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Journal of Chromatography A, 991 (2003) 241–253
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Large-volume programmed-temperature vaporiser injection for fast gas chromatography with electron capture and mass spectrometric detection of polybrominated diphenyl ethers

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Received 4 November 2002; received in revised form 24 December 2002; accepted 9 January 2003

Abstract

A large volume injection fast-GC–MS method has been developed, optimized and evaluated for the determination of polybrominated diphenyl ethers, including the decabrominated diphenyl ether (BDE-209). The programmed-temperature vaporiser injection parameters, temperature programming of the GC oven, and the physical dimensions of the narrow bore GC column were investigated to find the optimal operating conditions for the analysis. Depending on parameter settings the yield of the PBDEs and particularly BDE-209, varies significantly. Volumes up to 125 μl were successfully injected and a fast GC separation was performed, with retention times as short as 6.4 min for the last eluting compound, BDE-209. In a pilot study an air sample, collected at an electronics dismantling facility, was analyzed. Low-resolution mass spectrometry in electron capture negative ion mode was used for detection. Nine BDE congeners, including BDE-209, were identified and quantified.

Keywords: PTV injection; Injection methods; Polybrominated diphenyl ethers

1. Introduction

The limited injection volume of split/splitless- and on-column injectors, typically 1–3 μl, allows only a fraction of a sample to be introduced into a GC capillary column. This is a significant shortcoming in environmental trace analysis. With limited amounts of sample at low concentrations, there is a need for methodologies for large injection volumes.

Though the programmed-temperature vaporiser (PTV) has been used for over two decades and at an early stage was recognized as a potential large volume injector [1–3], the interest in development and applications has only recently arisen. It has proven to be a reliable technique for injection volumes up to 10 ml [4] and has been used for improved sensitivity in off-line methods, as well as an interface in coupled techniques [3,5,6]. Lately, applications of the PTV in combination with narrow bore columns have been reported [7,8]. Covaci et. al used this for the determination of tri- to hexa-BDE and tri- to deca-PCB in human adipose tissue [7]. These systems are powerful tools for environmental analyses, allowing large volume injections and short analysis times and thereby overcoming two of the

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0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00174-2

major weaknesses with conventional gas chromatography.

Fast gas chromatographic analyses have been a desirable aim and the subject of many papers through the entire history of capillary GC. As early as 1962, Desty et al. [9] proposed smaller inner diameters of the columns to decrease analysis times in GC. The exploitation of fast-GC utilizing narrow bore columns (I.D. $\leq$100 μm) was, however, held up by practical difficulties. Even though these obstacles essentially have been overcome today and the area has been both theoretically and practically investigated [10–17], the technique is still not considered as a standard operating procedure.

Narrow bore columns can also decrease the minimum detectable amount of the analytes [18], since sharp peaks increase the signal-to-noise ratio. Furthermore, for thermally labile compounds, the use of smaller column dimensions can be advantageous, as the analytes spend less time at elevated temperatures.

There are a large number of consumer products that need to be treated to reduce their flammability and to prevent fires. Therefore there is a demand for efficient and inexpensive flame-retardants, such as the commonly used polybrominated diphenyl ethers (PBDEs). Since these additive flame-retardants only are dissolved in the plastics polymer or added to the textiles and not covalently bonded, they have been shown to migrate to the environment. There are numerous reports about the presence of PBDE congeners in various samples such as sediments [19,20], fish [21–26], human blood [27] and breast milk [28]. The PBDEs are highly lipophilic and persistent, and the similarity in structure with polychlorinated biphenyls (PCB) give rise to concerns about the PBDEs as environmental contaminants. Thus, there is a great need for accurate and sensitive methods for determination of PBDE [29].

Commonly the determination of PBDE is performed on a gas chromatographic system equipped with an electron capture detector (ECD) or a mass spectrometric detector (MS). The split/splitless injection technique is the most frequently used according to an interlaboratory study organized by De Boer et. al [30]. High boiling compounds, such as the octa-, nona-, and deca-brominated diphenyl ethers, are however discriminated in the split/splitless injector and the high temperatures used may also increase the thermal degradation of the PBDE congeners [31]. This is one probable reason for the scarce number of papers in the literature, including the determination of the high-molecular mass congeners, e.g., deca-BDE. Consequently, alternative injection techniques for the GC analysis of PBDE are of great interest.

In this paper we present a practical optimization and evaluation of the large volume PTV injector in combination with narrow bore capillary columns for fast GC–ECD and fast GC–MS analysis of polybrominated diphenyl ethers, including the thermally labile, high-molecular mass hepta- to deca-BDE.

2. Experimental

2.1. Chemicals

In this paper we are using the IUPAC numbering system for PCB [32] to name the congeners of PBDEs in a similar manner. A PBDE standard stock solution was prepared by dissolving the congeners BDE 2, 3, 7, 13, 17, 47, 49, 99, 100, 153, 154, 183, 190, 203 and 209 in Supra Solve toluene (Merck, Darmstadt, Germany) (Table 1). Test mixtures of desired concentration were made by diluting the stock solution in either *n*-hexane of pesticide analysis grade (Scharlau, Barcelona, Spain), or isooctane of HPLC-grade (Merck)

2.2. Instrumentation

The optimization and evaluation experiments were performed on an Agilent 6980 series gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a PTV from Gerstel (CIS-4, Gerstel, Mülheim an der Ruhr, Germany) and a micro electron capture detector (μECD, Agilent). The detector temperature was 350 °C and nitrogen was used as make-up gas at a flow of 70 ml/min. The GC oven was temperature programmed, with the following instrumental maximum rates: 50–70 °C, 120 °/min; 70–115 °C, 95 °/min; 115–175 °C, 65 °/min; 175–300 °C, 45 °/min and 300–325 °C, 35 °/min. Helium was used as carrier gas at linear flow-rates in the range 20–170 cm/s. The PTV injector was operated in the solvent vent mode in order to make injections of 25–125 μl possible. The sample

