Identification of TBBPA-DBPE in plastics by thermal desorption GC-MS (TD-GC-MS)

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Introduction

Tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE) is a widely used flame retardant in polymers like high-impact polystyrene (HIPS), polypropylene (PP) and high density polyethylene (HDPE). Tetrabromobisphenol A (TBBPA) and its derivates are substitutes for RoHS banned brominated flame retardants (BFRs) and should be monitored to inform the industry about the sample composition and for purpose of public health protection. The phenol groups of TBBPA are practical due to its location to form ethers. TBBPA-DBPE is commercially known as Bromkal 66-8, Dibromopropydian, Fire Guard 3100, Flame Cut 121K, Flame Cut 121R or Pyroguard SR 720 [1,2].

Various analytical methods for the quantification/identification of BFRs in plastics are based on a solvent extraction followed by a time consuming sample clean-up and GC-MS or LC-MS analysis. A fast alternative method is the combination of x-ray fluorescence (XRF) and thermal desorption GC-MS (TD-GC-MS) analysis for the quantification of bromine and identification of the presented BFR respectively. If the plastic sample is positive for bromine by XRF a TD-GC-MS analysis is needed to identify the BFRs. The method described in this paper is routinely used for determination of poly-brominated diphenyl ethers (PBDEs), poly-brominated biphenyls (PBBs) and TBBPA in plastic materials.

Material and Methods

Chemicals

The sample described in this work was a HDPE pipe sample containing TBBPA-DBPE supplied by a customer to identify type of BFRs. A TBBPA-DBPE reference was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Calibration solutions for the XRF analysis were made of tetrabromomethane (Loba/Chemie, Wien) in toluene. All solutions were made with HPLC grade solvents.

XRF screening for bromine

The XRF analysis was performed with an Oxford Instruments ED 2000 Ag instrument under the conditions for measuring of medium elements in air, a tube voltage of 45 kV, the current to tube is 50 mA measuring time 30 seconds. The sample preparation for a XRF analysis requires cutting the samples in a size they fit in the XRF sample cup (optimal 22 mm diameter).

TD-GC-MS method for BFR identification

All experiments were carried out with a thermal desorption and pyrolysis unit PY-2020iD (Frontier Laboratories Ltd., Japan) with a 48 position auto sampler connected to a HRGC/LRMS QP2010plus (Shimadzu, Japan). A special metal capillary separation column (Ultra ALLOY-PBDE; 0.25 mm i.d. x 15 m, Frontier Laboratories Ltd., Japan) coated with a very thin (0,05 um) film of immobilized-polydimethylsiloxane is used for separation of the thermal desorption products. After optimising the desorption settings a thermal desorption temperature of 270°C for 10 minutes give the highest and stable peaks for BFRs. The ionisation mode is electron impact with ionisation at 70 eV. The peaks are monitored in FASST-mode (Fast Automated Scan/SIM Technique) which enables to acquire both Scan and SIM data on one peak. The SIM mode was programmed for the RoHS banned chemicals. The Scan mode is used to identify other BFRs.

Sample preparation for TD-GC-MS

Three ways of sampling of polymers for TD-GC-MS are possible: first one is "solving way", the second one "solid way". "Solving way" is preferred due to its better accuracy and reproducibility and it is used mainly for quantification. Sample is overnight solved in toluene and then dosed (few microliters via Hamilton syringe) in the sample cup. Dosing of solid polymer is then very precise. After solvent evaporation at a room temperature a thin film of analyte/polymer remains in the sample cup. "Solid way" is simply to cut the plastic and placing approx. 3 mg in a sample cup. Few microliters of toluene is then added so the sample will stick on the wall to avoid occasional sample loose during free fall of the sample cup into the desorption unit. For the purpose of only qualitative screening of BFRs in plastics third alternative sample preparation way is used. Sample is dipped in the toluene overnight and the toluene is then dosed in the sample cup and let evaporated (like the "solving way"). This procedure eliminate majority of the polymer matrix introduced in the chromatograph while enough amount of BFRs is surely extracted. For the purpose of simple identification this preparation is sufficient. TD-GC-MS have a big advantage comparing to the direct injections of polymer solution into GC as only minor part of matrix (only oligomers) are introduced to the GC and there are minimum looses of BFRs during the process of sample preparation. The sample cups are then placed into an auto-sampler and during thermal desorption heated in the furnace of the pyrolyzer. They are made of metal and are covered with a thin layer (< 1 µm) of fused silica (deactivated).

