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Short communication

Brominated flame retardants in laboratory air

C. Thomsen[a,*], H. Leknes[a], E. Lundanes[b], G. Becher[a,b]

[a]*Department of Environmental Medicine, National Institute of Public Health, P.O. Box 4404 Torshov, N-0403 Oslo, Norway*
[b]*Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*

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Abstract

During the development of a method for determination of brominated flame retardants in human plasma and serum using solid-phase extraction, several brominated flame retardants were found in the procedural blanks. The contaminants originated most probably from the laboratory air. The brominated flame retardants were found to be adsorbed on glass surfaces and to be acquired using solid-phase sampling. 2,4,6-Tribromophenol, 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) and 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99) were the most abundant brominated flame retardants in our laboratory air, however, large differences in contamination with respect to sampling time and place were observed.

Keywords: Flame retardants; Air analysis; Halogenated compounds

1. Introduction

Brominated flame retardants are widely used to protect various products from catching fire. The most important are tetrabromobisphenol A (TBBP-A) and polybrominated diphenyl ethers (PBDEs) (Fig. 1) with an estimated annual global use of 60×10^6 and 40×10^6 kg, respectively [1–3]. TBBP-A is usually incorporated as a reactive flame retardant, which means that it is covalently bound to the polymer, and is mainly employed in epoxy resins used in printed circuit boards [2]. Nevertheless, it has been shown that small amounts of TBBP-A might leak from the products [4]. PBDEs are used as polymer additives in plastics, textile coatings and electrical appliances [1]. Leakage of the brominated flame retardants into the environment might occur by evaporation from heated materials, as discharges from industry or from waste handling and deposition.

Following the identification of PBDEs and TBBP-A in air particulate in the vicinity of plants manufacturing brominated flame retardants [5], the compounds have been found in several outdoor air samples [1,2,6,7]. The air in different indoor environments such as computerized offices and at a recycling plant has also been found to contain PBDEs and TBBP-A [6,8,9]. The general distribution of brominated flame retardants in the environment has recently been reviewed [10,11].

We have recently developed a method for determination of brominated flame retardants in human plasma and serum using solid-phase extraction (SPE) and GC–electron-capture MS [12]. During the method development several PBDEs and TBBP-A were found in the procedural blanks (no plasma or serum present). The objective of this study was to verify

*Corresponding author. Tel.: +47-2204-2341; fax: +47-2204-2686.

E-mail address: cathrine.thomsen@folkehelsa.no (C. Thomsen).

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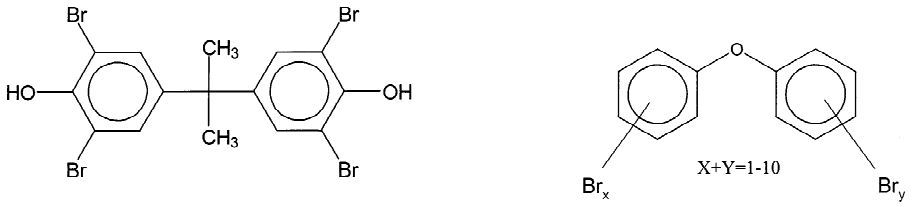

TBBP-A PBDE

Fig. 1. Structural formula of TBBP-A and PBDEs.

our hypothesis that the contamination of brominated flame retardants observed originated from the laboratory air. In addition, we wanted to examine whether there was any difference between two separate laboratories, one of which had been recently renovated.

2. Experimental

2.1. Materials and reagents

2,4,4′-Tribromodiphenyl ether (BDE-28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183) were kindly supplied by Wellington Labs. (Guelph, Canada). TBBP-A was supplied by the Wallenberg Laboratory (University of Stockholm, Sweden). 2,4,6-Tribromophenol (TriBP) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) were purchased from Aldrich (Milwaukee, WI, USA) and 1,3,5-tribromobenzene (TriBB) from Fluka (Buchs, Switzerland). All solvents were pesticide grade from Labscan (Dublin, Ireland). Helium (99.998%) and methane (99.99%) were obtained from Aga (Oslo, Norway).

The Isolute ENV+ SPE columns (200 mg, 6 ml) were purchased from International Sorbent Technology (Mid Glamorgan, UK).