Table 1
The standard solution

Congener	Bromines	Subst. pattern	Conc. (pg/μl)
BDE-2	1	3	2.61
BDE-3	1	4	2.68
BDE-7	2	2,4	1.97
BDE-13	2	3,4′	1.72
BDE-17	3	2,2′,4	1.43
BDE-49	4	2,2′,4,5′	1.21
BDE-47	4	2,2′,4,4	1.27
BDE-100	5	2,2′,4,4′,6	1.01
BDE-99	5	2,2′,4,4′,5	1.14
BDE-154	6	2,2′,4,4′,5,6′	1.04
BDE-153	6	2,2′,4,4′,5,5′	1.12
BDE-183	7	2,2′,3,4,4′,5′,6	1.05
BDE-190	7	2,3,3′,4,4′,5,6	1.01
BDE-203	8	2,2′,3,4,4′,5,5′,6	1.05
BDE-209	10	2,2′,3,3′,4,4′,5,5′,6,6′	0.98

was injected at constant speed, in the range 100–390 μl/min, the latter being the practical maximum of the pump, utilizing a syringe pump (Pump 11, Harvard Apparatus, Holliston, MA, USA), equipped with a 500-μl syringe (Hamilton, Reno, NV, USA). A fused-silica needle (200×0.05 mm, J&W Scientific, Folsom, CA, USA) was used to connect the syringe to the PTV injector. The end of the fused-silica needle was located about 30 mm down in the PTV injector liner. During injection, the injector body was kept at a low temperature and the solvent split was kept open. After injection the split was closed and the injector heated, to transfer the analytes to the column. The investigated domains of the injection parameters are shown in Table 2.

If nothing else is stated, the GC column was a 4 m long DB-1 (J&W Scientific), with an internal diameter of 0.1 mm and a film thickness of 0.1 μm. DB-1 columns from J&W with inner diameter of 0.05 mm and film thickness of 0.05 μm with lengths of 1 and 3 m were also investigated. For some experiments a 1 m×0.25 mm uncoated fused-silica capillary (Restek, PA, USA) was used as retention gap, connected to the analytical column with a Siltek deactivated press-fit connector (Restek). A 15 m×0.25 mm DB-1 MS analytical column from J&W with 0.1 μm film thickness was used as a reference GC column.

Table 2
The injection parameters

Parameter	Domain
Injection rate	50–390 μl/min
Injection temperature	35–125 °C
Vent flow	0–300 ml/min
Temperature rate	200–700 °/min
Transfer temperature	275–375 °C
Transfer time	0–2.5 min
Solvent elimination time	0–0.3 min

For the determination of PBDEs in air an LVI-PTV-fast-GC–MS system was used (Agilent 6980 series gas chromatograph connected to a 5973 mass selective detector). The optimized conditions from the GC–ECD experiments were applied on the GC–MS system. Methane was used as reagent gas at a pressure of 2.2×10^{-4} Torr, and the electron energy was set to −175 eV. The ion source had a temperature of 200 °C and the quadrupole was kept at 150 °C. Selective detection of PBDEs was performed by selected ion monitoring (SIM) in electron capture negative ion mode, monitoring the m/z 79 and 81 ions characteristic for the bromine ion, $[Br]^-$. A 2 m long DB-1 column with an inner diameter of 0.1 mm and a film thickness of 0.1 μm was used. The injector temperature was 80 °C, the vent flow 150 ml/min and the injection volume 50 μl. The PTV transfer rate was 700 °C/min, the transfer time 1–2 min and the temperature 325 °C.

2.3. Air sampling

Air samples were collected using AirCheck 2000 personal air sampling pumps (SKC, PA, USA) equipped with a sampling head of anodized aluminum containing a glass fiber filter (25 mm binder free borosilicate glass fiber filter (type A/E, Gelman Sciences, Ann Arbor, MI, USA) and two cylindrical polyurethane foam plugs (PUFs) (length 15 mm, diameter 15 mm, porosity 60 p.p.i., density 25 kg/m^3, Specialplast, Gillinge, Sweden) in series. The second PUF served as a control of sampler break through. The glass fiber filters were washed in an ultrasonic bath for 20 min in methanol, acetone and dichloromethane prior sampling. PUFs were first boiled in water for 4 h, followed by additional washing steps in water, acetone and dichloromethane, respectively. The PUFs were then Soxhlet-extracted in dichloromethane for 12 h. This is a standard operating procedure at our laboratory to remove impurities in the PUF adsorbent.

The pumps were adjusted to a flow of 3.0 l/min prior sampling, using a DC-Lite Calibrator (BIOS, Butler, NJ, USA). The sampling time was 12 h for all samples. Surrogate standard, 1490 pg of BDE-119, was added to both the filter and the PUFs. Filter and adsorbents were separately extracted by use of ultrasonic assisted solvent extraction in 5 ml of dichloromethane during 20 min. The extraction procedure was repeated once with a fresh portion of solvent giving a total extract volume of 10 ml. The solvent was changed to *n*-hexane and the volume reduced to 1 ml. To remove polar material, the sample was applied on a 1 g NH_2 solid phase extraction (SPE) cartridge (Isolute, International Sorbent Technology, UK) and eluted with 10 ml hexane.

3. Results and discussion

To achieve fast GC analysis with reproducible results, sufficient resolution and high yield of PBDEs, the LVI-PTV-fast-GC system was optimized in three steps that were assumed to be independent: the injection, the transfer of analytes from the PTV injector liner to the column, and the gas chromatographic separation. The order of the experiments was randomized within each parameter investigation.

