Fast analysis of decabrominated diphenyl ether using low-pressure gas chromatography-electron capture negative ionization-mass spectrometry

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Submitted to: Journal of Chromatography A

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Abstract

This paper reports the applicability of low-pressure gas chromatography-mass spectrometry operated in electron-capture negative ionization mode (LP-GC–ECNI-MS) for the analysis of decabrominated diphenyl ether (BDE 209). Particular attention were paid to find optimal injector and oven conditions for minimal thermal degradation of BDE 209. The analytical characteristics of the LP-GC–MS method were compared for a LP-GC setup (10 m x 0.53 mm internal diameter) with different film thickness (FT- 0.15 µm vs. 0.25 µm) and for a conventional GC setup (15 m x 0.25 mm x 0.10 µm FT). Short residence times (6.5 min and 9.8 min) of BDE 209 were found for the LP-GC systems with 0.15 and 0.25 µm FT, respectively, indicating that a lower FT is preferred for a shorter residence time. This also results in a lower elution temperature than the degradation limit of 300 °C. Additionally, baseline separation of 22 lower brominated BDE congeners (major components of PBDE technical mixtures) was possible in less than 12 min using the LP-GC–ECNI-MS system with 0.15 µm FT. The optimized method was applied for the determination of PBDEs in Belgian indoor dust samples. The obtained concentrations of BDE 209 (range 8 – 292 ng/g dry weight) were in the same range or lower than concentrations from other European countries.

Keywords: low-pressure gas chromatography, polybrominated diphenyl ethers, BDE 209, optimization, dust

1. Introduction

In the last years, the occurrence of brominated flame retardants (BFRs), and in particular of polybrominated diphenyl ethers (PBDEs), in the environment has raised growing concern and has become subject of intense research (Law et al., 2006). While analytical methods are readily available for quantifying tri- through octa-brominated BDE congeners found in the Penta-BDE and Octa-BDE technical mixtures, the analysis of higher brominated compounds, in particular of decabrominated diphenyl ether (BDE 209), has proven to be difficult. This has been recently highlighted by de Boer and Wells (2006), which have reviewed the results of several interlaboratory exercises for BFRs conducted in the last years.

Conventional chromatographic techniques for the determination of halogenated contaminants with very similar physical-chemical properties, such as polychlorinated biphenyls (PCBs), are not satisfactory for determination of PBDEs, especially for higher

brominated congeners [Bjorklund et al. 2004]. High temperatures are needed for the GC injection and column systems, while some higher PBDE congeners are thermally-labile compounds, particularly BDE 209, which starts to degrade at temperatures above 300 °C [WHO/IPCS, 1994]. Therefore, there is a need for techniques which can minimize thermal degradation of thermally-labile compounds, improving in this way the accuracy and precision of the measurements. Such technique is low-pressure gas chromatography (LP-GC) which may be used as an alternative to conventional GC for the analysis of BDE 209.

Already in 1962, Giddings [Giddings, 1962] has shown that the application of a vacuum at the column outlet would lead to reduced analysis time in GC. He also proposed another approach based on GC at sub-atmospheric pressure or low pressure. For many years, this alternative was not practical due to the lack of adequate instrumentation. However, this is now possible by connecting a wide bore capillary column (e.g. 0.53 mm internal diameter (ID)) to a narrow and short restriction capillary (e.g. 0.1 mm ID) that is positioned at the injector [Mastovska, 2001; de Zeeuw et al., 2000; van Deursen et al., 2000]. On the other hand, the use of MS detectors, which also require low pressure for analysis, can provide the vacuum for LP-GC, avoiding additional instrumentation.

There are several advantages of LP-GC–MS, such as speed of analysis, increased sample capacity and narrower peaks, thus higher sensitivity, compared to conventional GC methods. Moreover, it may provide an easier way of analyzing thermally-labile compounds, while lower column temperatures and higher flow rates may be used, reducing thus the oven cool-down time and reducing interactions with active sites in the column and consequently reducing degradation [Amirav et al., 1998; de Zeeuw et al., 2000].

