Identification of decabromodiphenyl ethane (DBDPE) in plastics by thermal desorption GC-MS

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Introduction

Decabromodiphenyl ethane (DBDPE) is a cost effective brominated flame retardant (BFR) for a wide range of polymers used in electrical appliances. The widespread of BFRs in plastics, electric and electronic equipment results in a higher fire safety but has the disadvantage of an overall pollution of BFRs and their derivates. In the European RoHS regulation polybrominated biphenyls (PBBs) and polybrominated diphenylethers (PBDEs) are restricted but other flame retardants like DBDPE, tertrabromobisphenol A (TBBPA) and their derivates should be also monitored. A fast method for determination of BFRs in plastics is a thermal desorption GC-MS (TD-GC-MS) analysis[1].
The objective of this paper is to see the thermal stability of DBDPE during thermal desorption and the possibility for quantitative analysis. Known is that DBDPE might undergo thermal decomposition by scission of C-C bound resulting in the formation of bromotoluenes or debromination forming lower polybrominated diphenylethanes[2]. Data from thermal gravimetric analysis of polymers prove that polymer decomposition starts usually at a temperature of 400˚C. Thermal desorption of BFRs in plastics generally occurs within a temperature range between 250 and 400˚C [3,4]. Another objective is to see if the DBDPE can be analyzed under the conditions for quantification of PBBs and PBDEs by thermal desorption in order to develop one universal analytical method for determination of BFRs in plastics.

Material and Methods

TD-GC-MS method

The measurements were performed with a thermal desorption and pyrolysis unit PY-2020iD (Frontier Laboratories Ltd., Japan) connected to a HRGC/LRMS QP2010plus (Shimadzu, Japan). Thermal desorption was performed at 370˚C isothermal (60 seconds) for checking the thermal stability of DBDPE. A routinely used method for quantification of PBBs/PBDEs in plastics at 270˚C isothermal (10 minutes) was used to check possibility of usage of one universal analytical method for determination of BFRs in plastics. 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 µm) film of immobilized-polydimethylsiloxane is used for separation of the thermal desorption products. The mass spectrometer operated in electron impact mode at 70 eV. The peaks were monitored in FASST-mode (Fast Automated Scan/SIM Technique) which enables to acquire both Scan and SIM data on one peak.

Sample preparation for TD-GC-MS

Two ways of sampling are possible: first one is “solving way”, the second one “solid way”. For the purpose of study of desorption process and for purpose of calibration “solving way” is preferred due to its better accuracy and reproducibility. 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 into the desorption unit. The sample cup is 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

A first attempt is a short thermal desorption from an ethylene vinyl acetate polymer sample at 370ºC isothermal for 60 seconds. The chromatogram shows a wide distribution of polybrominated diphenylethanes from hexaBDPE till decaBDPE-209 (Figure 1) in full scan (300-1000 amu). The distribution of technical BDPE in the sample has no majority of decaBDPE-209 but contains more octaBDPE and nonaBDPE. This is completely different from data taken from analysis of many samples doped by technical decaBDE where the majority is decaBDE-209. Further investigation need to be done to see if the decaBDPE-209 is not debrominating at those thermal desorption conditions or the congener composition in the sample is like we see it on the chromatogram.

