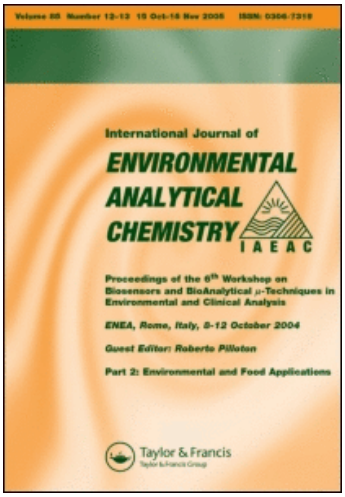

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Parametric evaluation for programmable temperature vaporisation large volume injection in gas chromatographic determination of polybrominated diphenyl ethers

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Parametric evaluation for programmable temperature vaporisation large volume injection in gas chromatographic determination of polybrominated diphenyl ethers

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This work is a thorough investigation on the major operating parameters of the programmable temperature vaporisation (PTV) inlet used for gas chromatographic injection, including injection mode and volume, inlet temperature, vent and purge flow rates. The results clearly demonstrate the advantage of large volume injection in enhancing the detection of polybrominated diphenyl ethers (PBDEs). Partial loss of injected PBDEs occurred during solvent venting and due to incomplete sample transfer. Such loss was minimised by lowering the initial inlet temperature and vent flow and elevating the final inlet temperature. The results show that 50 mL/min vent flow, as low as 0°C initial and higher than 300°C final inlet temperatures produced the relatively high responses. Two mass spectrometric parameters were also evaluated. Indoor dust, lake sediment and human placenta tissue samples were analysed to demonstrate reliability and sensitivity improvement of the PTV large volume injection.

Keywords: gas chromatography; PTV; large volume injection; polybrominated diphenyl ethers

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively as flame retardants in various industrial and consumer products. As a result, PBDEs have ubiquitously contaminated the environment [1–3]. More than often, the concentrations of PBDEs in biotic and abiotic matrices are at trace levels, i.e. less than parts-per-billion (ppb) or even parts-per-trillion (ppt). Therefore, sensitive instrumental analysis is essential for the reliable detection and quantification of PBDEs.

Analysis of PBDEs is commonly conducted using gas chromatograph (GC) coupled with mass spectrometer (MS) or electron capture detector (ECD). Traditional GC sample introduction techniques include cool on-column, hot inlet splitless and pulsed splitless, which usually allow an injection of only 1 or 2 μL of a solution; therefore, samples must be sufficiently concentrated in order for the trace level analytes to be detected. To lower the limits of the instrumental detectability, large volume injection techniques have been developed. Large volume splitless injection with concurrent solvent recondensation (CSR) allows up to 50 μL sample introduction with the control of sample evaporation in the

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injector and recondensation in the precolumn [4–7]. Cool on-column large volume injection uses solvent vapour exit (SVE) behind the precolumn to discharge the solvent vapour before sample transfer to the column. Up to 250 μL sample injection has been reported [8,9] and it is suitable for relatively clean samples with the advantage of minimising the degradation of thermally unstable compounds and the loss of volatiles [10]. The large volume programmable temperature vaporisation (PTV) technique allows as much as 500 μL of a liquid sample injection [11] and was designed to handle semi-volatile analytes in complex or dirty samples [12,13].

When PTV inlet is operated with solvent vent, a process in which the sample is introduced into the inlet at a temperature below the boiling point of the solvent, the majority of the solvent is stripped by and vented with a relatively high flow of carrier gas. Meanwhile, the much less volatile analytes are trapped on the wall or the packing material of the liner. This enables large volume injection without causing liquid invasion into the GC column. During a single GC run, multiple injections may be performed with time intervals in between to allow efficient solvent venting. After the completion of the injection, the vent is shut down and the inlet temperature increased rapidly, facilitating the evaporation and transfer of the analytes into the GC column [14].

In this study, we thoroughly evaluated the PTV operational parameters with the objective of lowering detection limits for PBDEs. The parameters investigated included injection mode, injection volume, initial and final inlet temperatures, and vent and purge flow rates. A few operational parameters of the mass spectrometric detector were also evaluated. Thirteen PBDE congeners, which are frequently detected in environmental and human samples, were selected, and their relative responses (peak areas) were compared under different parametric settings. The instrumental detection limits (IDLs) were given under the optimised conditions. A standard reference material of indoor dust was analysed to compare our results using PTV injection with the certified values obtained by other injection methods, and the enhancement of analytical sensitivity was demonstrated by the analyses of lake sediment and human placenta tissue samples. Although this study is focused on PBDEs, the results may be applicable to other semi-volatile compounds.