The method was designed for analysis of the PBDEs found in technical mixtures and environmental and indoor air samples, ranging from tetra-BDE to deca-BDE, rather than all the 209 possible congeners.

3.1. Sample introduction

The injection procedure is illustrated in Fig. 1. The sample was introduced at constant speed into the PTV injector, which was kept at a temperature in the range of 35–135 °C. During injection, the solvent was vented out through the PTV split, while the analytes are trapped in the injector liner. The high boiling points of PBDE, with molecular masses in the range of 249–959 Da, gives a wide dynamic range for the large volume injection, since losses through the solvent vent are improbable for most of the congeners. The lowest molecular mass analytes, mono- and di-BDE, were however found to be discriminated under some conditions. The injection temperature and the vent flow are crucial parameters both for the evaporation of solvent and for the trapping of analytes in the PTV liner.

Evaporation of the solvent must occur in the liner, prior to the column head if the analytes are to be trapped in a region of the liner from which they can be transferred to the column, after completed injection. It is suggested in the literature that the injection rate should be similar to the evaporation rate to avoid flooding of the injector [33]. Analytes reaching past the column head and further down in the liner cannot be quantitatively transferred or might be lost through the split exit [6]. On the other hand, at too high evaporation rates, low-molecular mass compounds might be lost through the split.

To optimize the injection, a number of parameters were investigated: injection flow, injection temperature, vent flow, solvent elimination time, and injection volume.

3.1.1. Injection flow

A plot of peak areas versus injection flow is shown in Fig. 2a, for three congeners, BDE-7, BDE-99 and BDE-209, representing low-, medium- and high-boiling BDEs. The flow was varied between

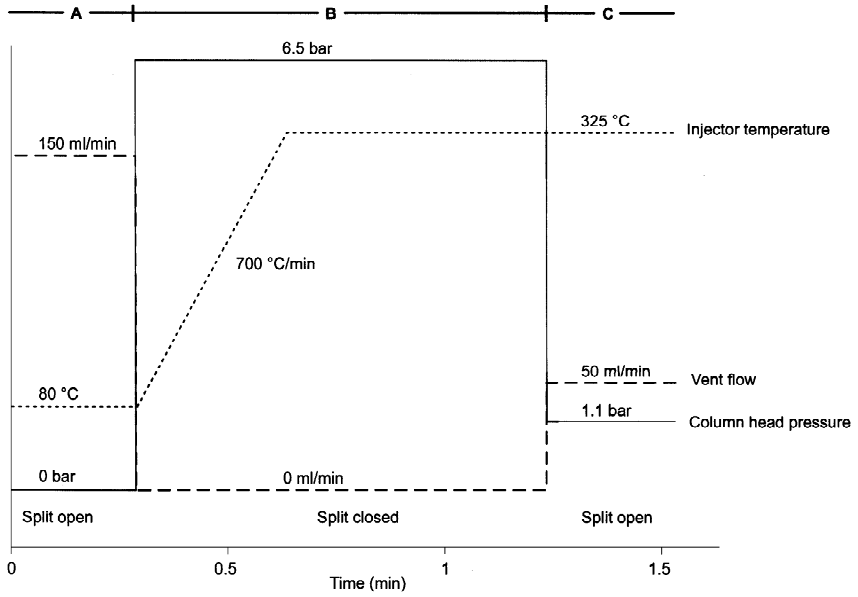

Fig. 1. The injection procedure, showing (A) the sample introduction phase, (B) the transfer phase and (C) the GC separation.

100 and 390 μl/min, while the temperature was kept at 80 °C and the vent flow at 150 ml/min. The areas for BDE-209 and BDE-99 increase up to about 300 μl/min, while the area for BDE-7 exhibits a slight decrease.

By observing the flow at the exit of the fused-silica needle, it was established that the sample solution leaves the injection needle in one of two modes. At low flow-rates the solvent leaves the needle as droplets, which cling to and spread over the needle tip, while at higher flow-rates the solvent bursts out from the needle forming a spray. The critical flow-rate was found to be about 200 μl/min, determined at ambient pressure and temperature. Due to an increased surface area-to-volume ratio, an efficient spray formation improves evaporation of the solvent. The high boiling components condense on the liner surface from which they can be effectively transferred to the column, which gives high yields (Fig. 2a,b). However, low-molecular mass congeners, such as BDE-7, are to some extent co-evaporated with the solvent and lost through the solvent split. At too high injection rates the evaporation site moves downwards in the liner and flooding occurs, which leads to decreased peak areas.

BDE-209 showed the strongest dependence on the injection flow-rate. To obtain the highest peaks the flow was set to 300 μl/min.

3.1.2. Temperature and vent flow

As illustrated in Fig. 2c,d, an increased evaporation rate, in terms of increased temperature and vent flow, showed to be favorable for all the investigated BDE congeners, up to a certain level. The injection flow was kept at 300 μl/min. When investigating the vent flow the temperature was set to 65 °C and during the injection temperature study the vent flow was set to 100 ml/min.

At the optimal settings the evaporation occurs in the liner, above the column, enabling a quantitative transfer. At very high temperatures, particularly BDE-7, but also BDE-99, is discriminated by losses through the solvent split.

A temperature of about 80 °C and a vent flow of 150 ml/min showed to be the optimum for all congeners, when using *n*-hexane as solvent.