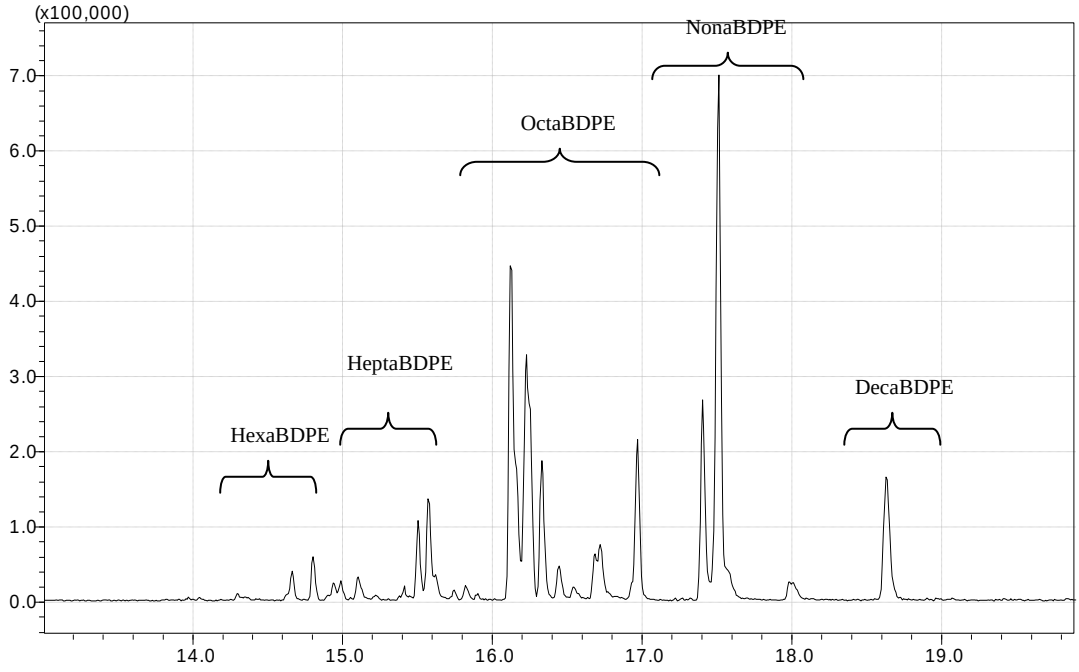

Figure 1: Detailed chromatogram of ethylene vinyl acetate polymer sample at thermal desorption temperature of 370ºC for 60 seconds.

To clarify the possibility that decaBDPE-209 is debrominating a decaBDPE-209 standard (DBDPE, Wellington Laboratories, Canada) was thermally desorbed. Again 370ºC for 60 seconds was chosen as an extreme temperature to check the thermal stability of the analyte. The full scan chromatogram (300-1000 amu) of 250 ng DBDPE shows only decaBDPE-209 at t_R 18,6 min (Figure 2). Surprisingly no thermal degradation products like bromotoluenes or lower brominated diphenylethanes were observed.

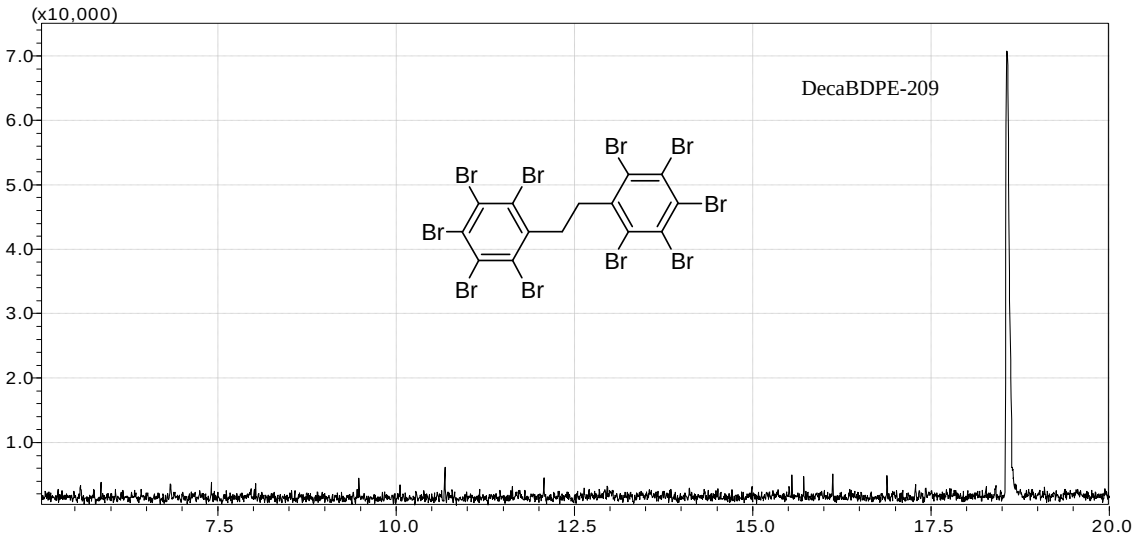

Figure 2: Detailed chromatogram of a 250 ng DBDPE standard at thermal desorption temperature of 370ºC for 60 seconds.

