

Identification of ``heavy`` and polymeric brominated flame retardants in polymeric consumer goods by reactive and non-reactive pyrolysis GC-MS: approach for primary identification

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Introduction

From the consumer goods evaluation perspective, several brominated flame retardants (BFRs) need to be identified and quantified in polymeric samples^{1,2,3,4}. As an example, in new electrical and electronic equipment by the Restriction of Hazardous Substances Directive (RoHS, 2002/95/EC of the European Parliament and of the Council 2003), polybrominated biphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) should not exceed the agreed 0.1 weight % threshold. The objective of the RoHS directive is based on the protection of human and animal health and the environment against hazardous substances. Nowadays, an update of the RoHS directive was issued (RoHS2; 2011/65/EU, European Commission 2011) also banning technical decaBDE. The RoHS2 directive proposed hexabromocyclododecane (HBCDD) as a substance of high concern and it is expected that HBCDD will be regulated in Waste Electrical and Electronic Equipment (WEEE) as a priority, this, due to the risks to human health and the environment arising from the use. The measures provided in this Directive are taking into account existing international guidelines and recommendations which are based on assessments of available scientific and technical information.

In the European Union BFRs presented in consumer goods are as well regulated by the Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH, European Commission 2006) containing the regularly updated Candidate List of Substances of Very High Concern (SVHC; under REACH article 59). This complementary law in Europe on consumer goods, REACH/SVHC restricts BFRs like HBCDD in consumer goods, mixtures and substances not to be higher than 0.1 weight % except for expanded polystyrene. Rather than a ban, these brominated substances are limited but not completely phased out.

In many cases a bromine positive sample might be evaluated for common additive flame retardants, however when the bromine balance is not fitting or common BFRs are not detected probably, beside the use of inorganic bromine salts, other BFRs were used. There is still the possibility that: 1) reactive BFRs (reacting to the polymer chain); 2) polymeric BFRs have been used or; 3) the BFRs have a low volatility or too high molecular weight in order to be detectable by common gas chromatography (GC) combined with mass spectrometry (MS). Therefore as a solution, pyrolysis as a sample introduction technique in front of GC-MS can be used to fragment the (semi) macromolecular into volatiles giving indication of the presented BFR.

The intention to use reactive BFRs and (high molecular weight/polymeric BFRs in polymers comes from the application, where generally a release of BFRs is not likely to happen. Within this paper the use of X-ray spectrometry (XRF) as a bromine screening method joined with 2 pyrolytic based analytical techniques with GC-MS are presented. One is based on pyrolysis GC-MS using a helium atmosphere and heat to decompose the macromolecular based BFRs. The other application uses as well pyrolysis GC-MS but a reagent to hydrolyse the condensed BFR into small derived fragments.

Materials and methods

Initial XRF-screening:

XRF spectroscopy has the ability to screen quickly many test points on one sample without a time-consuming sample treatment. Br was taken as the first indication for WEEE contamination due to the fact that BFRs are intensively used in electrical and electronic applications. Despite, there might be other non-brominated flame retardants used, BFRs are still prominently presented in the WEEE streams. XRF analysis was used initially to distinguish between Br positive and Br negative samples. The XRF analyses were performed on an Oxford Instruments ED2000 Ag spectrometer (Oxfordshire, United Kingdom) equipped with a Si(Li) cross section detector cooled by liquid nitrogen. To prove the presence of bromine in polymers, the measurement conditions for medium elements in air were selected and the instrument parameters were optimised for measuring total bromine in a hydrocarbon matrix. The acceleration voltage of the X-ray tube with a silver target was set to 45 kV

with a current towards the filament of 50 mA. The X-ray tube radiation is filtered with a silver source filter for background reduction and improvement of the fluorescence yield. The warming up time of the source was 10 seconds, while the measuring time was set to 30 seconds. For Br, the $K\alpha$ spectral line at 11.92 KeV is the most sensitive and therefore chosen as the analytical line for quantification. Unfortunately, this line can be overlapped by the $K\beta$ lines from As and also by the $L\beta_1$ and $L\beta_2$ lines from Hg.