No peak distortion due to overflow of the injector liner and liquid entering the column was observed during the experiments, which might be expected at such a low injection temperature as 35 °C. Very little of the total gas and vapor flow enters the column during the injection phase. This is due to the high

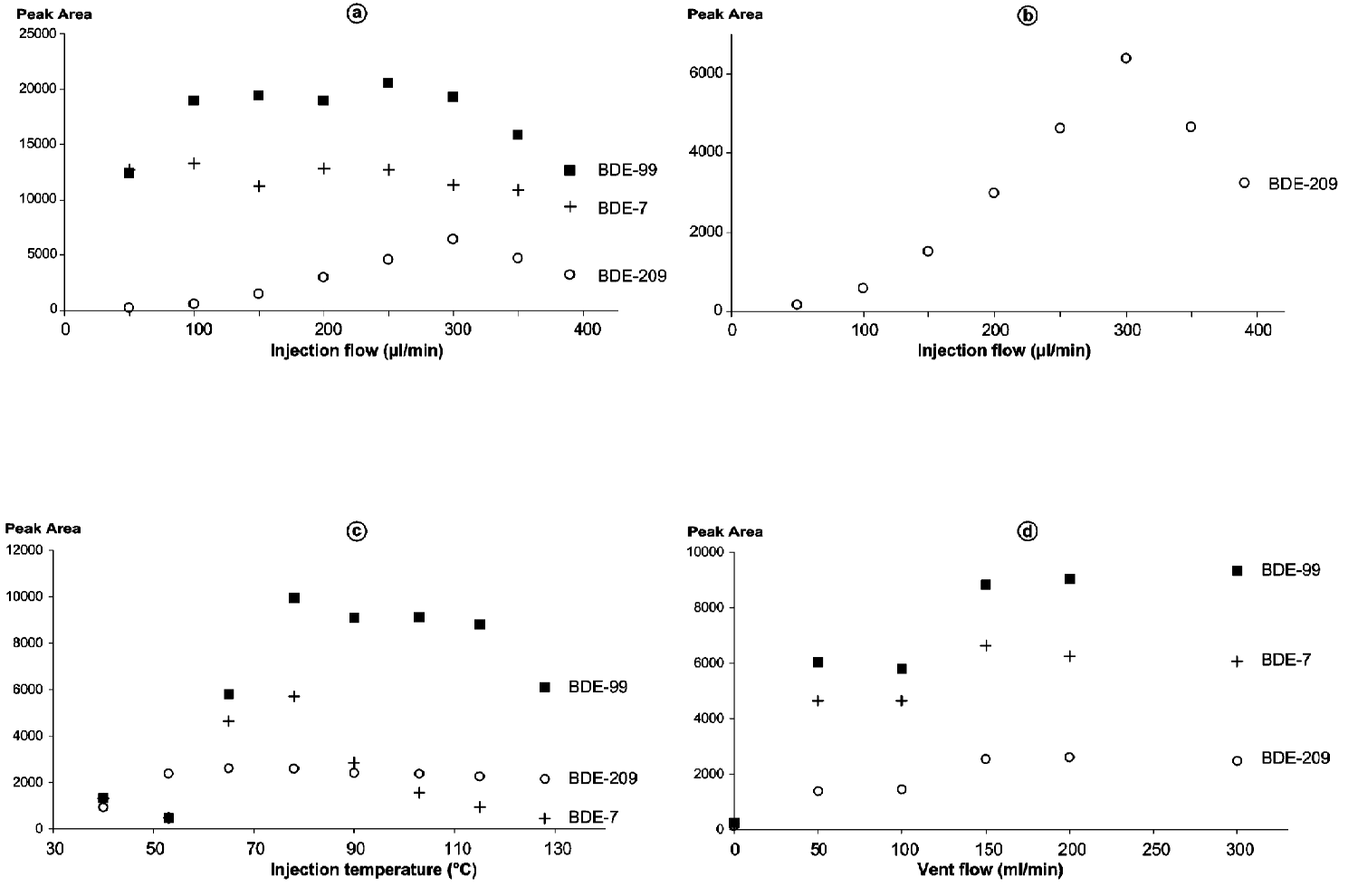

Fig. 2. Peak areas as a function of: injection flow-rate (a,b); of injection temperature (c); and vent flow (d); 74–147 pg in a 75-μl injection.

back pressure in the narrow bore column, in combination with the high injector vent flow that gives a extremely high split flow ratio, since the column flow during injection was set to zero. Furthermore, even if a part of the analytes actually would be introduced on to the column before transfer, the start band is refocused by the large difference in injector and GC oven temperatures during the subsequent transfer process.

Due to the gentle evaporation of solvent during injection and analytes during transfer the temperature programmed injection technique is favorable. When injecting 1 μl, the response for deca-BDE was almost 17 times higher with the PTV in this mode than in constant temperature splitless mode.

3.1.3. Solvent delay time

The influence on the yield of the time delay between the end of sample introduction and closure of the solvent split was studied. No effect could be observed in the range from 0 to 0.3 min and the time was set to 0.1 min to reduce the risk of any possible solvent residues entering the column and reaching the detector.

3.1.4. Injection volume

Volumes of 25, 50, 75, 100 and 125 μl of the same standard solution were injected. As was to be expected, a linear relationship of peak area versus injected volume was confirmed. Coefficients of correlation was high, with $r^2=0.9997$ for both BDE-47 and BDE-99, $r^2=0.9864$ for BDE-7 and $r^2=0.9897$ for BDE-209. This means that full advantage can be taken of large injection volumes in order to improve sample detection limits. When injecting 25 and 125 μl the system exhibited somewhat lower precision, Table 3. The absolute error of the system affects smaller volumes to a higher degree. At larger volumes the settings of the evaporation parameters become more critical and the stability of the system is decreasing.

Table 3
Relative standard deviation as a function of injection volume

Injection volume	RSD (%) ($n=3$)	
	Rel. area	Abs. area
25	5.3	18.1
50	2.4	4.2
75	1.3	2.4
100	1.4	9.0
125	4.0	22.0

The system shows excellent precision for injection volumes of 50–100 μl, which is sufficient for most off-line application. In this investigation a 75 μl injection is used unless else is stated.

