

Pyrolysis of Plastics Containing Brominated Flame Retardants

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Abstract

It is perceived that brominated flame retardants may form brominated dioxins and furans under certain circumstances. Online pyrolysis gas chromatography with mass spectroscopic detection (py-GC/MS) was optimized to identify polymers as well as brominated flame retardants. The results of the performed experiments demonstrate that the method is suitable to achieve this goal.

1. Introduction

In various applications, plastics have to fulfill flame retardancy requirements. Brominated hydrocarbons like brominated bisphenols (tetrabromobisphenol-A TBBA) or polybrominated diphenylethers (PBDE) are, up to a content of 10%, added commonly to polymers as reactive or additive flame retardants.

In Europe a public discussion concerning these substances started because they were supposed to affect the environment by forming brominated dioxins and furans during synthesis ¹⁾, compounding ²⁾ or under thermal stress ³⁾ as well as during the use of electrical appliances⁴⁾.

However, the world market for these substances is still increasing. For example 80 % of the total production of the brominated additives (in Europe: 64.000 t in 1995⁵⁾) are used for plastics in electrotechnical applications ⁶⁾.

In addition, the recycling activities on such materials are recently increasing. Due to the variety of flame retarded plastics, new rapid analytical methods are required. These methods should enable the online characterization of the polymers including the additive, polymeric or reactive flame retardants.

2. Experimental Methods

In order to meet the objective as described above, online py-GC/MS was applied to several samples of plastics from electrotechnical applications (Table 1).

Table 1
Analysed samples

| Sample | Source | Polymer |
|--------|---|---|
| I | Printed circuit board base material (FR3) | Epoxy resin (EPR) |
| II | Material as recieved | Acrylonitrile/butadiene/styrene-copolymer (ABS) |
| III | Material as recieved | Polybutylene terephthalate (PBT) |
| IV | Section of a household electrical appliance | Polypropylene (PP) |
| V | TV housing (20 years old) | High impact polystyrene (PS-HI) |
| VI | TV housing (21 years old) | High impact polystyrene (PS-HI) |

Py-GC/MS analysis

After grinding the sample material to a size of 1 mm using cutting and centrifugal mills, a few milligramms of the sample was injected into the pyrolysis oven by a solid sample syringe. This oven (shown in Fig.1, SGE PIU-II) consists of a sample inlet, an electrical heater (allowing to vary the temperature from 200-1000 °C) and a coupling device to the gas chromatograph.

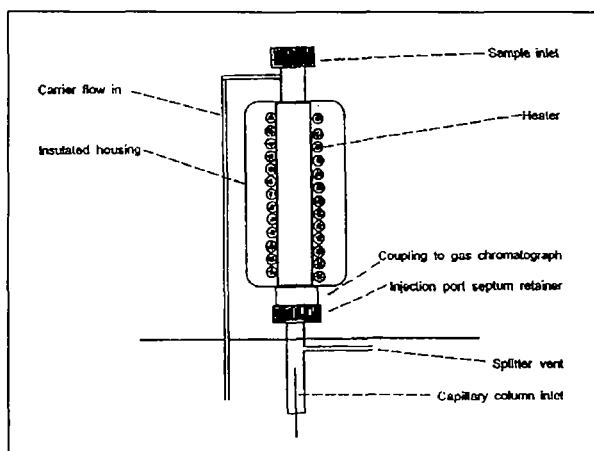


Fig. 1 Pyrolysis oven (SGE PIU-II)

The pyrolysis products are then separated in a gas chromatograph, a CARLO ERBA 8060, with an injector temperature of 280 °C. A SGE DB5 MS column (30 m length and 0.32 mm ID) was programmed starting at 100 °C, 20 °C/min to 180 °C, 5 °C/min to 280°C, 20 °C/min to 320 °C and hold for 15 min. Helium was used as carrier gas. The detection was performed with a FISONS TRIO1000 mass spectrometer in the scan modus (Ionisation modus EI, 70 eV).

Dioxin '97, Indianapolis, Indiana, USA

3. Results and Discussion

The results obtained are reported as the relative signal intensity versus the retention time. Figures 2 to 7 show the chromatograms (pyrograms) of the samples described in Table 1.