Therefore, in the present study, we have systematically investigated chromatographic parameters for the fast analysis of BDE 209 using LP-GC-MS. Additionally, the method performance to analyze lower PBDEs was also assessed. The analytical characteristics of the LP-GC-MS method were compared for columns with different film thickness (FT- 0.15 µm vs. 0.25 µm) and for a conventional column. The optimized LP-GC-MS method was applied for the determination of BDE 209 in indoor dust samples.

2. Experimental

2.1 Chemicals and materials

All solvents used for the analysis (acetone, dichloromethane, *iso*-octane, *n*-hexane, toluene) were of SupraSolv grade (Merck, Darmstadt, Germany). Individual reference standards of PBDEs were purchased from Wellington Laboratories (Guelph, ON, Canada).

The IUPAC numbering system for the PCB congeners [Ballschmiter and Zell, 1980] is here applied also for PBDEs. A PBDE standard mixture was prepared by diluting in *iso*-octane the following BDE congeners 28, 47, 66, 100, 99, 154, 153, 183. ^{13}C-labeled BDE 209 (99 % purity) was used as internal standard together with BDE 77 and 128. Solutions containing 1.25 ng/µL of each BDE 209 and ^{13}C-labeled BDE 209 were used during the LP-GC optimization and also for conventional GC experiments. The reference material SRM 2584 (Trace Elements in Indoor Dust) from National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, USA) for which indicative values of PBDEs were obtained by Stapleton et al. (2006a) has been used for the method validation.

Silica gel (0.063-0.200 mm, Merck) used for extraction was prewashed with *n*-hexane and used after heating overnight at 120 °C. The acidified silica was prepared as described by Covaci and Schepens (2001). Extraction thimbles (25 x 100 mm, Whatman® Schleicher & Schuell, England) were pre-extracted for 1 h with hexane/acetone (3/1; *v/v*) and dried at 100 °C for 1 h. Empty polypropylene columns for clean-up (25 mL) were from Alltech (Lokeren, Belgium).

2.2 Instrumentation

An accelerated soxhlet extractor B-811 (Büchi, Switzerland) was used for extraction of the analytes from standard reference material (SRM) and also from the indoor dust samples. The GC–MS experiments were performed using a Hewlett Packard 6890 GC (Palo Alto, USA) connected via direct interface with a HP 5973 mass spectrometer. The GC system was equipped with an electronic pressure control, a programmable-temperature vaporizer (PTV) and a HP 7673 autosampler. The mass spectrometer was operated in electron capture negative ionization (ECNI) in the selected ion-monitoring (SIM) mode at the *m/z* = 79 and 81 for all lower BDEs and at *m/z* = 484.7/486.7 and 494.7/496.7 for BDE 209 and ^{13}C-BDE 209, respectively. Dwell times were set at 40 msec. Methane was used as moderating gas, while the ion source, quadrupole and interface temperatures were set at 250, 150 and 300 °C, respectively.

LP-GC–ECNI-MS experiments were performed comparatively using a 10 m x 0.53 mm ID x 0.25 µm FT CP-SIL 8 CB capillary column (Varian, Middelburg, The Netherlands) and a 10 m x 0.53 mm ID x 0.15 µm FT AT-5 (Alltech, Lokeren, Belgium), respectively. In each case, the analytical column was connected to a 1m x 0.1mm ID x 0.1 µm FT narrow bore column (Varian) at the inlet end. The conventional GC experiments were performed using a 15 m x 0.25 mm x 0.10 µm DB-5 capillary column (J&W Scientific, Palo Alto, Ca USA). In

all cases, the stationary phase of analytical columns used was 5%-phenyl, 95%-dimethylpolysiloxane.