3.1.5. Liner insert

The liner insert has an important role in the trapping and transfer of the analytes. In this study four different liners were investigated: single-baffled, singled-baffled with glass wool, multi-baffled and sintered glass. The latter gave excellent results with respect to precision and especially trapping of the low boiling analytes. However, after only 30 injections, severe losses of high-molecular mass congeners were observed. When using glass wool as packing material in a single baffled liner the same problem occurred. This suggests that the materials in these liners were activated, causing irreversible adsorption or catalysis of thermal degradation of the analytes. Both the empty single- and multi-baffled liners were impaired by discrimination of low-molecular mass congeners, i.e., mono-BDE, di-BDE and tri-BDE, when operating the PTV in solvent vent mode. The yield of these congeners was 13, 37 and 66%, respectively, compared to a temperature-programmed pulsed splitless injection, whereas for higher molecular mass PBDEs 100%. The discrimination was even more pronounced when Siltek deactivated liners were used, suggesting that a better deactivation of the liner provides fewer sites where volatile compounds can be trapped. The single-baffled liner had low precision regarding both absolute and relative peak areas and was therefore not used in the further studies. The multi-baffled liner showed good precision and the discrimination of low boiling BDEs was reduced by adding 0.1–0.35% (v/v) of dodecane to the sample solution. This small amount of keeper was enough to efficiently trap the low boiling BDE congeners. The yield for mono-, di- and tri-BDE increased to 33, 66 and 98%, respectively. The RSD for absolute and relative peak areas were 4.1 and 1.8%, respectively. For 0.5 and 1% of dodecane results comparable to the splitless injection were obtained, but with distortion of the early eluting

peaks as a significant drawback. The yield of deca-BDE was not affected when using dodecane as dynamic trapping, as was the case when using glass wool or sintered glass liners.

The life span for all liners was limited. After about 100–200 injections the liner performance started to deteriorate, with discrimination of the heavier BDE congeners as a result. This suggests that the liners were activated, most likely due to the large amount of solvents being injected, in combination with steep and frequent temperature gradients. For this reason the liner has to be replaced regularly.

3.2. Analyte transfer

Transfer of the analytes from the PTV injector liner to the GC column, starts when the split valve closes and the PTV is rapidly heated to a suitable transfer temperature.

Four parameters were suspected of influencing the transfer: temperature ramp, final temperature, transfer time and transfer pressure. An initial screening showed that only the three latter parameters significantly affected the peak areas.

3.2.1. Transfer temperature ramp

Temperature ramps from 200 to 700 °C/min were applied for the transfer process, without any significant change in response for the BDE congeners. Therefore the maximum rate of 700 °C/min, providing the fastest injections, was used during the rest of the investigations.

3.2.2. Transfer temperature and time

A diagram showing the peak area for deca-BDE versus transfer time for different transfer temperatures is seen in Fig. 3. Short transfer times and low temperatures could discriminate high boiling compounds, such as deca-BDE. All BDE congeners followed the same pattern, but BDE-209 tended to be transferred a bit more slowly. At 375 °C the peak area for BDE-209 was considerably lower, suggesting that the compound was degraded in the injector. At a transfer temperature of 275 °C a high yield of deca-BDE was obtained, but the transfer time had to be extended to several min. When applying an even lower temperature, 240 °C, considerable band broadening due to the cold spot effect of the injector

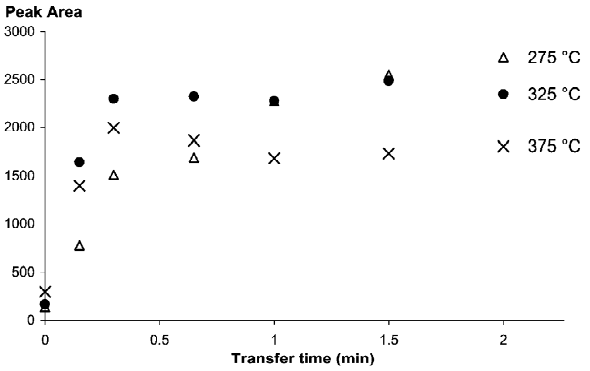

Fig. 3. Peak areas for BDE-209 as a function of transfer time and temperature.

was observed. We found 325 °C a good compromise, with maximum peaks obtained after only 0.3–0.6 min.

3.2.3. Transfer pressure

An increased carrier gas pressure during the transfer enhanced the transport of the analytes from the injector liner to the column. A carrier gas pressure of 650 kPa, which is close to the instrument maximum, increased peak areas three to four times, compared to using a column head pressure of 170 kPa, which was applied for the GC analysis.

The optimal settings of the injection are presented in Fig. 1.

3.3. GC separation

Separation efficiency and thus the time of analysis can be modified by selecting carrier gas, gas chromatographic column system and temperature program. The gas chromatographic system was designed for analysis of the PBDE found in products and real samples rather than to separate all 209 congeners.

3.3.1. Carrier gas

Because of its low viscosity, safety and compatibility to mass spectrometry, helium was used as carrier gas. The velocity was investigated in an interval from 20 to 140 cm/s and finally set to 60 cm/s since it proved to give the narrowest peaks. This was what could be expected from the normal van Deemter curve using helium as the carrier gas.

3.3.2. Column

Narrow bore columns gave sharp and narrow peaks with an average peak width at half peak height of 0.61 s, compared to 1.9 s for a conventional 0.25 mm column. The latter value had to be calculated without the contribution from the deca-BDE peak, since this congener could not be detected using the standard GC column system (see Section 3.5).