All glassware was washed in 2.5% RBS 25 foaming cleaner (Chemical Products, Brussels, Belgium), rinsed with distilled water and heated at 450°C for 4 h.

2.2. Sampling and sample preparation

Two different sampling methods were used; adsorption to glass at ordinary laboratory air circulation or pumping air through a SPE column. A Dymax 30 pump from Charles Austen Pumps (Surrey, UK) was used for air sampling.

2.2.1. Adsorption to glass — (A) samples

Clean glass funnels of upper diameter 38 mm were heated at 450°C for 4 h, room temperated in the oven and directly placed on to cleaned and burned Petri dishes of glass, which were put at the locations described in Table 1. Two glass funnels were placed at each location. After 48 h, 6 ml of dichloromethane–methanol (7:3, v/v) were poured through the funnel and collected in a Kimax tube. Care was taken to ensure that all interior surfaces of the funnel

Table 1
Locations for glass funnel or solid-phase sampling

Sampling location	Abbreviated
Laboratory bench in a newly renovated laboratory	Room A, bench
Laboratory hood in a newly renovated laboratory	Room A, hood
Laboratory hood in the customary laboratory	Room B, hood

were rinsed with the solvent. The tube was capped and kept at −18°C until derivatization.

2.2.2. Adsorption in solid-phase column — (B) samples

The SPE column, containing a sorbent of a styrene–divinylbenzene copolymer, was prewashed and conditioned by subsequently applying 3 ml methanol, 3 ml dichloromethane and 6 ml dichloromethane–methanol (7:3, v/v). Thereafter, the SPE column was connected via a PTFE tube to the pump, and placed at a location described in Table 1. Air sampling was performed for 45 min at an approximate rate of 4 l/min. The brominated flame retardants were eluted using 6 ml dichloromethane–methanol (7:3, v/v). One sampling was performed at each location for two following days.

The further procedure was identical for (A) and (B) samples.

Prior to derivatization the sample extracts were concentrated under a gentle stream of nitrogen at 50°C to about 30 μl. Subsequently 50 μl of diazomethane solution was added, and the derivatization was performed as described in Ref. [13]. Finally 15 μl of GC–MS quantification standard solution of 1.78 pg TriBB/μl ethyl acetate was added and the samples were stored at −18°C until analysis. The GC–MS calibration solutions were prepared in the same way, using 30 μl of the standard solutions described below.

Both sampling locations were laboratories containing different electrical appliances, analytical instruments and computers. The oldest laboratory (room B in Table 1) was installed in 1990 and had a separate ventilation system. The other laboratory was recently renovated and was connected to the main ventilation system of the building. The sampling on the laboratory bench was performed as far as possible from any electrical equipment.

2.3. Instrumentation

A HP (Avondale, PA, USA) 6890 gas chromatograph equipped with a HP 7683 automatic liquid sampler was operated by ChemStation B 02.05. A CP-Sil 5 CB fused-silica capillary column (30 m× 0.25 mm I.D., 0.25 μm film thickness, Chrompack, Middelburg, Netherlands) was connected to the injector via a deactivated retention gap of 1.5 m× 0.32 mm I.D. (J & W Scientific, Folsom, CA, USA). The injector temperature was 250°C and samples of 2 μl were injected in pulsed splitless mode with a pulse pressure of 1.72 bar for 1.5 min. Helium was used as carrier gas and separation was performed at a constant flow of 1.2 ml/min. The column temperature was initially 90°C for 1 min, then raised by 20°C/min to 250°C, 10°C/min to 300°C and 30°C/min to 325°C, which was held for 3 min.

The mass spectrometer, a HP 5973 MSD instrument with chemical ionization (CI) option, was operated in the electron-capture mode with methane as buffer gas. The compounds were monitored at m/z 79/81 and confirmed by controlling the isotope abundance ratio. The temperature was 106, 250 and 300°C for the quadrupole, the ion source and the interface, respectively, and an electron energy of 235 eV was used.