2.3. Sampling and sample preparation

Indoor dust samples (n = 8), taken in Antwerp (Belgium) in 2004, were collected with a vacuum cleaner, a new empty bag being used each time. Samples were sieved through a 1000 μm sieve and stored in polypropylene containers in dark at the room temperature until analysis. Additionally, two samples were collected also from Romania (n = 1) and Spain (n = 1) and treated in a similar way.

The method used for the sample extraction and clean-up has been previously described and validated [Covaci et al., 2005] and is briefly presented below. Weighted samples of around 250 mg of indoor dust were spiked with internal standards 50 ng BDE 77 and 128 and with 125 ng ^{13}C-BDE 209 and extracted for 2 hours by hot Soxhlet with 100 mL of hexane/acetone (3/1; *v/v*). The extract was concentrated and then cleaned-up on 8 g of acidified silica. After elution of the analytes with 15 mL of hexane and 10 mL of dichloromethane, the cleaned extract was concentrated using a rotavapor and further under nitrogen to approximately 250 μL. Injections of 1 μL final extract were performed using the optimized LP-GC–ECNI-MS method. Procedural blanks (no sample added) were processed in a similar way.

3. Results and discussion

3.1 Optimization of PTV injector parameters

Since some PBDE congeners, and in particular BDE 209, decompose at temperatures just above 300 °C, it is important to select appropriate injector and column conditions to minimize thermal degradation. According to Korytár et al. (2005), who used comprehensive two-dimensional GC, the principal degradation products of BDE 209 were the nona-BDE congeners, with the intensities of the decomposition curves decreasing in the order: BDE 207 > BDE 208 > BDE 206. In order to establish the chromatographic conditions in which the degradation of the BDE 209 was minimal, the area of BDE 209 and BDE 207 were measured together with ratio between these two areas. Furthermore, a mixture of BDE 209 and ^{13}C-labeled BDE 209 was used for all injections to assess whether there is a difference between the profiles of unlabeled and labeled BDE 209. A minimal difference between these would also prove the suitability of using ^{13}C-labeled BDE 209 as internal standard for the analysis of BDE 209.

PTV injection has become a popular choice, particularly for the analysis of PBDEs [de Boer et al., 2001; Covaci et al., 2003]. A PTV injector can be operated in hot splitless mode similar to a traditional splitless injector, but also in cold or hot pulsed splitless or even in solvent vent mode. Being more complicated than the conventional split/splitless injectors, the PTV injector must be optimized prior to use [Stapleton, 2006b]. If this injector is operated in hot splitless mode, a severe discrimination of the high molecular BDE congeners may be observed [Bjorklund et al. 2004].

Initial experiments with the PTV injector in solvent vent and cold pulsed splitless mode have shown that no significant difference in the area of BDE 209 could be obtained, while an double area of BDE 207, the main thermal degradation product of BDE 209, was noticed when cold pulsed splitless was applied (data not shown). Therefore, for further experiments, the injector was operated in solvent vent mode and each programmable parameter was changed in order to assess optimal conditions for which the degradation of BDE 209 is minimal, but also to achieve a higher sensitivity. Subsequently the following injector parameters were optimized: initial inlet temperature, time for purge flow to split vent (splitless time), vent flow, final injector temperature and vent time (Table 1).

Modifying the initial inlet temperature, a slight decrease of the BDE 209 area together with constant values for the BDE 207 peak areas were obtained. This shows that these parameter does not influence thermal degradation in the inlet, but only the sensitivity of the instrument to BDE 209. Thus, 90 °C was set as initial temperature for the following experiments.