A similar method is described in an international standard published in 2009 by the European Committee for Standardization (CEN) concerning the analytical support of the RoHS directive namely standard EN 62321. This CEN standard was taken as a guide for the Br quantification. For calibration of the instrument a RoHS standard set of Sumika Chemical Analysis Service, Ltd (Osaka, Japan) was used. As a control measurement, the certified reference material ERM®-EC591 (JRC-IRMM, Geel, Belgium) which is a PBDE/PBB doped PP in pellet form with an overall Br concentration of $2.08 \pm 0.07 \text{ g kg}^{-1}$ and ERM-EC680K PP pellets (JRC-IRMM, Geel, Belgium) spiked with inorganic pigments having an elemental Br concentration of $96 \pm 4 \text{ mg kg}^{-1}$ has been used. Samples with a total elemental Br concentration higher than 40 mg kg^{-1} were considered as Br positive with this concentration as the limit of detection (LOD).

Measurements and instrumentation - pyrolysis GC-MS:

Pyrolysis GC-MS spectrometry was used as an additional instrumental method that enables a reproducible characterization of (co-)polymers either as a major component or as a trace contaminant. This method detects monomers and significantly abundant pyrolysis degradation products to get a full composition overview of the polymer matrix and polymeric BFRs. For the pyrolysis analysis up to 20 μl of sample extract (toluene) was placed in an 80 μl sample cup and by free fall injected and heated up to 650°C for 2 minutes in a helium stream. The hardware configuration uses a thermal desorbing unit coupled to GC-MS (PY-2020iD, Frontier laboratories, Japan/ GC-MS QP2010 Plus, Shimadzu, Kyoto, Japan) using an PBDE-UA column (0.25 mm i.d. x 30 m x 0.25 μm film thickness, Ultra-Alloy, Frontier laboratories, Japan). The mass spectrometer was programmed in full scan mode from 30-1000 Da with electron impact ionization (70 eV) and a detector dwell time of 0.30 seconds. All peaks from the pyrograms were identified by using the NIST 05 library (National Institute for standards and Technology, USA). Similar to the thermal desorption GC-MS method, all measurements were repeated twice and compared to blank measurements to check the cleanness of the system and to avoid potential carry-over issues.

Measurements and instrumentation - Reactive Pyrolysis GC-MS:

For reactive pyrolysis GC-MS the same hardware configuration was used with a relatively low pyrolysis temperature of 440°C kept for 2 minutes. This due to the fact that the creation of pyrolytic fragments should be suppressed and mainly the TMAH/MeOH reagent should react with the polymer or extracted substances. Reactive pyrolysis GC-MS enables to chemically cut the polymer or extracted additives at specific functional places *e.g.* esters/amides and methylate the remaining fragments.

As a sample preparation, the sample (dried toluene extract) was mixed with TMAH (25 weight %) in MeOH (Sigma-Aldrich). TMAH is a very strong base and therefore perfect for this thermo-chemolysis. The ability to hydrolyse ester or amide bonds in combination with methanol (trans-) esterification makes this method a useful tool. Moreover amines and alcohols are also converted into methylethers and (di-)methylamines. As a disadvantage, due to the extent of formed aliphatic amine substances *e.g.* 2-(dimethylamino)ethanol, the pyrogram need to be cut at the beginning in order to save the filament lifetime from the ion source and the MS detector. Therefore, information about small target analytes cannot be obtained; however, these substances might be detected after pyrolysis GC-MS as there a screening of very volatile fragments is favoured.

The selected samples:

For our evaluation, 2 samples were selected containing bromine (evaluated by XRF spectrometry) but not giving after thermal desorption/pyrolysis GC-MS analysis the full picture of the bromine balance. Several such a samples ``in question`` were selected for further evaluation.