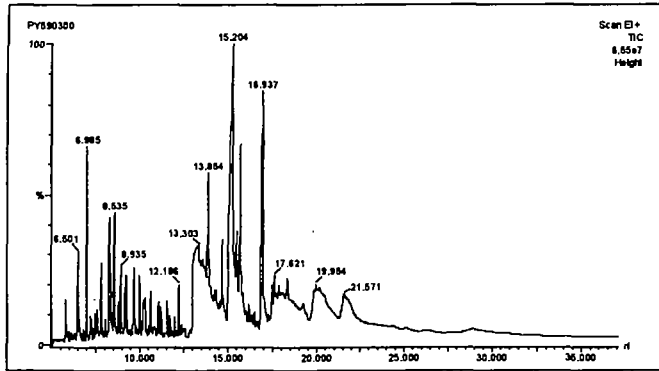


Fig.2 Pyrogram of sample I, EPR

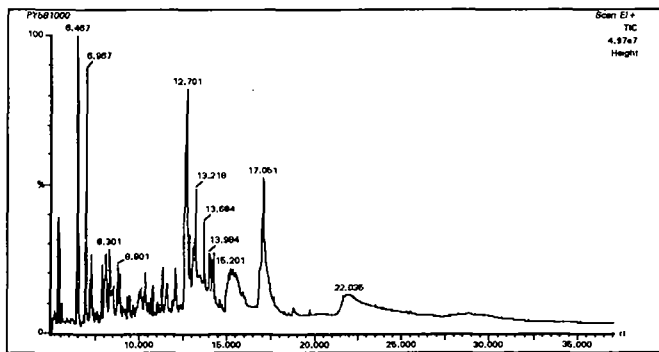


Fig.3 Pyrogram of sample II, ABS

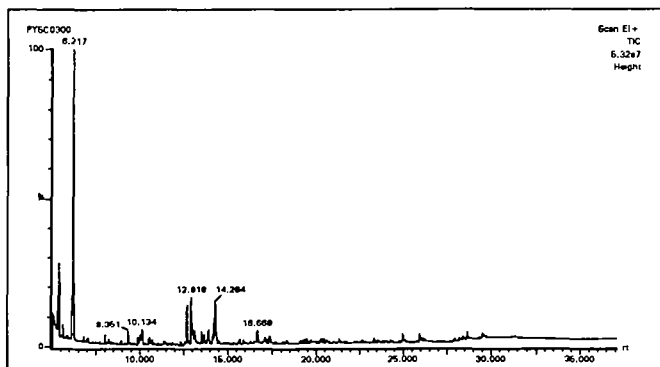


Fig.4 Pyrogram of sample III, PBT

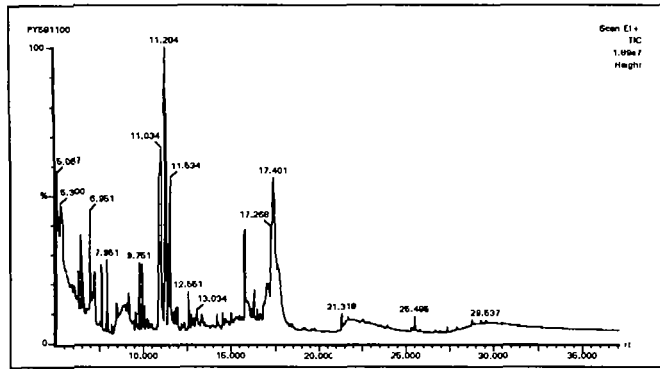


Fig.5 Pyrogram of sample IV, PP

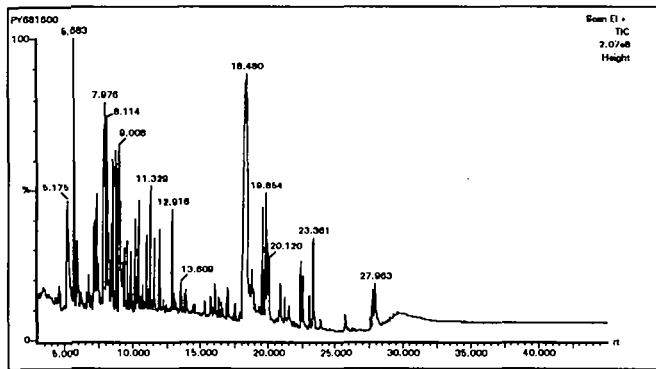


Fig.6 Pyrogram of sample V, PS-HI

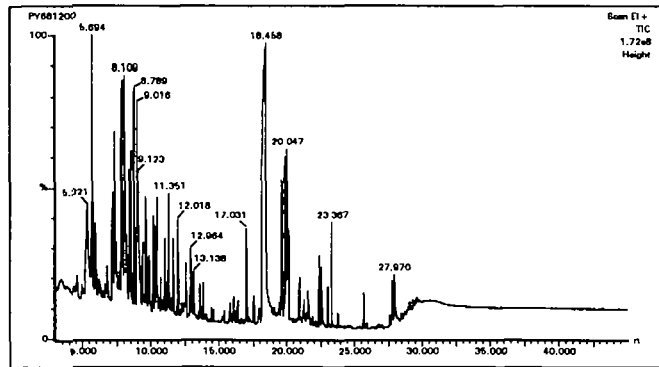


Fig.7 Pyrogram of sample VI, PS-HI

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Figure 8 is an example of how the flame retardants are identified in the pyrograms shown in Figures 2 to 7:

Under pyrolysis conditions flame retardants show a characteristic thermal reaction behaviour. For example, in the case of decabromodiphenylether, the main decomposition products are hexabromobenzene and pentabromophenol. TBBA reacts by elimination of bromine under formation of lower brominated products.

It follows that the pyrogram of the reference material (pure flame retardant) has to be compared with the pyrogram of the sample to be examined in order to identify the flame retardant class.

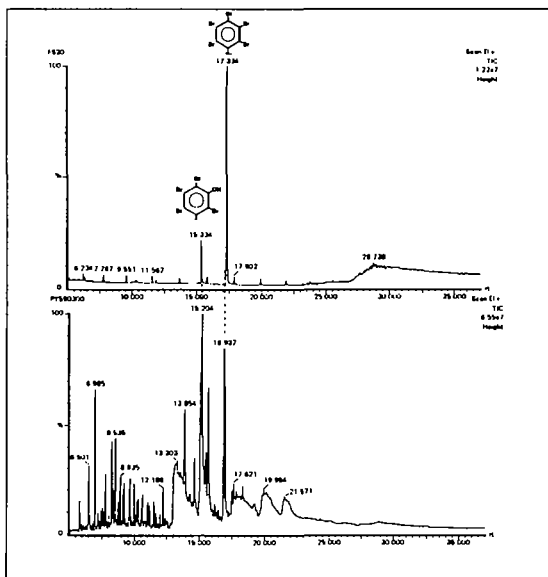


Fig. 8 Identification of flame retardants.

Pyrogram of decabromodiphenylether (reference) and identification of the characteristic decomposition products in the sample material (epoxy resin, sample I).