When the splitless time was varied, the same profile was obtained for area ratios between BDE 209 and BDE 207 peaks and also for BDE 207 area for mass chromatograms for *m/z* = 484.7/486.7 (corresponding to unlabelled BDE 209) and also for *m/z* = 494.7/496.7 (for ^{13}C-BDE 209). The minimum value for BDE 207 area, corresponding to a minimal thermal degradation of BDE 209, was achieved for a splitless time of 1.25 min. A maximum value for the BDE 209/BDE 207 areas was found for the same splitless time. The influence of the splitless time and of the final injector temperature on the response of 1.25 ng of BDE 209 and ^{13}C-BDE 209 injected is shown in Figure 1a and 1b. A clear correspondence between the final injector temperature and area ratio BDE 209/BDE 207 was obtained by modifying this parameter and the maximum sensitivity for BDE 209 was achieved when injector temperature was set at 305 °C. No significant differences on the investigated areas were obtained when vent flow and also vent time were modified (data not shown).

3.2 Oven temperature program and column parameters

The following parameters were optimized: initial and final oven temperature, oven ramp, column flow and column thickness (Table 1).

In order to achieve a short retention time for BDE 209, a range between 90 and 180 °C was applied for the initial oven temperature. However, even for initial oven temperatures close to 100 °C, the necessary time to cool and keep the inlet at the optimized value of 90 °C was too high. Therefore, the total time needed for an injection cycle was considered to be unsatisfactory, because the gain in retention time was found to be smaller than the total run of an injection. As a consequence, the initial oven temperature was set to 90 °C. During optimization of the final oven temperature, due to the thermal degradation, a clear decrease of BDE 209 area, paralleled by a decrease of the peak width were observed with the increase of the final oven temperature (Figure 2a and 2b). A minimal value for BDE 207 area, indicating a minimal thermal degradation of BDE 209, was the main criteria for selecting 295 °C as the optimal final oven temperature.

Several column flows ranging from 1.0 to 2.0 mL/min, corresponding to respectively 13.4 and 25 psi column head pressure at 90°C for the narrow bore restriction, were investigated (Figure 3). Higher flow rates were not investigated because the increase in the gas flow would result in a higher gas pressure in the ionization chamber (leading to filament burning) and also in exceeding the limits of the vacuum pumps (maximum admissible pressure 2.5 x 10^{-4} torr) which would ultimately affect the detection performance [Mastovska, 2001]. All experiments were conducted in constant flow regime. Figure 3 shows the chromatograms obtained by injecting BDE 209 at five different column flows on each LP-GC setup. A reduction in the retention time of BDE 209, without increasing too much the carrier gas flow, was the main purpose of this step. Thus, for further experiments, a constant flow of 1.5 mL/min helium corresponding to a column head pressure of 19.75 psi at 90 °C was used.

When the oven rate was optimized, two different end-points were targeted: 1) to find the maximum oven rate which can give the shortest retention time of BDE 209 without a loss in sensitivity when only BDE 209 has to be analysed; 2) to find the oven rate which can give a complete separation of the lower PBDE congeners.

If only BDE 209 has to be investigated, then a faster program can be used by combining an oven ramp of 60 °C/min with a constant column flow of 2.0 mL/min (Figure 4). Short residence times (6.5 min and 9.8 min) of BDE 209 were found for the 0.15 and 0.25 μm FT LP-GC systems, respectively, indicating that a lower FT is preferred for a shorter

residence time. The retention time of BDE 209 obtained using the conventional GC column (with 0.10 µm FT) in the same conditions as above was 11.6 min.

If the separation of lower PBDE congeners is also an important issue, the LP-GC methods can be tuned to allow elution times for BDE 209 of 10.8 min and 14.8 min using the 0.15 µm and 0.25 µm FT LP-GC setups, respectively (Figure 5). Even in these conditions, a good separation of major PBDEs was obtained. In contrast, the conventional GC setup allowed the separation of BDE congeners and the elution of BDE 209 in 21.3 min. Table 2 presents the retention times of selected PBDEs on both LP-GC columns and on the conventional GC column. The separation power of the investigated methods was also evaluated, expressed here as the number of theoretical plates (N) calculated using the formula: $N = 16*(t_r/W_h)^2$ in which t_r is the retention time of the analyte and W_h represent the width at the base of the peak (Table 2).