Results and discussion

Sample 1: reactive pyrolysis from a PBT sample extract

A black sample of PBT from an electric computer fan was measured by XRF for bromine content. The bromine content gives an indication for the possible BFRs presence and semi-quantitative concentration value. The sample of interest contained more than 1.0 weight % bromine. The sample preparation was done by a static ``over night`` extraction of the polymer additives in toluene, the sample extract was spiked (approximately 20 ul) into a stainless steel sample cup and pyrolysed without TMAH addition. After that, the toluene extract was evaporized and TMAH reagent was added, after shaking, the extract was spiked (approximately 2 ul) into a stainless steel sample cup which contains a small disc made of high quality glass fibres (Auto-Rx Disc, frontier laboratories, Japan). This disc adsorbs the liquid and so avoids ``creeping`` of the TMAH from the inner of the cup towards the outer side. By an initial pyrolysis GC-MS experiment three bromine containing peaks were identified namely: 2,4,6-tribromo-phenol, tetrabromobisphenol A (TBBPA) and an unknown higher MW molecule (figure 1).

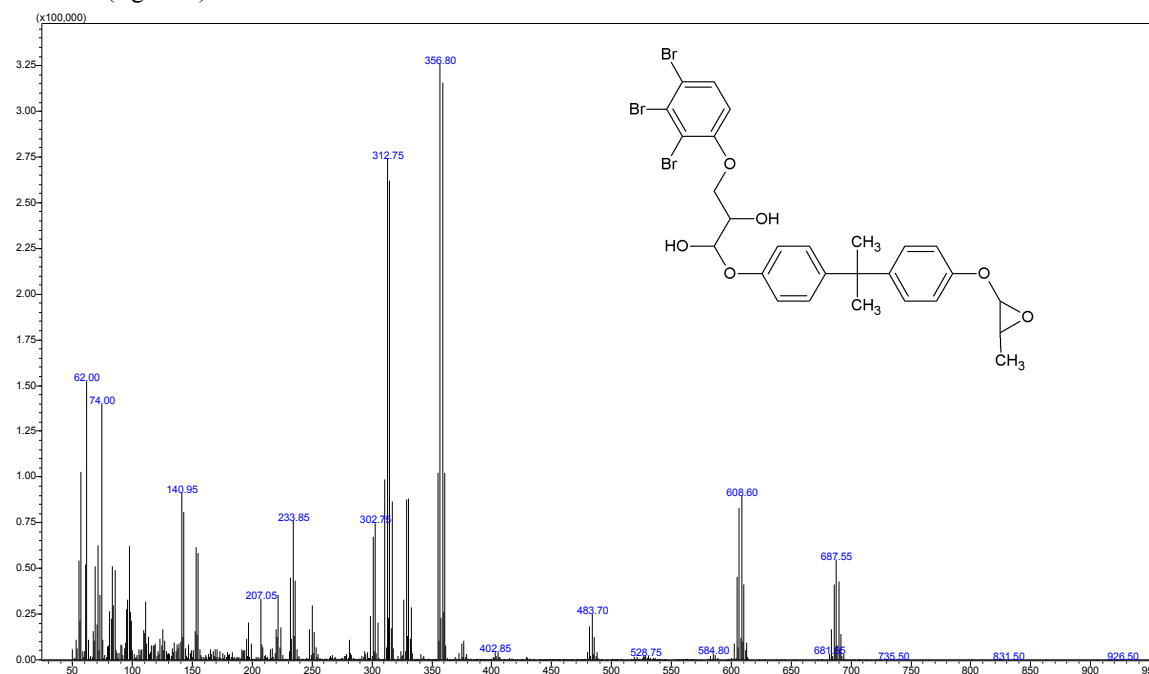


Figure 1: Electron impact mass spectrum of an ``unknown`` peak at t_R 21,6 minutes with a specific peak of M/e 356 showing the neutral loss fragmentation of a bigger tribromophenol based derivate.