2. Experimental

2.1 *Materials*

PBDE standards (BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 206, 207 and 209) and $^{13}C_{12}$-labelled BDE118 (BDE118L) and $^{13}C_{12}$-labelled BDE209 (BDE209L) were purchased from Cambridge Isotope Laboratories (Andover, MA) and AccuStandard (New Haven, CT). Bio-beads S-X3 (200–400 mesh) were purchased from Bio-Rad Laboratory (Richmond, CA). Bondesil (C18, 4 μm) was purchased from Varian Inc. (Palo Alto, CA). Solvents, anhydrous sodium sulfate and silica gel (100–200 mesh, Davisil Grade 644) were purchased from Fisher Scientific. Hexane, dichloromethane and acetone were GC grade. The indoor dust standard reference material (SRM 2585) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD). A surface sediment sample was collected from Maple Lake in Cook County, Illinois. A fresh full-term human placenta was collected from the University of Illinois at Chicago Medical Center with signed consent of a patient after she gave birth to a child.

2.2 *Sample treatment*

Duplicate indoor dust SRM and sediment samples were mixed with anhydrous sodium sulfate, transferred to Whatman cellulose thimbles, and spiked with a known amount of BDE118L and BDE209L. The spiked samples were Soxhlet-extracted for 20 hours with 150 mL of 1:1 (v/v) hexane-acetone mixture. Extraction of the placenta tissue was achieved by the matrix solid phase dispersion (MSPD) method [15]. The placenta was homogenised using a commercial blender and 20 g of the homogenate was freeze dried. The dried tissue was then combined with sorbent C18 in 1:4 sample-to-sorbent ratio and thoroughly ground in a glass mortar until a fine powder was obtained. Then the sample was packed into a glass column (30 cm × 2.6 cm ID) and extracted using 100 mL of hexane.

The sample extracts were concentrated on Kuderna-Danish (K-D) concentrators, solvent-exchanged to hexane, and reduced in volume to around 2 mL by N_2 blow. Then, the samples were cleaned up using the bio-beads packed gel permeation chromatographical (GPC) column (30 cm × 2.5 cm ID) and multi-layer acidic, basic and neutral silica gel chromatographic column (40 cm × 1.1 cm ID). The eluates were concentrated again on the K-D concentrators and then N_2 blown down to about 1 mL. The solutions were then transferred to volumetric flasks to make exact 2 mL for dust and sediment samples or 1 mL for placenta tissue samples. Before GC injection, octachlorobiphenyl PCB204 was added to the SRM sample as the injection standard to normalise the peak areas in the quantification of tri- through hepta-BDEs; and decabromobiphenyl (BB209) was used as the injection standard for octa- through deca-BDEs.

2.3 *PTV and GC/MS*

The PTV injection port used in this work is Model CIS 4 made by Gerstel (Germany). It was the inlet for an Agilent Model 6890 GC. The inlet used a single-baffled glass liner (71 mm × 2 mm ID) packed with about 10 mm deactivated glass wool. The following were the default settings except when a particular parameter was evaluated. Each sample in hexane was introduced into the PTV inlet operated in the solvent vent mode at the initial temperature of 40°C (holding for 1.5 min). Fast injection was performed for all the samples. A total of 60 μL was injected with three injections of 20 μL and 10 s intervals in between. The split vent was kept open until 1.4 min with the flow rate of 100 mL/min. After the injections were completed, the PTV inlet temperature was increased from 40 to 300°C at 600°C/min. The purge flow of 50 mL/min was applied from 2.75 min until 10 min, and then gas saver flow of 20 mL/min was used until the end of the run. Figure 1 illustrates the timelines of the inlet temperature programme and gas flows.

The GC had a DB-5MS (15 m × 0.25 mm ID, 0.25 μm film thickness; J&W Scientific) capillary column. Helium was the carrier gas at the constant flow of 1.5 mL/min from 1.4 min until the end of the run. The initial oven temperature was 90°C, which lasted for 3 min, then increased to 140°C at 10°C/min and further to 300°C at 5°C/min. The final temperature was kept for 15 min to complete the run. The detector was an Agilent Model 5973 electron capture negative ionisation mass spectrometer (ECNI-MS). The GC/MS interface temperature was 280°C. The mass flow controller of the reagent gas CH_4 was set to 40%. The temperatures of the ion source and quadrupole were 150 and 106°C, respectively. The MS was turned on after a solvent delay time of 10 min, and operated in selected ion monitoring (SIM) mode. The ions monitored were m/z 484.6 and 486.6 for

