

Short communication

Determination of bromophenols as dioxin precursors in combustion gases of fire retarded extruded polystyrene by sorptive sampling-capillary gas chromatography–mass spectrometry

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Abstract

Extruded polystyrene (XPS) is often treated with hexabromocyclododecane (HBCD) as fire retardant (FR). Because of its aliphatic structure, HBCD is not suspected to cause formation of polybrominated dioxins upon combustion. Precursors of polybrominated dioxins, namely bromophenols, were detected during tubular furnace combustion experiments of FR-XPS in combination with sorptive enrichment on polydimethylsiloxane followed by on-line thermal desorption-capillary GC/MS. The highest concentration of mono- and tribromophenols detected were 85.9 and 3.7 mg kg⁻¹, respectively, at a temperature of 700 °C, while a temperature of 500 °C yielded the highest concentration of dibromophenols namely 10.4 mg kg⁻¹. At a combustion temperature of 900 °C no bromophenols were detected.

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1. Introduction

For several decades, flame-retardants (FRs) are added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage. Brominated flame-retardants (BFRs) are presently most frequently used, because of their low cost and high performance efficiency. Concerns for this emerging class of chemicals have, however, risen because of their occurrence in the environment and in human biota. In addition, formation of hazardous products upon thermal degradation of these substances has been stated. In particular, fires involving polymeric materials containing BFRs, with aromatic moieties, are suspected to lead to the formation of brominated polyaromatic compounds such as polybrominated dioxins [1–3].

There are five major classes of BFRs namely brominated bisphenols, diphenyl ethers, cyclododecanes, phenols and phthalic acid derivatives. The first three classes represent the

highest production volumes. In fact the five overwhelming BFRs on the market at the moment are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and three commercial mixtures of polybrominated diphenylethers (PDBEs). At present, the use of BFRs in general is highly dynamic because of the ongoing debates in many countries concerning their risk to wildlife and humans and whether their use should be phased out [1,4,5].

The present research was concentrated to HBCD. HBCD is a non-aromatic, brominated cycloalkane used primarily as an additive flame retardant in plastic materials, textiles and electronics. HBCD has to some extent replaced the usage of PDBEs in several applications. Its total production was about 15,900 ton in 1999 and Europe accounts for 56% of the total global use. This makes HBCD a relatively minor contributor to the total BFR economy. The European market share for HBCD is, however, significantly higher than for other BFRs, where Europe only accounts for about 10–15% of the global consumption. Extruded polystyrene (XPS), mainly used as an insulating building material, is the main product, that is flame retarded with HBCD. All European XPS contains about 1–2% HBCD [4].

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Because of its aliphatic nature, HBCD is not suspected to be a source of brominated aromatic species upon combustion. However, to the best of our knowledge, the interaction of the thermal decomposition products of HBCD and polystyrene has not been studied. To this purpose, samples of FR-XPS were combusted in a tubular furnace and the combustion gases were trapped using tubes packed with polydimethylsiloxane (PDMS) particles followed by thermal desorption-capillary GC/MS. This methodology, applying a moveable tubular furnace over a quartz tube containing the sample, is commonly used for the quantitative analysis of combustion gases [6] while sorptive extraction on PDMS has proven to be superior over adsorptive extraction for the analysis of both apolar and polar solutes from gaseous samples [7–9]. Special attention was given to the detection and quantification of bromophenols which are known precursors of polybrominated dibenzodioxins and dibenzofurans [10].

2. Experimental

2.1. Sampling

A set-up composed of a tubular furnace (MTF10/25/130, Carbolite, Hope Valley, UK) on a moveable plateau, a 1 m quartz tube and an electromotor was used (Fig. 1). Compressed air (Messer, Machelen, Belgium) was used as combustion gas at a steady flow of 500 ml min^{-1} , using a flowmeter (Aalborg-Alltech, Lokeren, Belgium). The set-up allowed the oven to move at 1 cm min^{-1} over the polymer sample in a direction opposite to the airflow, thus limiting condensation effects. In this way, the set-up mimics DIN 53436 (Deutsches Institut für Normung) [11]. The inside temperature of the quartz tube was measured using a thermocouple, allowing accurate temperature regulation and measurement. The combustion effluent was directly sampled for 20 min on a polydimethylsiloxane sorbent tube obtained from Gerstel GmbH (Mülheim a/d Ruhr, Germany). The sorbent tubes ($17.6 \text{ cm} \times 4 \text{ mm i.d.}$) contained 300 mg of particulate polydimethylsiloxane material with an average particle size of 1 mm.