2.4. Calibration solutions and quantification

All dilutions were made in ethyl acetate using volumetric equipment. The calibration solutions covered the concentration range 0.15–0.6 pg/μl for all compounds except for TriBP, which was 0.0095–0.038 pg/μl to give a similar MS-response as the others. Thus, the total amount of each brominated flame retardant in the GC–MS calibration solutions ranged from 4.5 to 18 pg (n=3) for all compounds except TriBP, which was from 0.825 to 1.14 pg (n=3). A GC–MS quantification standard solution was made by diluting TriBB to a final concentration of 1.78 pg/μl. Both standards and samples were injected twice. The samples were quantified by external standard calibration using area ratios related to the quantification standard.

3. Results and discussion

A chromatogram of a procedural blank prepared according to the method developed for determination of brominated flame retardants human plasma or serum using SPE [12], is shown in Fig. 2. Procedural blanks were frequently performed during the method development and usually similar peak patterns were observed, however, the amount of the different

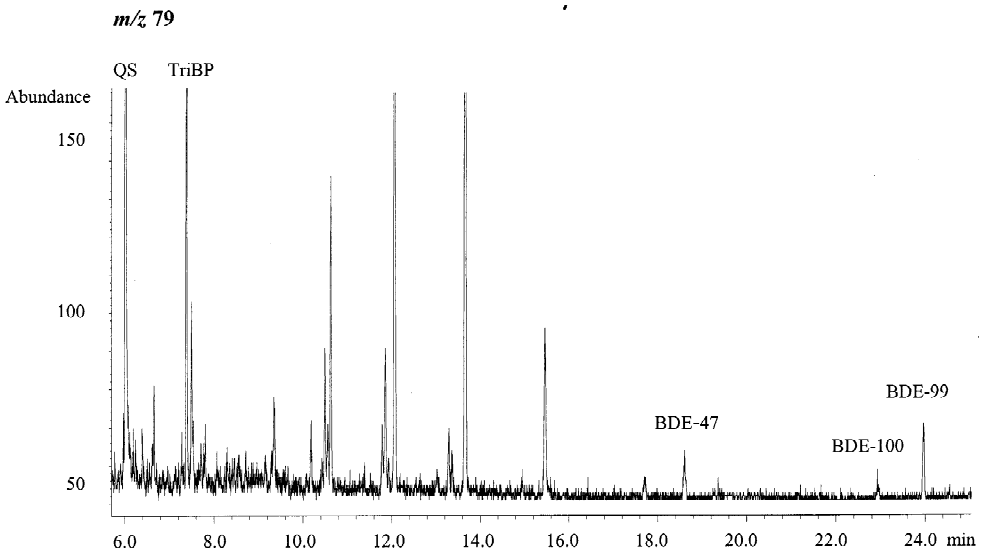

Fig. 2. Chromatogram of a procedural blank prepared according to the method described in Ref. [12]. The temperature program was 90°C for 1 min, then 20°C/min to 190°C, 5°C/min to 230°C, 1°C/min to 235°C, 3.5°C/min to 250°C and finally 30°C/min to 325°C, which was held for 3 min. The compounds were detected as m/z 79/81 (m/z 79 shown) and 2 μl of the extract were injected. The compounds were identified by retention time and isotope ratio.

contaminants varied. Some of the contaminants were identified as brominated flame retardants (Fig. 2). Thus, in order to achieve reliable quantification of low levels of brominated flame retardants in plasma and serum samples, the sources and level of contaminants were identified. Possible sources were solvents, equipment and the laboratory air.

The airflow through the individual SPE columns and across the glass funnels is expected to vary slightly. Therefore, the total amount of the brominated flame retardant in the different sample extracts rather than amount per m^3 air was calculated and compared.

TriBP, BDE-47 and BDE-99 were the most abundant brominated flame retardants acquired using these sampling techniques. The total amounts in the different sample extracts are shown in Fig. 3a–c. At the lowest calibration standard level of 4.5 pg BDE-47, 4.5 pg BDE-99 and 0.825 pg TriBP, the signal-to-noise ratios (S/N) of these analytes were 6, 4 and 3, respectively, and these amounts were used as quantification limits (QLs).

TriBP is the most volatile of the investigated compounds and this is probably the reason why a higher amount of this compound was observed in the SPE extracts compared to the glass funnel extracts. BDE-47 and BDE-99 have been found to be the dominant BDE congener in air and biota [10,11]. Based on an approximate sampling rate of 4 l/min the estimated concentrations of BDE-47 and BDE-99 in our laboratory air were in the range 12–59 and 7–20 pg/m^3, respectively, which are consistent with concentrations previously reported in indoor air [6,9].