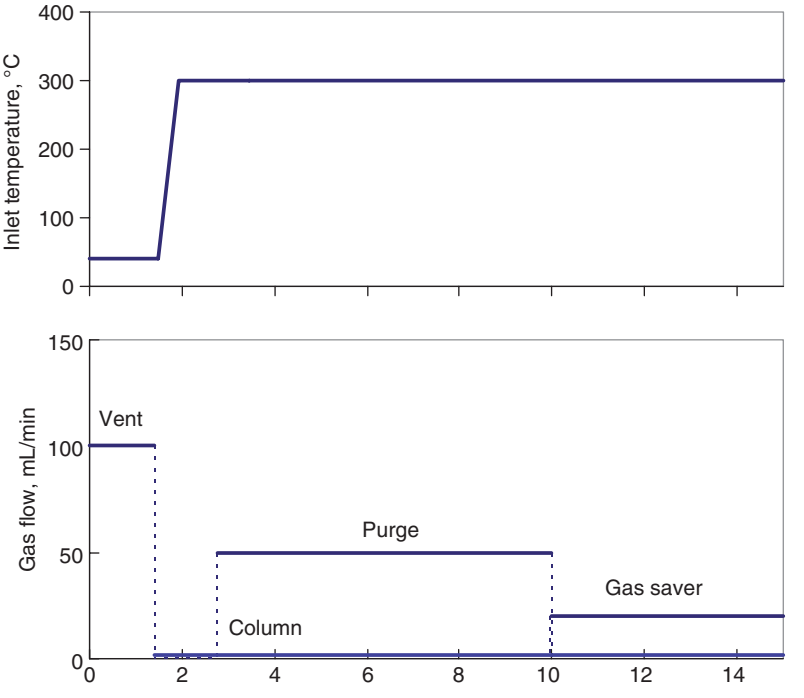

Figure 1. The timelines of PTV inlet temperature programme and gas flows. The carrier gas was at a constant flow of 1.5 mL/min from 1.4 min until the end of the run.

BDE209, 494.6 and 496.6 for BDE209L, and 79 and 81 for the other PBDEs and BB209. The m/z values 428, 430 and 432 were used for PCB204.

3. Results and discussion

3.1 *Injection mode*

Three injection modes, solvent vent, pulsed splitless and splitless, are available with the PTV inlet. Björklund *et al*. [16] recommended not using the PTV inlet in the splitless mode for PBDEs due to the low sensitivity, especially for heavier congeners; but a quantitative comparison with the solvent vent mode was not provided. Although the splitless injection could suffer from analyte discrimination in transferring to GC column as well as thermal degradation of heavier PBDE congeners [16,17], it avoids the venting loss that might occur when the PTV is operated in the solvent vent mode. To investigate the significance of the venting loss and the discrimination, 2 μL of PBDE standard solution was injected with each of the three injection modes and the results were compared in Figure 2.

For tri- through hepta-BDE congeners, the responses using pulsed splitless and splitless were similar. However, pulsed splitless yielded higher responses than splitless for heavy congeners from BDE196 to BDE209, indicating that the pressure pulse facilitated the transfer of these congeners and might have also helped to minimise thermal degradation [18]. Compared with the pulsed splitless, solvent vent yielded a response 17–39% lower for tri- through hept-BDE congeners, suggesting that they were partially lost during solvent

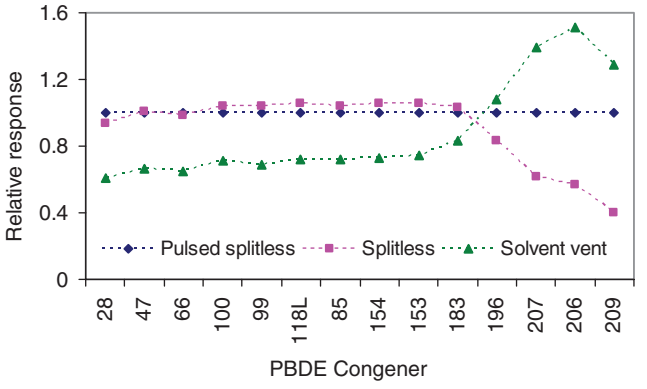

Figure 2. Comparison of different PTV injection modes. 2 μL of a PBDE standard solution was injected for all three modes. The responses using the pulsed splitless mode were set to 1. The inlet temperature was kept at 300°C for the splitless and pulsed splitless modes. The pressure of 30 psi was used for the pulsed splitless. The injected concentrations are 14.4 ng/mL for BDEs 28 to 183, 60 ng/mL for BDEs 196, 206 and 207, and 120 ng/mL for BDE209.

venting; and such loss was more significant than thermal degradation, if any. For heavy congeners BDE196 to BDE209, the responses were in the order of solvent vent > pulsed splitless > splitless injection modes. The lower responses using the splitless and the pulsed splitless modes may result from less efficient transfer to the GC column or degradation in the hot glass-wool-packed liner.