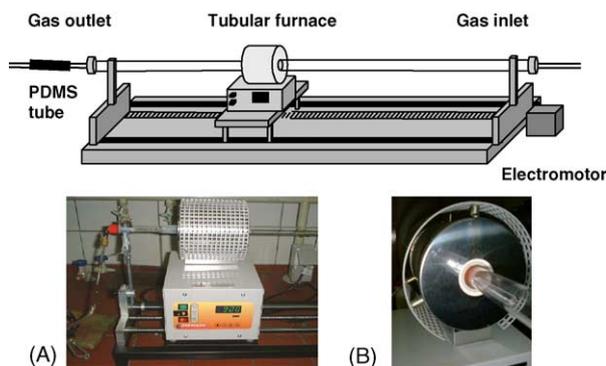


Fig. 1. Overview of the tubular furnace set-up and photographs showing a front (A) and side view (B) on the tubular furnace.

2.2. Thermal desorption capillary GC/MS

The sorbent tubes were desorbed thermally using a TDS-2 thermal desorption unit from Gerstel. The thermal desorption unit was heated from 50 to 300°C at $60^\circ\text{C min}^{-1}$ with an initial time of 1 min and a final time of 5 min. Compounds were swept towards a programmed temperature vapourising injector (PTV-Gerstel) at 100 ml min^{-1} and trapped at a temperature of -150°C in an empty baffled liner. When desorption was completed, the PTV-injector was heated from -150 to 300°C at 12°C s^{-1} . All samples were injected at a 1/100 split ratio, except for the Bunsen experiment for which a 1 min splitless time was applied. The TDS-2 was mounted onto a 6890 GC-5973 MSD (Agilent Technologies, Little Falls, DE, USA). The MSD was used in the electron impact mode (70 eV) generating full scan spectra between 50 and 450 amu. Peak identification was performed using the Wiley sixth edition mass spectral data library. Quantitative data on bromophenols were recorded using the following mass window settings: for 2-bromophenol retention time and mass window 3–10 min, 160–185 m/z , respectively, quantification ion 172; for 2,6-bromophenol retention time and mass window 10–13 min, 245–260 m/z , respectively, quantification ion 252 and for 2,4,6-tribromophenol retention time and mass window 13–30 min, 325–340 m/z , respectively, quantification ion 330. The scan speed was 30 scans s^{-1} .

Separation was performed on a HP-5MS fused silica capillary column (Agilent Technologies, Little Falls, DE, USA), $30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m } d_f$. Carrier gas was helium set at a constant flow of 1.2 ml min^{-1} . The oven was programmed from 40°C (1 min) to 300°C (1.5 min) at $10^\circ\text{C min}^{-1}$. For quantification of the individual bromophenols, standard solutions were prepared, ranging from 10 to 1000 mg l^{-1} for mono- and dibromophenol and solutions ranging from 10 to 140 mg l^{-1} for tribromophenol in dichloromethane (Biosolve, Valkenswaard, The Netherlands). 2-Bromophenol, 2,6-dibromophenol and 2,4,6-tribromophenol were obtained from Fluka (Buchs, Switzerland). One microliter of the solutions was injected onto PDMS tubes and subsequently desorbed.

3. Results and discussion

Due to its aliphatic structure hexabromocyclododecane is less suspected, compared to “aromatic moiety” containing flame-retardants, to lead to the formation of brominated toxic substances when undergoing thermal degradation. Preliminary combustion experiments of FR-XPS, however, indicated the presence of various brominated aromatic species in the combustion gases (Fig. 2). In these experiments extruded polystyrene samples were exposed to a Bunsen flame and the combustion gases formed, were actively sampled on a PDMS tube. The Bunsen flame gave temperatures between 700 and 900°C with a non-uniform distribution of heat around the polystyrene sample. This can be deduced from the burn pat-

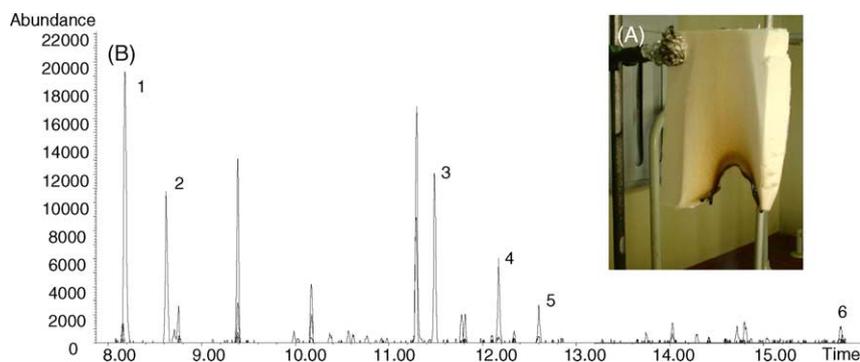


Fig. 2. Combustion products formed upon FR-XPS Bunsen exposure (A), 5 min sampling at 500 ml min^{-1} on PDMS, desorption and analysis conditions see text; (B) extracted ion chromatogram (172, 196, 252, 330 m/z) indicating the various brominated species formed: 2-bromophenol (1), benzylbromide (2), 1-allyl-2-bromobenzene (3), 2,4-dibromophenol (4), 2,6-dibromophenol (5), 2,4,6-tribromophenol (6).