BDE-100, BDE-153, BDE-154 and TBBP-A were occasionally identified in some of the samples at levels below the quantification limits. BDE-100 was detected in both sample replicates in all of the samples, while BDE-153, BDE-154 and TBBP-A were more arbitrarily detected, though most often observed in the SPE extracts. One sample extract was injected without derivatization, however, native methylated TriBP and TBBP-A were not present at amounts above the detection limit.

Generally, large differences in contamination level with respect to sampling time and location were found, thus no unambiguous trends in contamination pattern were observed. However, the contamination level in the newly renovated laboratory seemed to be decreasing during the time aspect of the method

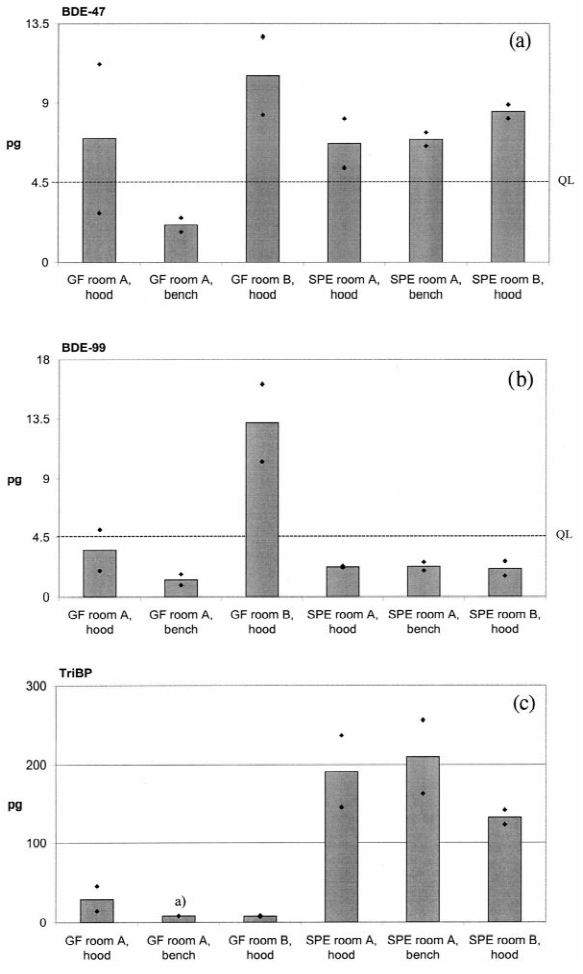

Fig. 3. The total amount of BDE-47 (a), BDE-99 (b) and TriBP (c) in the different sample extracts. Each bar represents the mean of the two sample replicates and the diamonds indicate the individual amounts (mean of two injections). 'a)' in panel (c): one of the sample replicates was not derivatized.

development and this study. This might be an indication of leakage of brominated flame retardants from the new building materials and laboratory furnishing, which is expected to decrease after installation.

All solvents, reagents, the SPE columns and different equipment used in the sample preparation were extensively investigated for possible contamination of brominated flame retardants, however none were present above the detection limit. Synthesis of standards or fortification with concentrated standard solutions has never taken place in the investigated laboratories. These facts also support the hypothesis that the contamination arises from the laboratory air. Thus, in order to avoid a high content of brominated flame retardants in the procedural blanks it is important that all glassware involved in the sample preparation are properly cleaned, and that direct exposure of the sample to the laboratory air is minimized.

The PBDEs and TBBP-A are likely to originate from the electronic equipment or flame-retarded materials used in the laboratory, or in nearby offices. TriBP is also used as a flame retardant; however, this compound has also been reported in exhaust from cars using leaded fuel [14], and might also originate from the heavy traffic road close to the laboratory building.

4. Concluding remarks

The brominated flame retardants observed in the procedural blanks are most probably originating from the laboratory air. They are adsorbed to glass surfaces or acquired using solid-phase sampling. Relatively large differences in the degree of contamination appeared with respect to sampling time and location. Therefore, it is extremely important to include procedural blanks when preparing samples, in order to assess the contamination from laboratory air and correct the results if necessary.

Acknowledgements

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