According to GC theory, capillary columns with an I.D. of 0.05 mm and a stationary phase of 0.05 μm should improve the separation even further by reducing band broadening due to resistance to mass transfer, compared to the column with I.D. of 0.1 mm. This could, however, not be confirmed in this study when using such columns, indicating significant extra-column band broadening.

To minimize band broadening due to the injection, injection band focusing by the solvent effect was applied. The GC oven start temperature was investigated within the interval 50–127 °C using *n*-hexane as solvent in the temperature interval 50–80 and using isooctane in the interval 67–127 °C. Furthermore, retention gap focusing was investigated by connecting a 1 m×0.25 mm uncoated guard column

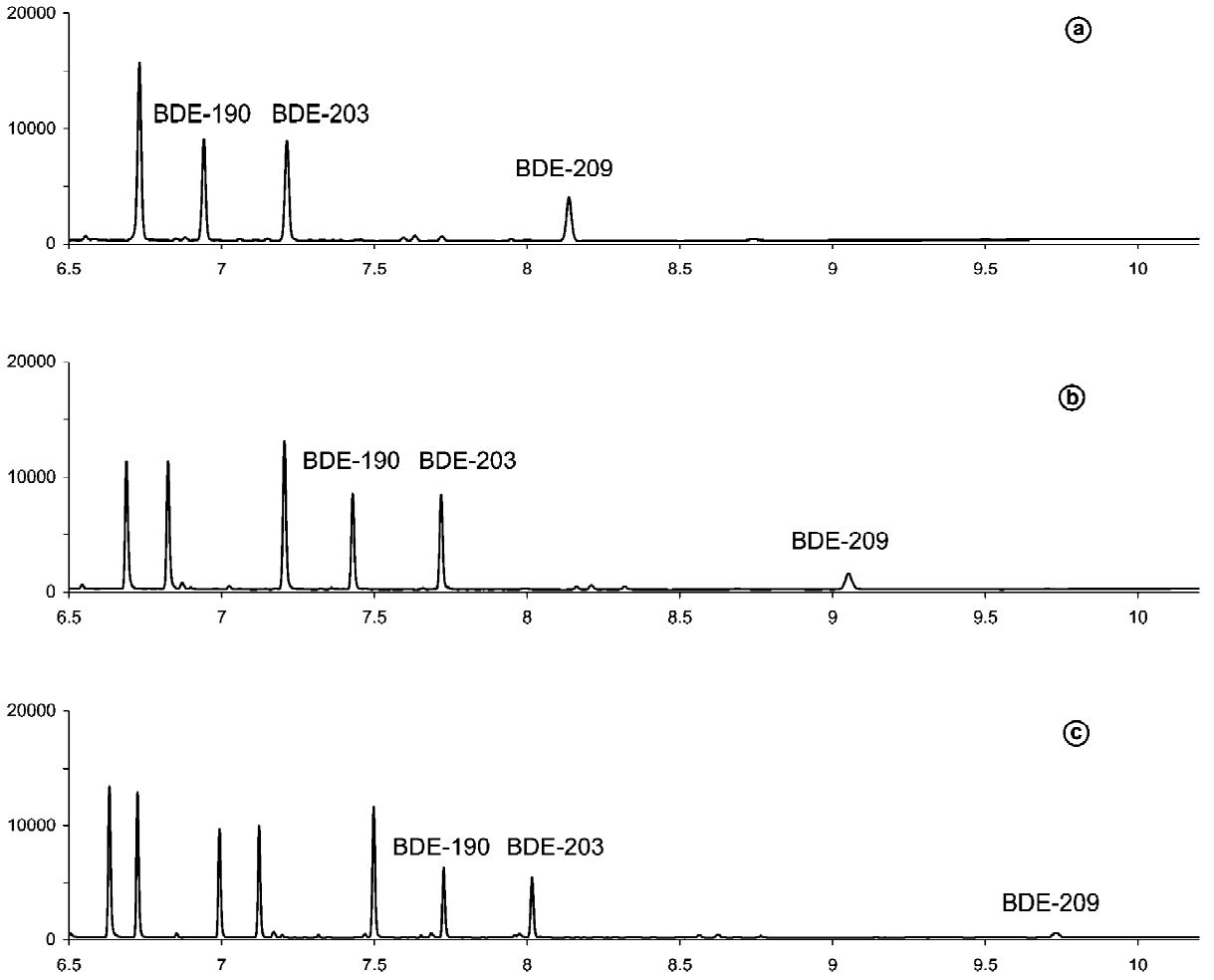

Fig. 4. GC–ECD chromatograms obtained using 2, 4 and 8 m×0.100 mm, respectively. Injection volume, 75 μl containing 73.5 pg of BDE-209.

to the analytical column. However, no additional decrease of peak width could be verified by any of these methods.

These results single out the detector of this standard GC system to be a strong contributor to the extra-column band broadening. The make up gas and detector base temperature were varied from 45 to 120 ml/min and 300 to 350 °C, respectively. However, the peak widths could not be reduced any further.

The length of the column is significant for the resolution, since it is increased with the column length. On the other hand, longer columns increase the analysis times, and since thermally labile, high boiling BDE congeners, in particular BDE-209, will spend a longer period of time at an elevated temperature, the degradation phenomenon will become more pronounced, as shown in Fig. 4. The peak area for BDE-209 increased about six times when going from a column length of 8 to 2 m. Except for the column length the conditions were identical. The degradation is most evident for the deca brominated congener, but also noticeable for BDE-190 and BDE-203.

3.3.3. Temperature program

A slow temperature program will increase the resolution. Analyses with linear temperature programming rates of 3, 5, 10, 15, 25 and 45 °C/min were performed. However, due to band broadening the improvement is not as evident as could be expected. When comparing the program rates 5 and 45 C°/min, the small gain in resolution for the peak pair BDE-49 and BDE-47, $R=5.49$ and $R=4.91$, respectively, is overshadowed by the long analysis time which increases from 8.5 to 46 min.