Results and Discussion

After thermal desorption of the polymer lots of peaks were seen in the chromatogram. Most of the peaks are coming from the polymer itself. The chromatogram of the toluene extract give a cleaner overview (Figure 1) of the additives. After thermal desorption of the toluene extract 3 major peaks at retention times (t_R 16,0, 16,6 and 19,3 min.) were seen with a similar looking mass spectrum (Figures 2-4). The masses m/z 119, 201, 383, 529 and 544 are in all spectra presented which indicates they are related to each other.
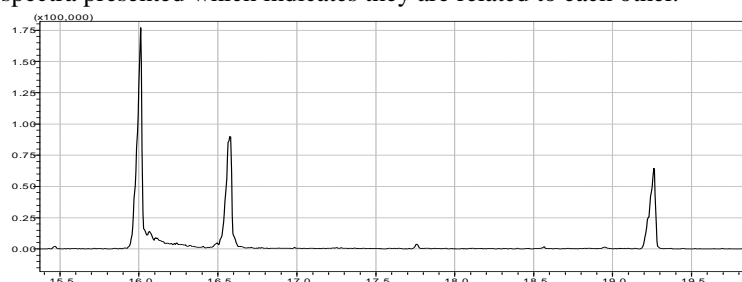

Figure 1: Detailed chromatogram of a TBBPA–DBPE in HDPE after toluene extraction and TD-GC-MS
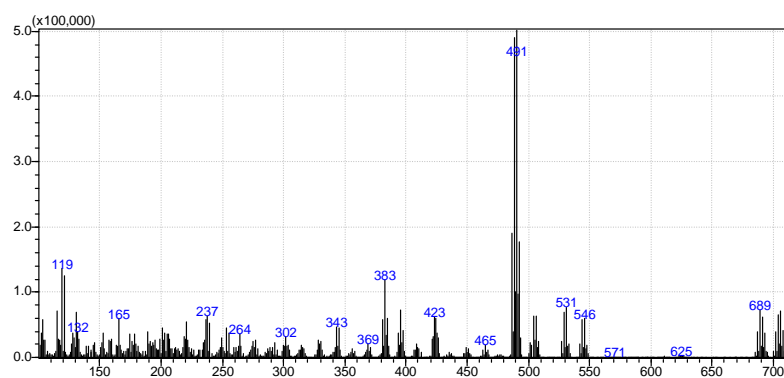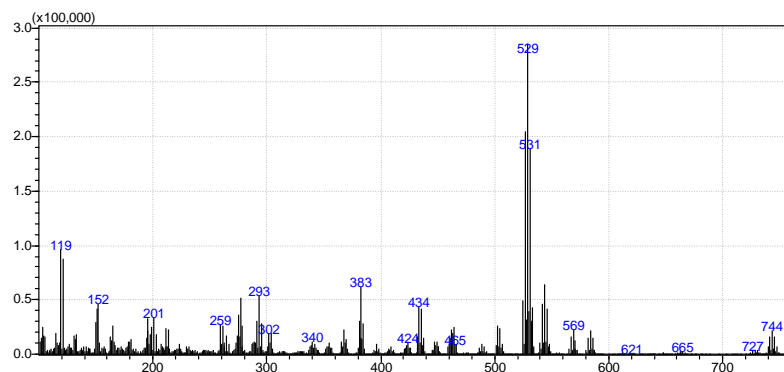

Figure 2: Mass spectrum of peak at t_R 16,0 min

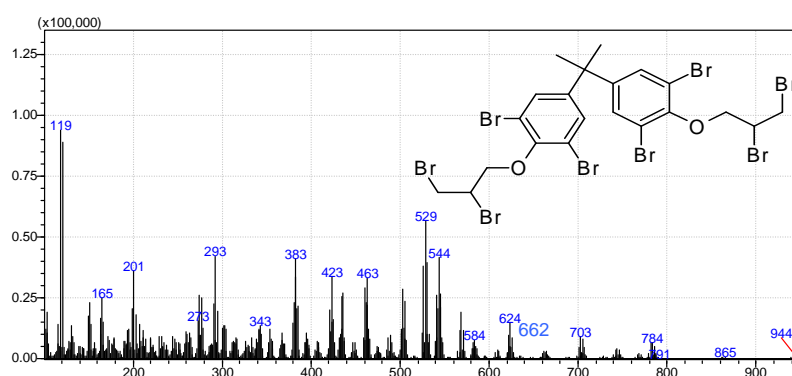**Figure 3: Mass spectrum of peak at t_R 16,6 min**

Figure 4: Mass spectrum of peak at t_R 19,3 min

The mass spectrum of the peak at t_R 19,3 min has been studied carefully because it gives the highest molecular ion. The molecular ion $[M]^+$-ion is seen at m/z value 944. The pattern of the molecular ion cluster proves that this product is octabrominated. The big signal at m/z value 544 and 529 are characteristic masses for the molecular ion of TBBPA and the $[TBBPA-15]^+$-ion respectively. The signal at m/z value 201 gives the answer for finding the $[M]^+$-ion. The m/z value 201 is the mass of 1,2-dibromopropane. This is forming ether on both sides of TBBPA resulting in TBBPA-DBPE. The structure of TBBPA-DBPE is shown in Figure 4.

