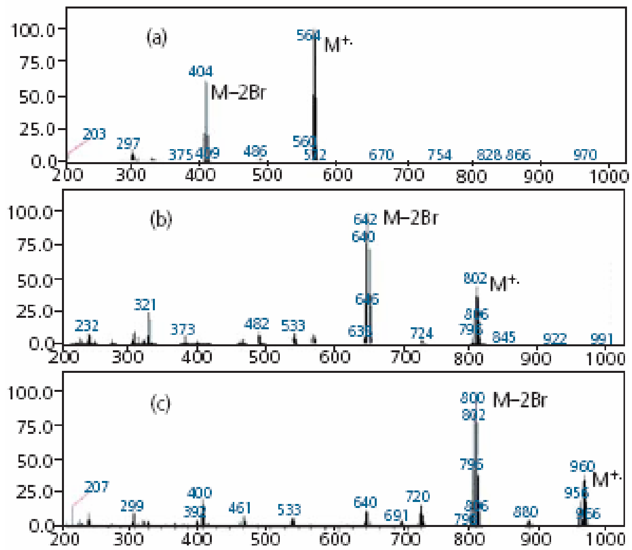
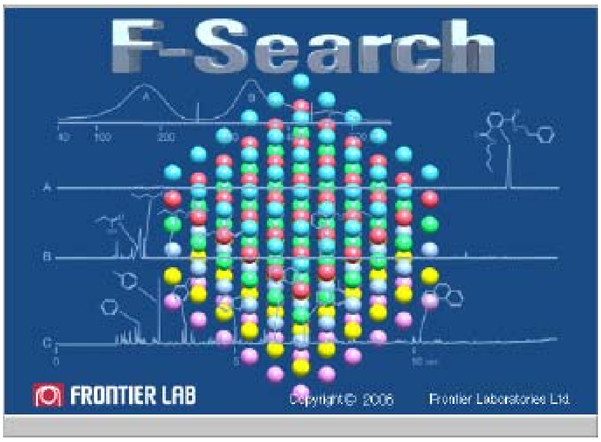


Fig.3: Mass spectra of the PBDE´s



Autosampler AS-1020E

Particularly for a screening method, the use of the autoshot auto sampler for the Py-200iD is of great advantage. It can analyze up to 48 samples.

Fig. 4: Pyrolysis autosampler with carousel for 48 samples and cup receiver

Quantitative analysis

For the quantitative analysis of PBBs and PBDEs, a sample preparation in the laboratory is required. In a first step, the samples are extracted. For soluble polymers, the samples are dissolved in the corresponding solvent and subsequently the brominated flame retardants are extracted by liquid/liquid or Soxhlet-Extraction. For non-soluble polymers, a Soxhlet-Extraction is used directly. The extract is cleaned afterwards by solid phase extraction or by GPC (gel permeation chromatography). The best cleaning of the samples for sure is achieved by using GPC, but GPC also requires more time and effort then solid phase extraction. The sample is then prepared for the GCMS analysis with liquid injection. Figure 5 shows the quantitative detection of PBDE in a polystyrene sample.

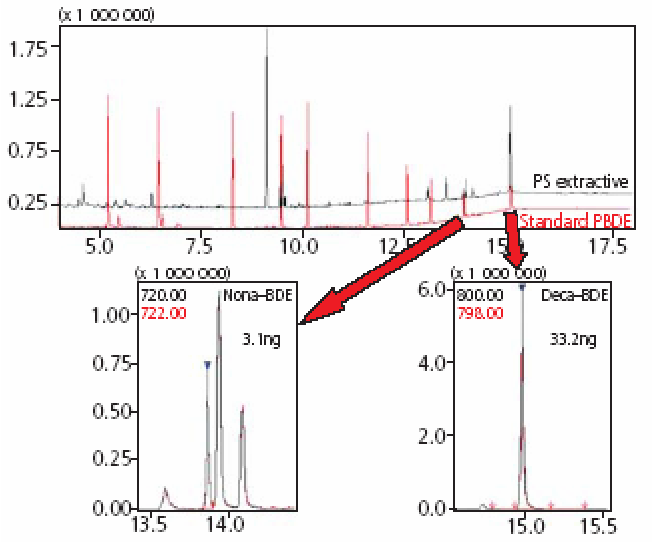


Fig. 5: Quantitation of PBDE´s in a polystyrene sample

Summary

GCMS is a fast and efficient method for the analysis of Brominated Flame Retardants in polymers. For a rapid screening, Pyrolysis GCMS is used, where the samples are analyzed without any sample preparation. The PBDE´s can be identified easily by their specific mass spectra (Fig. 3). Using the method of Double-shot pyrolysis not only information on the PBDE content but also on the polymer itself can be obtained. Identification of the polymer can be achieved by using the F-Seach software and data base. If quantitation is required the samples are extracted by Soxhlet or GPC and subsequently the extracts are injected into the GCMS.