Due to this high thermal stability decaBDPE-209 should be possible to screened simultaneously by methods for determination of PBBs and PBDEs in plastics by TD-GC-MS. DBDPE standard was tested under the conditions for the measurement of PBBs and PBDEs in plastics which were thermally desorbed for 10 minutes at 270ºC (Figure 3). Unfortunately debromination products like octaBDPE (t_R 14,5-16,0 min) and nonaBDE (t_R 16,5-17,5 min) were identified. The peak of decaBDPE-209 was very small (t_R 18,6 min).

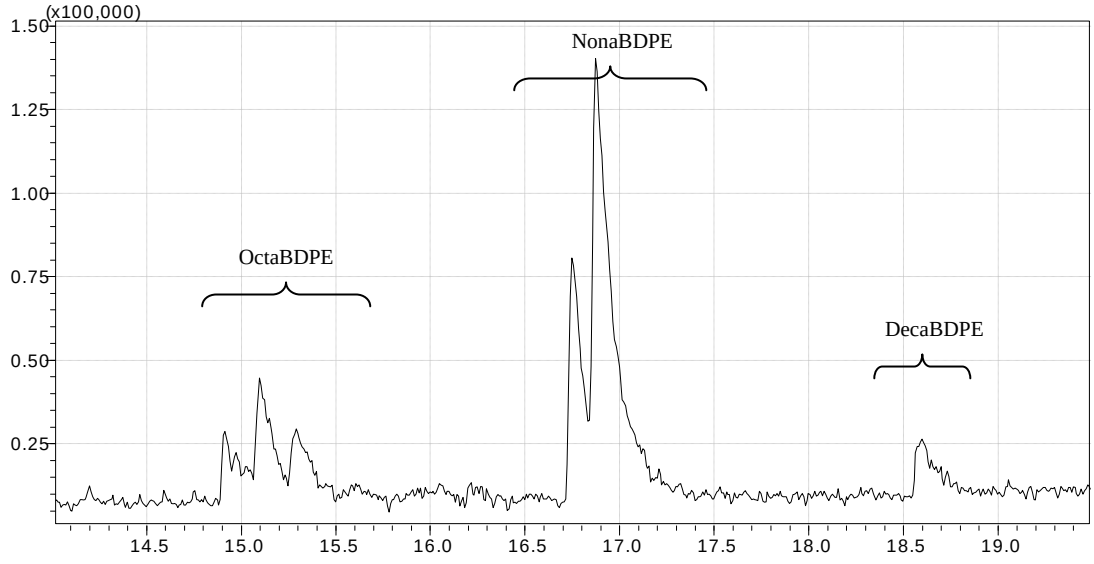

Figure 3: Detailed chromatogram of a 750 ng DBDPE standard at thermal desorption temperature of 270ºC for 10 minutes.

Conclusion

Thermal desorption is an excellent tool for determination of DBDPE in plastics. No thermal degradation products of decaBDPE-209 were observed by thermal desorption at higher temperatures for a shorter time (370°C for one minute). If thermal desorption is performed for a longer time (270°C for 10 minutes) debromination of decaBDPE-209 occurs.
The duration of heat exposure seems to be an important factor for debromination of decaBDPE-209. Screening for the presence of DBDPE can be done under conditions for analysis of RoHS banned BFRs by TD-GC-MS (270°C for 10 minutes) but we have to count with inducing of debromination to octaBDPE and nonaBDPE congeners. As for most of the BFRs thermal induced debromination occurs easier than scission of C-C bounds.
The sample of ethylene/vinylacetate polymer contained mainly octaBDPE, nonaBDPE and decaBDPE-209. Unfortunately technical DBDPE can not be quantified due to missing of commercial BDPE congener standards.

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