tern shown in Fig. 2A. Precursors of brominated dioxins such as bromophenols [10] were easily identified. Fig. 2B shows the ion-extracted chromatogram (IEC) at 172, 196, 252 and 330 m/z in which the following brominated compounds are depicted: 2-bromophenol and benzylbromide (172 m/z), 1-allyl-2-bromobenzene (196 m/z), 2,4- and 2,6-dibromophenol (252 m/z) and 2,4,6-tribromophenol (330 m/z).

No relationship between bromophenols and hexabromocyclododecane upon thermal degradation was described in the literature. Studies by Barontini et al. [12–14] on the thermal decomposition products of HBCD, indicated that the compound is thermally unstable at relatively low temperatures (230 °C) and that, when heated in air, the main decomposition product is hydrogen bromide, corresponding up to 58% of the total HBCD weight or up to 78% of its bromine content. Various other brominated organic species were produced next to hydrogen bromine. However, no oxygenated brominated organics, such as bromophenols, or other dioxin precursors, were identified.

The high yield of hydrogen bromide reflects the fire retardant properties of HBCD according to the flame poisoning mechanism. In this mechanism, hydrogen bromine reacts with the partial oxidation products in the gas phase, ultimately leading to flame extinction, hence flame poisoning. There is a general consensus that hydrogen bromide interacts with high energy O, H and OH radicals, reducing them to less energetic Br radicals [15]. This mechanism can, however, cause halogenation to take place, as suggested by Kanters et al. [16], who studied the bromination of phenols when combusted in the presence of hydrogen bromide. The obtained data follow this mechanism, which suggest that the interaction of XPS decomposition products, containing phenol and other aromatic structures [17], and bromine radicals produce new brominated species.

To investigate this phenomenon quantitatively in function of temperature FR-XPS was combusted in a tubular furnace. The use of a DIN furnace set-up provides combustion simulation and a reproducible combustion gas atmosphere, allowing quantitation of individual compounds of interest. In general this approach is used to identify major degradation compo-

nents. To this purpose amounts up to grams are introduced in the DIN furnace and grab sampling or split sampling is performed using adsorbents as trapping material [6]. In this work, however, it was the intention to detect minor components formed during combustion. Due to the low concentration of bromophenols in the combustion gases an adapted analysis methodology was developed. Directly connecting the exhaust to a PDMS tube followed by split thermal desorption allowed to effectively transfer the trapped bromophenols. The use of mass spectroscopic windows was preferred above single ion monitoring, because it allows bromine isotope differentiation, which in turn enhances identification.

In each combustion experiment only 10 mg of XPS was used. In order to investigate the breakthrough of bromophenols on PDMS, an XPS sample was combusted at 700 °C. and a second PDMS tube was added to the sampling set-up and consequently desorbed in splitless mode. No bromophenols were detected in the second tube.

In order to quantify the bromophenol concentrations given off under combustion conditions, calibration graphs were made using standard injections directly onto the PDMS tubes. A relative standard deviation of less than 10% was found for each of the selected bromophenols ($n = 6$) indicating the repeatability of analysis. A linearity factor greater than 0.99 was obtained for each component. The limit of detection based on the standard deviation was determined as 0.07, 0.2 and 0.5 ng, for monobromophenol, dibromophenol and tribromophenol, respectively. A limit of quantitation (LOQ) of 0.2, 0.6 and 1.8 ng was calculated based on the standard deviation for monobromophenol, dibromophenol and tribromophenol, respectively. The formation of bromophenols from FR-XPS was monitored at four different temperatures, namely 300, 500, 700 and 900 °C. The results are denoted in Table 1 and shown in Fig. 3.