The theory that the used additive is tetrabromobisphenol A bis (2,3-dibromopropyl ether) is once more proved by the fact that the frequent difference which appears between some ion clusters is 41 m/z. This difference is the mass of the $[CH_2=C-CH_2]$-radical coming from an allyl-X group. This can be seen in the mass spectrum of peak at t_R 19,3 min between m/z value 703 and 662 (Figure 4). If this happens twice for TBBPA-DBPE, the mass loss is nearly the mass of bromine (m/z value 80). This is the reason why the isotopic cluster of the $[M-(C_3H_5Br_2)_2]^+$-ion (m/z value 544) is the same isotopic cluster like the $[M-Br_5]^+$-ion. The following Table 1 gives the explanation of the main ion clusters seen in the mass spectrum from TBBPA-DBPE.

Table 1: Identified m/z values for TBBPA-DBPE

m/z value	Explanation of the ion cluster
944	$[M]^+$-ion, tetrabromobisphenol A bis (2,3-dibromopropyl ether)-ion
865	$[M-Br]^+$-ion
784	$[M-Br_2]^+$-ion
744	$[M-C_3H_5Br_2]^+$-ion
703	$[M-Br_3]^+$-ion
662	$[M-C_3H_5Br_3]^+$-ion
624	$[M-Br_4]^+$-ion
544	$[M-(C_3H_5Br_2)_2]^+$-ion, $[M-Br_5]^+$-ion
463	$[M-Br_6]^+$-ion
383	$[TBBPA-Br_2]^+$-ion and $[M-Br_7]^+$-ion
201	$[C_3H_5Br_2]^+$-ion
119	$[C_3H_5Br]^+$-ion

Result is that TBBPA-DBPE is the basic product and the peaks at t_R 16,0 and 16,6 min are the thermal degradation products of TBBPA-DBPE. These unknown peaks are identified as following in Table 2.

Table 2: The identification of peaks at t_R 16,0 and 16,6 min

Peak at t_R 16,0 min 3,3´,5,5´-TBBPA -4-(2,3-dibromopropyl ether) -4`-(2-propenyl ether) Intermediate with loss of HBr and Br_2.	
Peak at t_R 16,6 min 3,3´,5,5´-TBBPA-4-(2,3-dibromopropyl ether) Loss of 1,2-dibromopropane	

As known from the thermal degradation of BFRs chain cleavage and debromination are the main processes. The chromatographic results from the thermal desorption of TBBPA-DBPE proves that the debromination occurs much more forming 3,3´,5,5´-TBBPA -4-(2,3-dibromopropyl ether) -4`-(2-propenyl ether) than chain cleavage forming 3,3´,5,5´-TBBPA-4-(2,3-dibromopropyl ether).

Conclusion

TD-GC-MS is quick analytical method used for rapid identification low-molecular additives in plastics. One universal method can be used for many types of matrix (polyolefins, styrene-based polymers, acrylates, polyesters etc), regardless their solubility, polarity or other behavior of the complex matrix. The main advantage is minimum sample preparation. Disadvantage is thermal cleavage of the analytes, but there are still more positives than negatives. The qualitative analysis of TBBPA-DBPE by TD-GC-MS was done by 2 different sample preparation methods. Thermal desorption of toluene extracts gives in this case far better results than the direct thermal desorption of the plastics. But both methods are possible to use. TBBPA-DBPE is a thermal labile molecule and we have to count with thermal degradation products in the chromatogram after thermal desorption. The chromatographic data proves that debromination is a more dominant process than chain cleavage. Quantification of TBBPA-DBPE with TD-GC-MS will be difficult unless a compromising thermal desorption temperature has been found.

References:
1. Masten S. *Tetrabromobisphenol A bis(2,3-dibromopropyl ether) Review of Toxicological Literature* 2002:1.
2. BSEF, *Bromine Science and Environmental Forum*, http://www.bsef.com