Because thermal degradation of BDE 209 is a function of time and temperature; not only a fast elution is important for an accurate determination, but also the elution temperature. Comparing the determination methods used by other laboratories and the results of the present study (Table 3), two different situations can be observed. In some studies, BDE 209 was analyzed with a low residence time in the column, but with high elution temperatures (> 300 °C), while in some other studies, low elution temperatures were combined with high retention times. The results of the present study show that the optimum conditions for a minimal thermal degradation of BDE 209 are simultaneously obtained through low retention times and low elution temperature of BDE 209 using LP-GC.

3.3 Analytical characteristics

Validation parameters, such as calibration linearity, accuracy, precision (repeatability and intermediate precision) and limit of detection (LOD) and quantification (LOQ) for all target PBDEs in each set of conditions were calculated in order to compare the results obtained using the LP-GC columns configuration with those obtained using the conventional GC capillary column.

The linearity of the calibration curves was examined by the correlation coefficient r^2. The area ratio between the analyte and IS was plotted against the corresponding absolute amount ratio. Nine levels were used in the calibration curves for BDE 209 and for the lower BDEs seven calibration levels were applied using linear fit (Table 4) and all correlation values were in the range 0.997 – 1.000. Since the error on the measurements for calibrations should not increase with the concentration, the homoscedasticity was checked by plotting the residual

error in function of concentration. Calibration curves were accepted if errors showed a random distribution or if the occurring errors were not significant in comparison to the obtained results.

Accuracy was estimated by comparing the difference between the indicative values available for SRM 2584 [Stapleton et al. 2006a] and measured values with their uncertainty (i.e. the combined uncertainty of indicative and measured value). If there is no significant difference between the measurement result and the indicative value, the absolute difference between mean measured value and indicative value for BDE 209, Δ_m, should be equal or smaller compared to the expanded uncertainty of the same difference, U_Δ [Lisinger, 2005]. To perform such estimation, a number of 10 replicates of SRM 2584 were analyzed and the expanded uncertainty corresponding to a confidence interval of 95% was calculated for each of the used methods. For both LP-GC systems used and also for the conventional GC, no significant difference between the measurement results of BDE 209 concentration (ng/g) and the indicative values was found. The values for Δ_m and U_Δ for selected PBDEs measured in SRM 2584 are presented in Table 5.

The repeatability of the measurements was tested for all systems using two concentrations of BDE 209 (1 ng/µL and 50 pg/µL). A number of 9 replicate injections from the same solution, together with two injections from 4 solutions containing the same concentration were tested. Intermediate precision was calculated on the nine replicates over a period of time of two weeks using the same concentration of the standard analyte as for repeatability. The repeatability (% RSD) for LP-GC methods was < 4.8 % at 1 ng/µL and < 7.8 % at 50 pg/µL. These values were lower compared to the repeatability obtained using conventional GC (< 7.4 % at 1 ng/µL and < 11.6 % at 50 pg/µL).

The instrumental LODs and LOQs of PBDE congeners were calculated for a signal/noise (S/N) ratio equal to 3 and 10, respectively, at the chosen quantification ion(s). The method LODs and LOQs were calculated as 3 x SD of the procedural blanks above the blank mean values and 10 x SD of the procedural blanks, respectively and taking into account the amount of sample taken into analysis (typically 0.25 g dust). Calculated values of instrumental and method LODs and LOQs are presented in Table 4. They are in the same range or lower than reported values (Stapleton 2006a).