3.2 *Injection volume*

The dependence of response on injection volume was examined using the PTV in the solvent vent mode. Multiple injections of 20 μL were made in each run to reach different total injection volumes up to 200 μL. The vent flow and initial inlet temperatures were held until 2.5 and 2.6 min, respectively, so that up to 10 injections can be completed. Time intervals of 0, 5, 10 s between injections were compared, and no significant difference was found. The relative standard deviations of PBDE responses from five parallel 3 × 20 μL injections of the standard solutions were in the range of 1–11% with a mean of 4%.

As shown in Figure 3, the MS responses increased linearly with increasing total injected volumes in the range of 20 to 200 μL. The linearity for BDE209 ($R^2 = 0.997$) was stronger than for other congeners ($R^2 = 0.970$–0.985), and the relative responses of heavier congeners increased more dramatically than those of lighter ones (Figure 3). Norlock *et al.* [19] also observed a linear relationship between MS response and injection volume for polycyclic aromatic hydrocarbons using multiple injections. Tollbäck *et al.* [20] made single injections of 25, 50, 75, 100 and 125 μL and found a good linearity between PBDE peak area and injected volume.

These results clearly indicate that PTV inlet with solvent vent large volume injection is superior to splitless injection in enhancing analytical sensitivity. This is particularly beneficial to the analysis of heavier PBDE congeners, which are often difficult to detect and quantify in air and biological matrices due to their low concentrations. The substantial increase in sensitivity with large volume multiple injections would reduce the

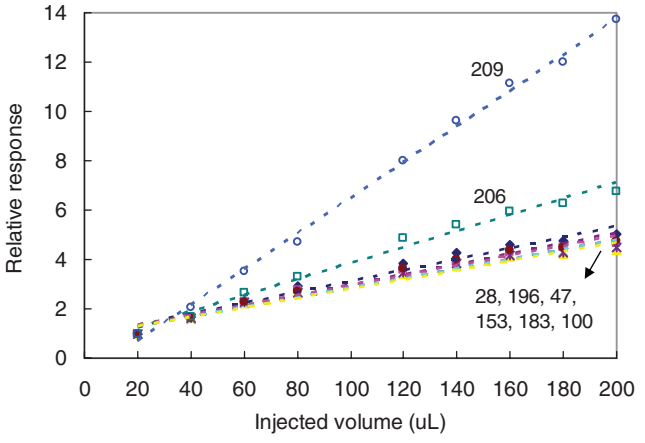

Figure 3. The relative responses of selected PBDE congeners as a function of total injected volume (20 μL × number of injections). One congener from each PBDE homolog with 3 to 10 bromines was used. The responses for 20 μL injection were set to 1. The injected concentrations are 3.6 ng/mL for BDEs 28 to 183, 14 ng/mL for BDEs 196 and 206, and 48 ng/mL for BDEs 209.

occurrence of non-detects. However, a large volume of injected solvent may overwhelm the inlet. Norlock *et al.* [19] found that their PTV inlet was flooded after 25 μL × 8 injections at 0°C inlet temperature, evidenced by the chromatogram with huge tailing solvent peak and distorted analyte peaks, due to the invasion of solvent liquid into the column. To avoid this, it is necessary to ensure the liner, with its baffled wall or inert packing, can hold the solvent from a single injection. For multiple injections, the injected liquid volume should also be balanced with the vapour elimination rate, which depends on the initial inlet temperature and pressure, injected volume, venting duration and vent flow rate.

3.3 *Initial inlet temperature*

Inlet temperature controls the vaporisation of the solvent and analytes and affects the transfer of the analytes into GC column. In this study, higher response was achieved at 0°C than at higher initial temperatures (Figure 4a), indicating increased loss of PBDEs at elevated inlet temperature. The temperature effect was more dramatic for light congeners. At 120°C, it appears that large fractions of the light PBDEs were vented before entering the GC column. For BDEs 196, 206, 207 and 209, the relative responses at 40, 80 and 120°C were similar, suggesting similar venting loss. Tollbäck *et al.* [20] used BDEs 7, 99 and 209 in the temperature range of 35 to 125°C with single large volume injection and found that increased initial inlet temperature can cause a high loss of PBDEs, in accordance with our observations.