All combustion experiments were repeated six times and the relative standard deviation of the bromophenol responses remained below 12%. Concentrations found, are in the range of milligrams per kilogram. The results indicate a rise in the formation of monobromophenol when the combustion temperature increases while the maximum concentration of di-

Table 1
Quantitative results for bromophenols in the combustion gases of FR-XPS

	Temperature					
	300 °C	±S.D.	500 °C	±S.D.	700 °C	±S.D.
Monobromophenol	3.0	0.2	31.1	2.7	85.9	2.7
Dibromophenol	2.5	0.1	10.4	1.1	7.1	0.7
Tribromophenol	1.3	0.1	3.7	0.1	3.7	0.2

All concentrations are expressed as milligrams bromophenol per kilogram FR-XPS.

bromophenol is already reached at 500 °C. The general concentration of tribromophenol remains low even at increasing temperatures. At a temperature of 900 °C none of the bromophenols was detected, indicating that the formation of

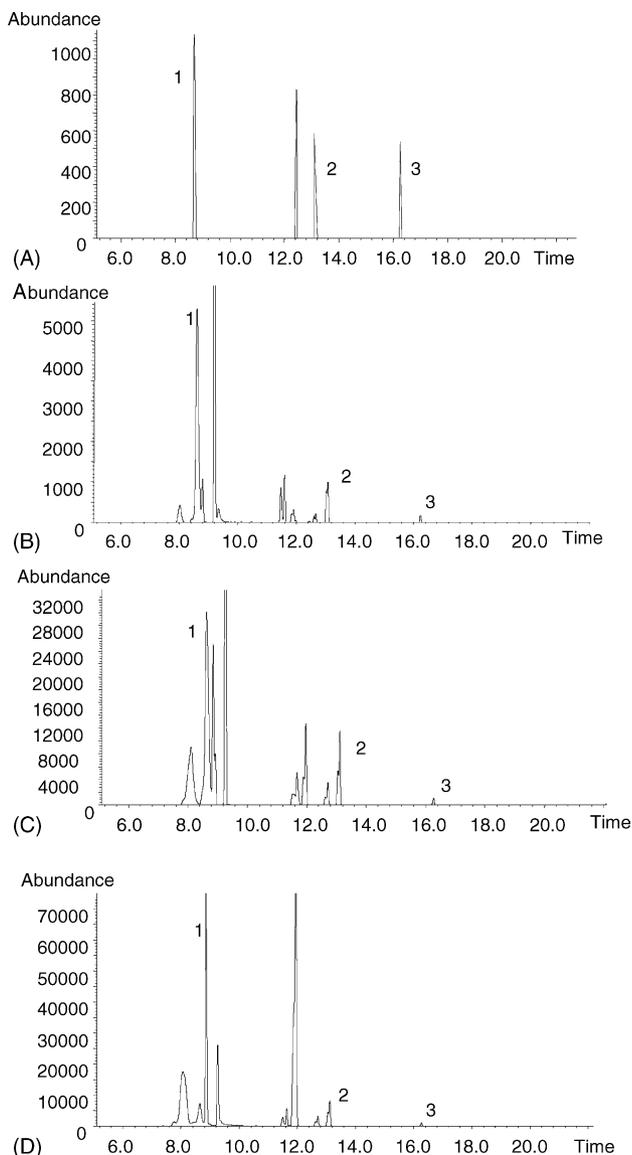


Fig. 3. Extracted ion chromatograms at 172, 252 and 330 m/z , respectively corresponding with monobromophenol (1), dibromophenol (2), tribromophenol (3); response corresponding with 1 ng standard injection (A); DIN combustion run at 300 °C (B), 500 °C (C) and 700 °C (D), conditions see text.

bromophenols is hindered. It seems that the decomposition of the combustion products has the upper hand over the gas phase formation of bromophenols at these high temperatures.

The formation of bromodioxins was not investigated in the present study. The formation of dioxins from bromophenols has, however, been intensively studied. Borojovich et al. [18] indicated that short-term exposures of brominated phenols yield brominated dibenzodioxins and some furans. Evans and Dellinger [19] investigated the mechanism of dioxin formation from the pyrolysis of 2-bromophenol. Sidhu et al. [20] further indicated a maximum yield of 25% for the gas phase formation of tetra-brominated dioxin isomers from 2,4,6-tribromophenol. From this figure, a theoretical maximum yield, based on 3.7 mg kg^{-1} at 700 °C, of ca. 0.9 mg tetra-brominated dioxin from 1 kg of FR-XPS (0.9 ppm) can be calculated. Most probably this yield will be lower due to the presence of other reactive organic species with which tribromophenol can react. It is, however, highly probable that various brominated dioxin isomers will be formed and this is the subject of present studies using the MS in the negative chemical ionisation mode.

4. Conclusion

Hexabromocyclododecane (HBCD) when used as flame retardant in polystyrene forms various bromophenols upon combustion. This formation seems to be inherent to the flame retardant mechanism of HBCD. The data presented, suggest that the use of halogenated flame retardants should not only be scrutinised from their inherent ability to form halogenated dioxins in thermal decomposition reactions, but that an interaction with the polymer breakdown products which could lead to the formation of well known dioxin precursors such as halogenated phenols should also be taken into account when evaluating the impact of BFR-treated materials on the environment.

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