During the performance of the experiments it was observed that the selection of the pyrolysis temperature is most important. A compromise between mobilisation of the flame retardants and minimisation of thermal reaction products has to be found. An oven temperature of 430 °C gave the best results. Using the optimized temperature the following flame retardants were identified in the samples:

Table 2
Identified flame retardants

| Sample | Polymer | Identified flame retardants |
|--------|---|-----------------------------|
| I | Epoxy resin (EPR) | TBBA |
| II | Acrylonitrile/butadiene/styrene-copolymer (ABS) | TBBA |
| III | Polybutylene terephthalate (PBT) | TBBA |
| IV | Polypropylene (PP) | PBDE |
| V | High impact polystyrene (PS-HI) | PBB ¹⁾ |
| VI | High impact polystyrene (PS-HI) | PBB |

¹⁾ PBB = Polybrominated biphenyls

Another analytical aspect of pyrolysis-GC/MS is the characterisation of the polymer matrix. Samples V and VI (Fig. 6 and 7) show nearly the same pyrogram, characteristic for high impact polystyrene under these pyrolysis conditions („fingerprint“). The other polymers (samples I - IV, Fig. 2 -5) show different, but also pyrograms characteristic for that specific polymer.

Conclusion

It has been shown that the employed analytical method (py-GC/MS) is suitable to characterize the flame retarded plastics effectively. The selection of the pyrolysis temperature is most important in order to obtain characteristic data.

4. Acknowledgement

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5. Literature Cited

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