According to the data obtained, the peak at 21,6 minutes indicates that there is another higher molecular weight BFR presented in the sample and not only 2,4,6-tribromo-phenol and tetrabromobisphenol A. The link between these 2 known BFRs can be done when performing reactive pyrolysis, as this analysis is ``smoother`` and very specific for condensed polymers as well as condensed additives. Reactive pyrolysis of the sample extract with TMAH resulted in the detection of a peak of trimethylglycerol (t_R at 4,7 minutes, meaning that the original substance detected was glycerol). By completing all data, the original used BFR was based on a tribromophenol end capped brominated epoxy polymer based on tetrabromobisphenol A diglycidyl ether (F 3014).

Sample 2: detection of polymeric BFRs by pyrolysis GC-MS

An environmental friendly approach is the incorporation of bromine into the polymeric chain (like tetrabromobisphenol A in PC) or as a polymeric additive (like brominated polystyrene in PET or PA6). Polymeric BFRs are mainly used for high-temperature applications like polyesters and polyamides. Flame retardant thermoplastics contain generally 5-20% polymeric BFR which is for this analytical method an advantage. Most common polymeric BFR is produced by the copolymerization of di- and tribromostyrene. The sample preparation was done by a static extraction of the polymer in toluene. Approximately 20 ul sample extract was spiked into a stainless steel sample cup, dried at room temperature in the fumehood and pyrolysed.

In figure 2 there is shown a pyrogram of isolated brominated polystyrene from a PA6 leachate in toluene. Main peaks seen in this pyrogram are the isomers from di-, tri- and tetra-bromostyrene from the unzipping process. The relative peak areas between the mono-, di-, tri- and tetra-bromostyrene were used to calculate the degree of bromination in this polymeric additive. In this case the brominated polystyrene had a bromine level of 2.7 (2% RSD, n=3).

Technical data from a supplier confirmed that this polymeric BFR had an average bromination degree of 2.7. Further are seen a mixture of cyclic by-products from radical recombination, mainly brominated polyaromates and cyclic hydrocarbons.

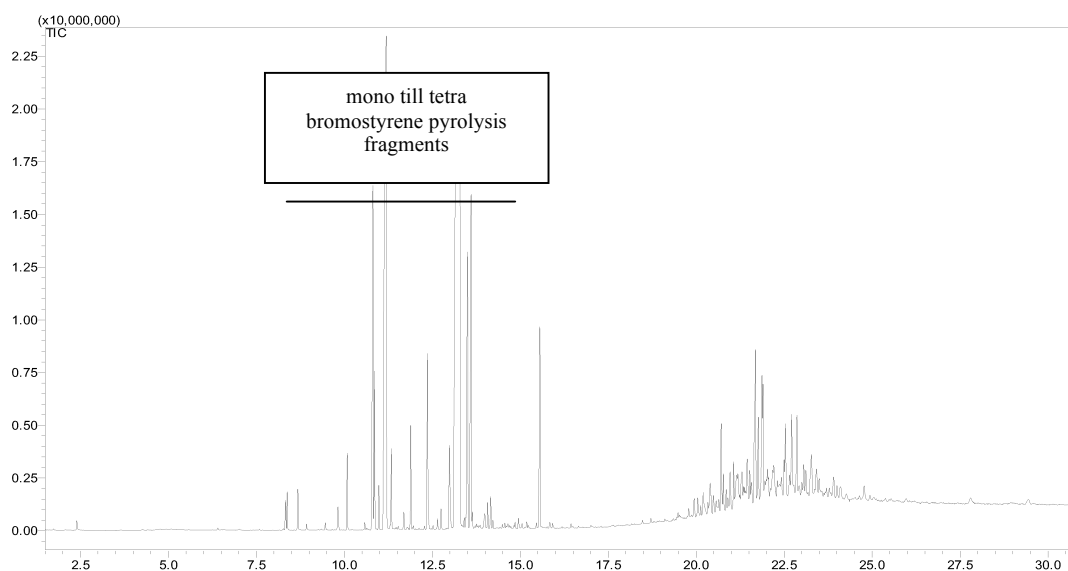


Figure 2: Pyrogram of isolated brominated polystyrene from a PA6 sample

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