In the solvent vent mode, the majority of the solvent is vented out and the residual solvent acts as a pseudo stationary phase to retain analytes in the liner. For this reason, the initial temperature 10°C lower than the solvent boiling point is recommended [14]. Although initial inlet temperature higher than the boiling point of hexane (69°C) was involved in this and other studies [20] for testing purposes, the use of temperatures higher than the solvent boiling point should be avoided because it can cause sudden evaporation

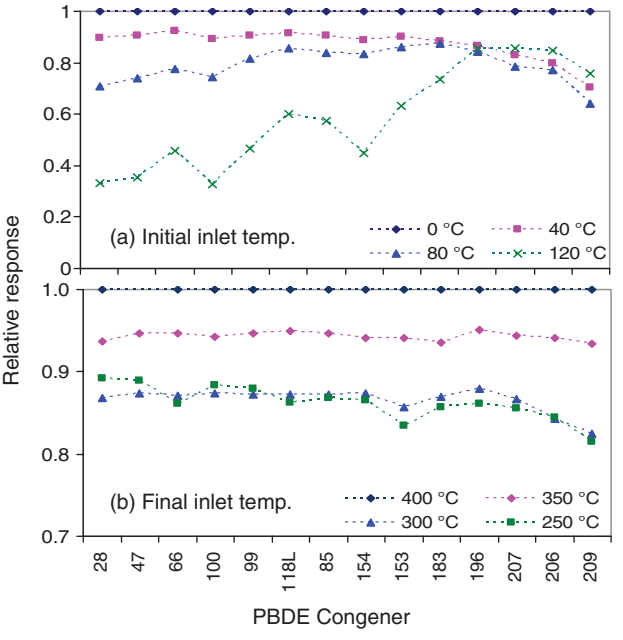

Figure 4. The relative responses of selected PBDE congeners at different initial (a) and final (b) inlet temperatures. (a) The responses at 0°C were set to 1. The injected concentrations are 7.2 ng/mL for BDEs 28 to 183, 40 ng/mL for BDEs 196, 206 and 207, and 60 ng/mL for BDE209; (b) The responses at 400°C were set to 1. The injected concentrations are 3.6 ng/mL for BDEs 28 to 183, 16 ng/mL for BDEs 196, 206 and 207, and 36 ng/mL for BDE209.

of the introduced solvent, and the solvent vapour could expand into other areas of the inlet, resulting in incomplete transfer and severe venting loss of analytes. The injection volume, temperature and pressure in the inlet interrelate with each other. Their applicable ranges can be estimated by the ideal gas law using the Agilent GC Pressure Flow Calculator software [21].

3.4 *Final inlet temperature*

Rapid increase from the initial to the final temperature of the PTV inlet facilitates the transfer of PBDEs to the GC column. Figure 4b shows that the higher the final inlet temperature resulted in higher response, especially for heavy congeners. BDE209 was reported to be thermally labile and began to degrade around 300°C [22]. However, the highest BDE209 response at 400°C observed in this study suggests that the enhancement in transfer efficiency is more significant than the loss due to degradation at elevated inlet temperature. The study by Björklund *et al.* [16] also recommended that the inlet temperature be kept as high as possible to improve the transfer of PBDEs, especially BDE209. As for the inlet temperature ramp rate, 600°C/min was used for all runs in this work. Tollbäck *et al.* [20] found no significant response change using ramp rate ranging from 200 to 700°C/min. Additional inlet temperature ramp may help thermally clean the inlet during purging. After purging, the inlet temperature can be lowered to relieve the heat stress on the inlet [14].

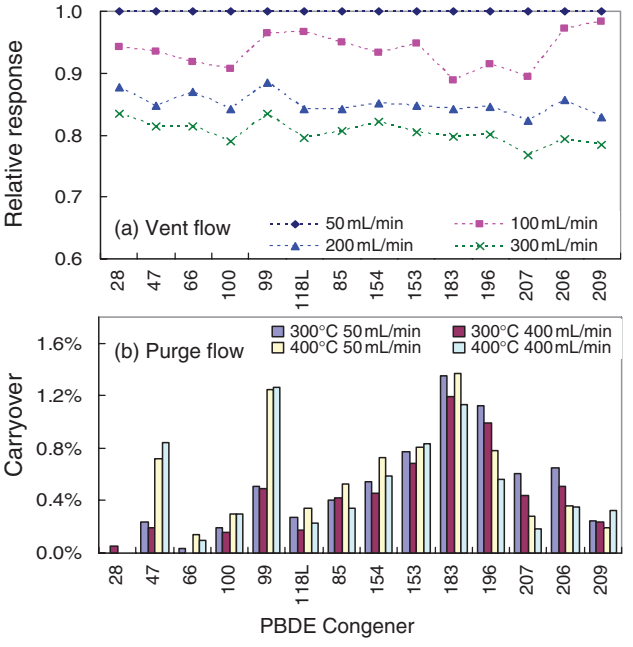

Figure 5. (a) The effect of vent flow rate on the responses of PBDEs. The responses at 50 mL/min were set to 1. The injected concentrations are 1.8 ng/mL for BDEs 28 to 183, 8.0 ng/mL for BDEs 196, 206 and 207, and 24 ng/mL for BDE209. (b) The percentages of PBDE carryover in the total injected mass after purging. Final inlet temperatures of 300 and 400°C and purge flows of 50 and 400 mL/min were used. The injected concentrations are 7.2 ng/mL for BDEs 28 to 183, 40 ng/mL for BDEs 196, 206 and 207, and 60 ng/mL for BDE209.