In the optimal analysis, the temperature program was set to the maximum program rate for the GC (see Section 2). The last eluting component, BDE-209 had a retention time of 8 min, giving a total analysis cycle time of 12 min with a 4 m×0.1 mm column. A typical chromatogram is shown in Fig. 5.

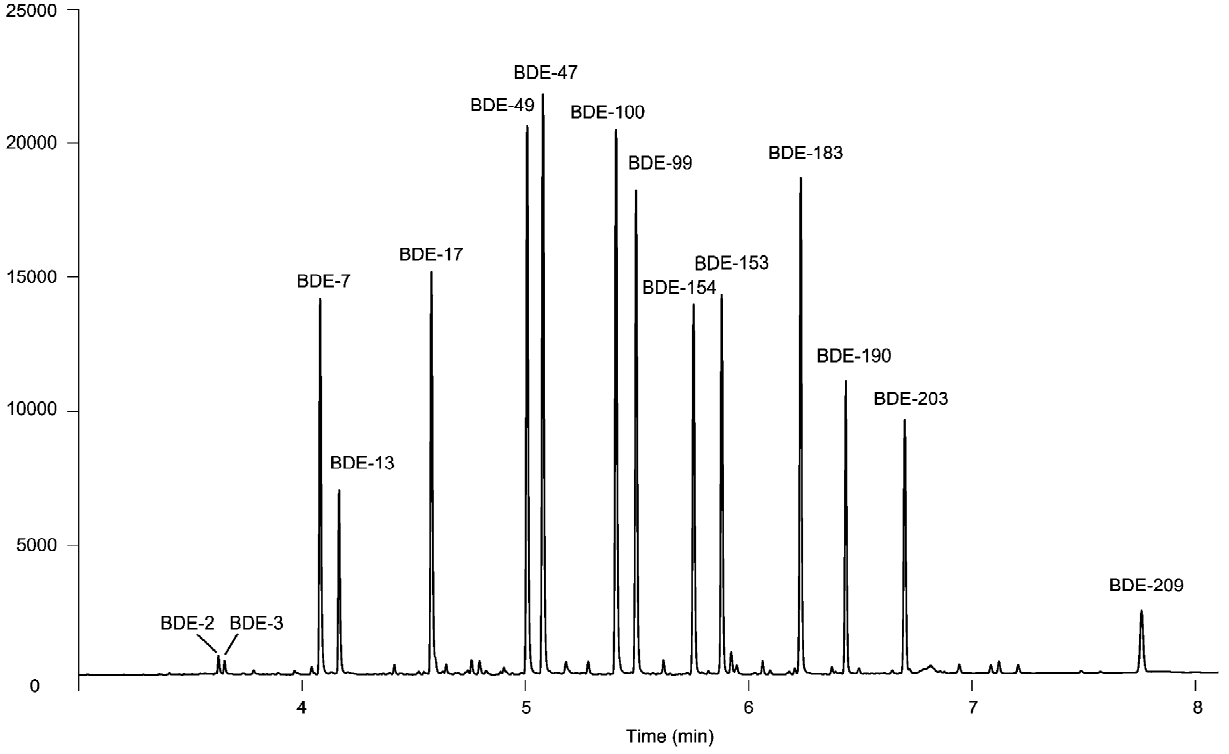

Fig. 5. A typical LVI-PTV-fast-GC–ECD chromatogram: 74–147 pg in 75 μl solvent injected.

3.4. Carry-over

Seventy-five μl of a standard containing 100–200 pg of the individual BDE congeners were injected and the separation was followed by a blank analysis injecting 75 μl of solvent. The carry-over was calculated as the ratio between the peak areas obtained from the chromatogram of the standard and the following blank chromatogram. It was found to be less than 0.3% for all the 13 investigated PBDEs.

3.5. Comparison to a conventional GC system

The performance of the LVI-PTV-fast-GC–ECD system for the analysis of PBDEs was compared to a ''conventional'' column and a splitless injector. The latter instrumentation had a lower resolution and an increased discrimination of high boiling BDE congeners. The peaks were considerably broader when the 25 m×0.25 mm ''conventional'' column was used and consequently the resolution was poorer when the same temperature program was employed. For the peak pair BDE-49 and BDE-47, the resolution was 4.6 with the narrow bore column and 1.5 with the conventional column when a linear temperature programming rate of 45 °C/min was applied on both columns. Loss of high boiling BDE congeners in the ''conventional'' system is a result of degradation in the hot injector liner during injection as well as inside the column during separation. Discrimination of BDE-209, the most temperature unstable of the BDE congeners, was severe in the conventional system and the congener could not be detected when the conventional column system was used in combination with either a splitless injector or the LVI-PTV, injecting around 80 pg of BDE-209. This verifies the assumption that the time in the column has a strong influence on the yield of thermally labile analytes.