3.5 *Vent flow*

As mentioned above, the solvent in the liner acts as a stationary phase and retains analytes. Higher vent flow eliminates more solvent, resulting in higher loss of PBDEs. When the vent flow was increased from 50 to 300 mL/min, the PBDE responses decreased by 16–23% (Figure 5a). No chromatographic problem caused by the liquid invasion to the column was observed at all tested vent flow rates. The vent flow rate of 50 mL/min is considered a good choice with higher response and lower gas consumption. Staniewski and Rijks [23] developed a model to estimate the solvent elimination rate based on solvent properties and inlet and outlet conditions. The model suggests that the solvent elimination rate can be increased by increasing the vent flow, reducing the inlet pressure, and/or increasing the inlet temperature. Venting time was also examined in this study, and longer venting time yielded lower PBDE response.

3.6 *Purge flow*

To investigate the effectiveness of purge flow in eliminating PBDE residuals from the inlet, solvent hexane was injected after a run of a concentrated PBDE solution. Purge flow was set to 50 or 400 mL/min at the final inlet temperatures of 300 or 400°C (Figure 5b). The carryover was represented by the ratio of peak areas from the hexane chromatogram to those from PBDE solution chromatogram. The carryovers ranged from $<0.1\%$ to 1.4%;

and for most congeners, they did not differ significantly under the four different combinations of inlet temperatures and purge flows. Under all conditions, the carryover was more severe for BDE183 than for other congeners, which could be partially attributed to the debromination of heaver congeners in the hot inlet. For congeners BDEs 196 to 206, carryovers were higher at 300°C than at 400°C. The opposite was observed for lighter congeners, especially BDEs 47 and 99. We suspect that, at 400°C, partial thermal debromination of retained heavy congeners occurred in the inlet and contributed to the observed BDE47 and BDE99 carryovers.

Substances with high boiling point temperatures, such as lipids and polymers, should be eliminated from the samples during the laboratory pretreatment, but nonetheless may be present in samples for GC analysis. They tend to remain inside the liner or be retained at the front of the column after the sample transfer, causing response decrease due to degradation, analyte carryover, retention time shift and peak trailing. The liner should be replaced and the front of the column should be trimmed after the observation of such problems. Alternatively, these substances can be flushed out from the column and the inlet using the backflushing techniques developed by some GC manufacturers such as Agilent Technologies [24] and Thermo Electron Corporation [13].

3.7 *MS reagent gas flow*

In ECNI-MS, reagent gas is bombarded with high energy electrons from the filament to produce low energy thermal electrons, and then the thermal electrons interact with electrophilic molecules, such as PBDEs, to form negative molecular and fragmental ions for subsequent sorting by the quadrupole mass analyser [25,26]. In this study, methane was used as the reagent gas and mass flow rates of 20, 40 and 60% were compared. PBDE responses at 20% methane flow were only half of those at 40% (Figure 6a). At 60%, the responses were basically equal to those at 40% for tri- through hepta-BDEs, but lower for more brominated congeners.

3.8 *MS ion source temperature*

Stemmler and Hites [27] found that high ion source temperature generally enhances molecular fragmentation in ECNI-MS. Increasing ion source temperature could promote C-Br and C-O bond cleavages and thus enhance the abundance of bromide or pentabromophenoxide ions used for quantification. As shown in Figure 6b, PBDE responses increased with increasing ion source temperature, with the effect being more significant for heavy congeners. BDE209 response dropped most dramatically by almost 40%, when the ion source temperature was decreased from 250 to 150°C. The native BDE209 (m/z 484.6 and 486.6) and ^{13}C-labelled BDE209L (m/z 494.6 and 496.6) had essentially the same relative responses to the variations in ion source temperatures (Figure 6b) and methane flow rates (Figure 6a), implying they have the same level of molecular fragmentation caused by electron capture triggered ionisation.

3.9 *Sample analyses*

The total ion chromatograms (TICs) of SRM, sediment and human placenta samples are presented in Figure 7. The retention times were within ± 0.05 min of those of the standards

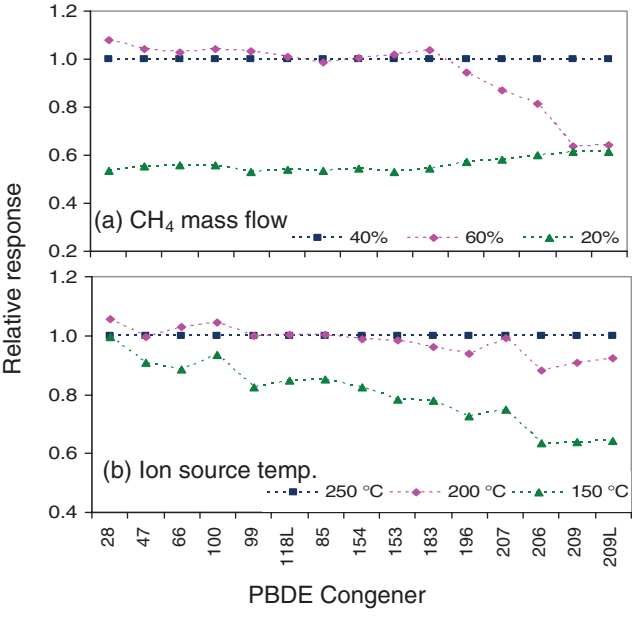

Figure 6. The relative responses of selected PBDE congeners using different methane mass flow rates (a) and ion source temperatures (b). (a) The responses at mass flow rate of 40% were set to 1. The injected concentrations are 2.7 ng/mL for BDEs 28 to 183, 12 ng/mL for BDEs 196, 206 and 207, and 30 ng/mL for BDEs 209 and 209L; (b) The relative responses of selected PBDE congeners at different ion source temperatures. The responses at 250°C were set to 1. The injected concentrations are 0.72 ng/mL for BDEs 28 to 183, 6.0 ng/mL for BDEs 196, 206 and 207, and 12 ng/mL for BDEs 209 and 209 L.

despite different matrices. The instrumental detection limits (IDLs) are presented in Table 1. With the 120 μL injection, as low as 6 – 12 pg/mL of BDEs 28 – 183 and 180 pg/mL of BDE209 can be detected.

Certified concentration values of PBDEs in indoor dust SRM 2585 were obtained using the on-column and splitless injection techniques [28]. Our analysis using PTV injection generated the results within 78% to 101% (average 90%) of the certified values. The relative standard deviations from duplicate measurements (including both sample treatment and GC/MS analysis) varied from 0.2% to 13%, with a mean of 3.1%, among thirteen individual PBDEs. These results demonstrate that PTV large volume injection technique is valid and reliable for PBDE determination.

For the sediment and placenta tissue samples, injections of 2 μL in splitless and 60 and 120 μL in solvent vent were performed under similar GC/MS operational conditions. The splitless injection did not generate clear PBDE peaks, indicating that PTV inlet is not a good choice for isothermal splitless injection. This finding is in accordance with the recommendation by Björklund *et al.* of not using the PTV inlet as a splitless injector in constant temperature mode [16]. In contrast, the large volume injections in the solvent vent mode produced not only quantifiable responses for the eight primary congeners (BDEs 28, 47, 99, 100, 153, 154, 183 and 209) [29], but some unambiguous peaks of octa and nona-BDEs, which were frequently reported as under detection limits for human samples with splitless injection.