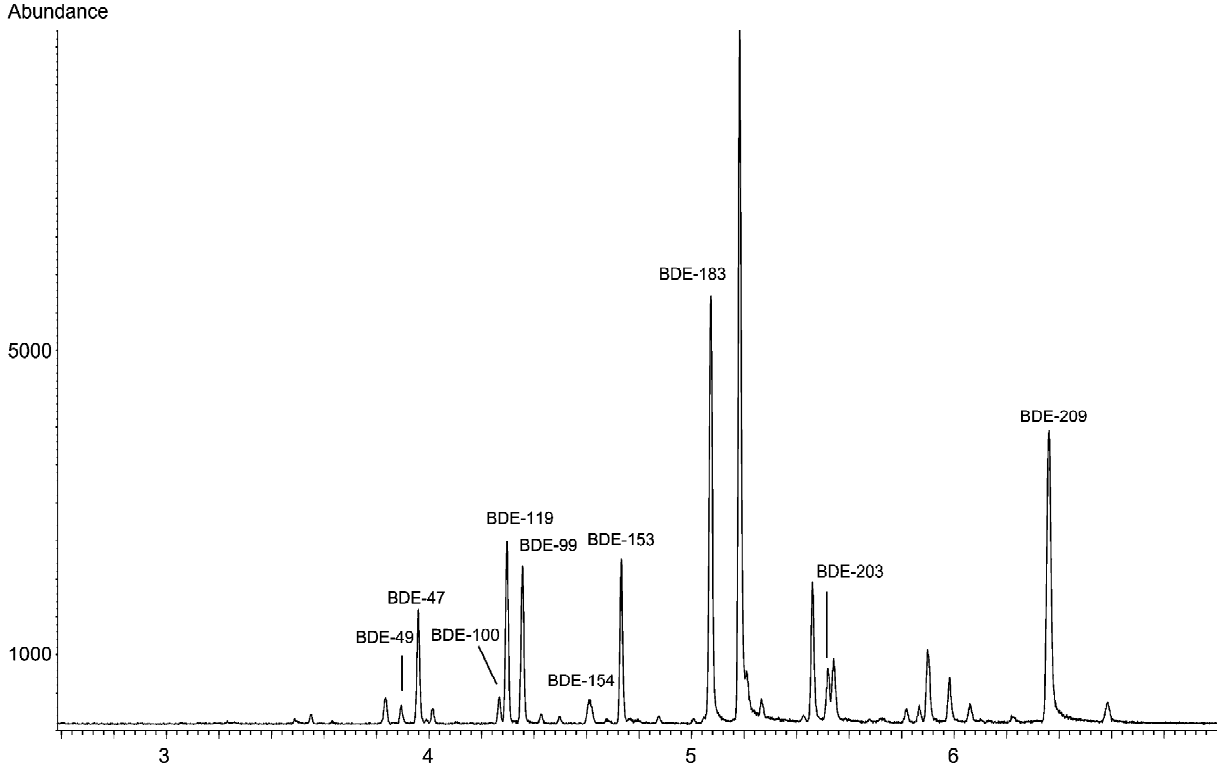

Fig. 6. LVI-PTV-fast-GC–MS chromatogram of the particulate fraction of an air sample from an electronics dismantling plant.

3.6. Application of LVI-PTV-fast-GC–MS

After optimization of the LVI-fast-GC, the optimum conditions were used for setting up an LVI-fast-GC–MS system. The last eluting component, BDE-209, had a retention time of 6.4 min and the total cycle time for the analysis was 9 min. Limits of detection were between 0.04 pg, for BDE-100, and 0.87 pg, for BDE-209. When injecting 50 μl this corresponds to sample solution concentrations of 0.8 and 17.4 fg/μl, respectively. Concentration-based LOD would of course be lower for larger injection volumes.

The average RSD for the relative areas obtained from the standard mixture, i.e., the relative response factors, was 2.8% ($n=5$) when using BDE-119 as internal surrogate standard. Though the determination of deca-BDE exhibits a quite low RSD (3.2%, $n=5$), a more high boiling alternative as the internal standard is desirable for the quantification of BDE-209 if further sampling and analyses are to be performed.

To evaluate if the LVI-fast-GC–MS systems separation capacity was sufficient for the determination of PBDEs in real samples, an air sample from an electronics dismantling plant was investigated. As can be seen in Fig. 6 the separation proved to be satisfactory. A rough quantification of the detected BDEs is shown in Table 4, where the concentrations are the average of three repeated injections of the sample. The precision in the determination is good with an RSD for BDE-209 of 5.7% ($n=3$) and an average RSD of 3,8% for all congeners except that of BDE-49 and BDE-100. Although these congeners are minor constituents, the cause of the large RSD has to be further investigated.

Table 4
Concentrations of detected PBDEs in an air sample from an electronics dismantling facility

	Conc. (ng/m^3)	SD	RSD
BDE-49	0.19	0.06	29.6
BDE-47	0.76	0.05	6.0
BDE-100	0.27	0.07	25.7
BDE-99	1.18	0.01	1.2
BDE-154	0.46	0.05	9.9
BDE-153	1.55	0.01	0.9
BDE-183	4.53	0.18	4.0
BDE-203	0.96	0.03	3.6
BDE-209	33.3	1.42	4.3

No PBDEs were detected in either of the PUFs, indicating that the analytes are only present in the particulate phase, as could be suspected considering their high molecular masses.

4. Conclusions

The injection and separation of 13 PBDE congeners have been optimized and evaluated to provide high yield and good precision for the analysis of PBDEs, particularly regarding the high boiling and thermally labile BDE-209.

The large injection volumes decrease the limits of detection, based on concentration, up to 125 times compared to a 1 μl injection, which is advantageous when samples with low concentration are to be analyzed. The response of the PBDE congeners is strongly dependent on the injection parameter settings, which therefore have to be optimized. A high solvent evaporation rate showed to be important to achieve maximum sensitivity. Also transfer times and temperatures have to be chosen carefully. Low temperatures decrease the transfer rate, whereas too high temperatures induce thermal degradation.

Though compromises between speed, resolution and sensitivity are inevitable, we have shown that a large volume PTV injection in combination with narrow bore columns is not only possible, but also beneficial in many aspects. Analysis times as short as 6.4 min with sufficient separation was achieved. This is a significant gain of time, but also a strong advantage when determining BDE-209, which is strongly degraded with the time it spends in the GC column.

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