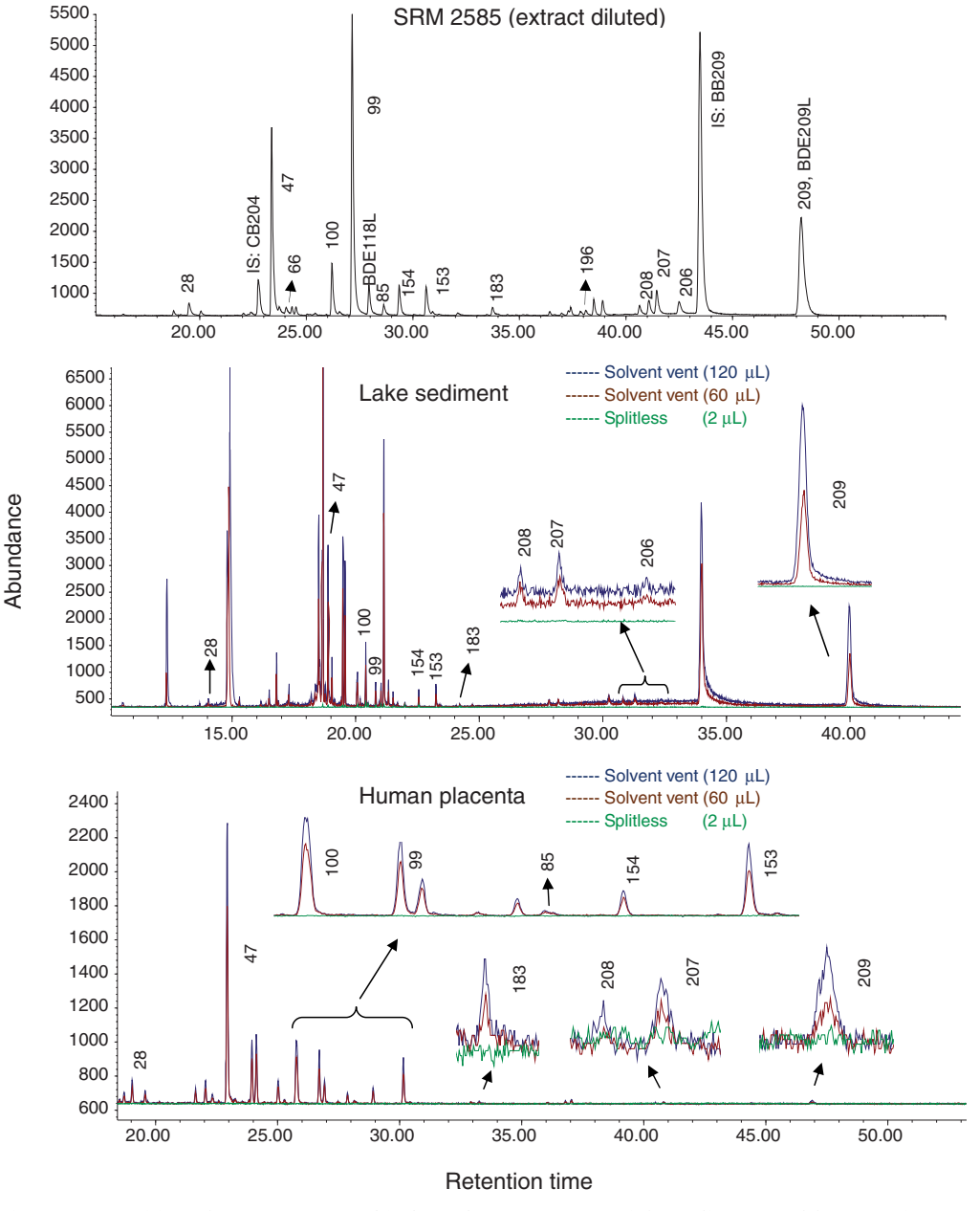

Figure 7. Total ion chromatograms of indoor dust SRM 2585, lake sediment and human placenta samples.

4. Conclusions

The results of this work demonstrate that GC/MS analysis of PBDEs using PTV injection is sensitive, reproducible and reliable. The increased volume with multiple injections increased the responses dramatically for PBDE congeners, especially for heavy congeners,

Table 1. Instrumental detection limits of PBDEs.

	Instrumental detection limit*	
Congener	Concentration ng/mL	Mass pg
BDE28	0.006	0.72
BDE47	0.006	0.72
BDE66	0.012	1.4
BDE85	0.012	1.4
BDE99	0.009	1.1
BDE100	0.006	0.72
BDE153	0.012	1.4
BDE154	0.006	0.72
BDE183	0.012	1.4
BDE196	0.03	3.6
BDE206	0.12	14
BDE207	0.04	5
BDE209	0.18	22

Note: *Concentration or mass required to produce a signal three times greater than the noise level. Based on 120 μL injection with optimised parameters using GC/ECNI-MS.

compared with other injection methods. However, our results showed that significant loss of injected PBDEs could occur during the solvent venting. To reduce such loss, the initial temperature of the PTV inlet should be maintained at least 10°C below the solvent boiling point. Lowering the vent flow rate also helps minimise the loss of PBDEs and yield higher responses, as long as efficient solvent elimination is maintained. High final inlet temperature was found to improve the efficiency of sample transfer into GC column and thus increase analytical sensitivity. Furthermore, high ion source temperature enhances the molecular fragmentation in ECNI-MS, thus increasing the PBDE response substantially when bromide or pentabromophenoxide (for BDE209) ions are used for quantification. Methane flow of 40% is a good choice for all PBDEs, particularly the heavy congeners. In addition, we demonstrated the reliability of the PTV injection by comparing our results with the certified values obtained using other injection techniques for PBDEs in an indoor dust SRM sample. Finally, we illustrated the advantage of large volume injection for the lake sediment and human placenta tissue samples with extremely low level of PBDEs, some of which were not detectable when the traditional splitless injection was used.

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