3.4 Application to indoor dust samples

To assess the feasibility of LP-GC for the quantitative analysis, BDE 209 was measured in several indoor dust samples (Table 6). Procedural blank values were found to be

consistent (RSD < 50 %) and therefore the mean procedural blank value was used for subtraction. No significant difference could be found between concentrations of BDE 209 measured by using LP-GC or conventional GC. Although the main purpose of the present study was to investigate the optimal conditions for the analysis of BDE 209, the optimized parameters allowed also a good separation of lower PBDE congeners. In the studied indoor dust samples, the following levels (mean ± SD) were found: BDE 47 (24 ± 14 ng/g), BDE 99 (32 ± 10 ng/g), BDE 100 (4 ± 2 ng/g), BDE 153 (8 ± 9 ng/g), BDE 207 (42 ± 23 ng/g) and BDE 209 (127 ± 92 ng/g). The dominance of BDE 209 in the Belgian samples is in accordance with the exclusive use of Deca-BDE technical product in the European Union. The presence of BDE 47 and BDE 99 at lower levels corresponds with a cessation in the use of Penta-BDE technical mixture. The concentrations found in the Belgium indoor dust samples are comparable with the levels of sum PBDEs from Portugal (2005), Belgium (2005), Spain (2005 and 2006) and United Kingdom (2006) [Fabrellas et al., 2005; Regueiro et al., 2006; Harrad et al., 2006], but are lower than levels measured in dust samples from Germany (2003), Italy (2005) and Sweden (2007) [Knoth et al., 2003; Karlsson et al., 2007]. The levels of PBDEs found in dust sample from Spain are also comparable with previous published data (Fabrellas et al., 2005, Regueiro et al., 2006). The low concentrations of PBDEs found in the dust sample from Romania are also in agreement with low levels reported for these contaminants in serum [Dirtu et al., 2006] and environmental samples [Covaci et al., 2006].

4. Conclusions

The determination of BDE 209 has been successfully optimised for a LP-GC system. Very short residence times of BDE 209 in the studied chromatographic systems and a lower elution temperature than the degradation limit of 300 °C were obtained. The method shows sufficient sensitivity for BDE 209 and provides repeatable quantification for a wide concentration range. Additionally, a good separation of 22 major PBDE congeners was possible in less than 12 min using LP-GC-ECNI-MS system with an analytical column of 0.15 μm FT.

5. Acknowledgements

Dr. Adrian Covaci acknowledges the financial support granted by a postdoctoral fellowship by Flanders Scientific Funds for Research (FWO).

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Table 1. Chromatographic parameters studied for the optimization of BDE 209 analysis using LP-GC-ECNI-MS technique.

	Studied range	**Optimized value**
Inlet parameters		
Splitless time (min)	0.60 - 1.50	1.25
Vent flow (mL/min)	50 - 100	75
Final injector temperature (°C)	290 - 320	305
Vent time (min)	0.02 - 0.05	0.04
Initial inlet temperature (°C)	90 - 115	90
Oven and column parameters		
Column flow (mL/min)	1.0 - 2.0	1.5
Column thickness (μm)	0.15 and 0.25	0.15
Initial oven temperature (°C)	90 - 180	90
Rate (°C/min)	15 - 60	25
Final Oven temperature (°C)	290 - 310	295

Table 2. Retention times (min) and theoretical plate numbers of selected PBDEs for LP-GC methods (0.15 and 0.25 μm FT) and conventional GC.

PBDE congener	Retention time - t_r (min)			Theoretical plate number - N (x 10^3)		
	LPGC 0.15 μm	LPGC 0.25 μm	Conventional GC	LPGC 0.15 μm	LPGC 0.25 μm	Conventional GC
28	5.45	6.44	9.80	201	124	400
47	6.30	7.27	11.16	226	235	457
77	6.58	7.59	11.70	301	369	698
100	6.88	7.86	12.13	410	293	540
99	7.05	8.05	12.45	451	238	465
154	7.51	8.50	13.21	392	397	775
153	7.74	8.76	13.62	434	250	853
128	8.26	9.37	14.63	516	333	1132
183	8.36	9.41	14.70	430	524	899
197	9.05	10.23	16.04	433	207	643
209	10.87	14.82	21.28	97	24	61

Table 3. Comparison between elution conditions of BDE 209 reported in the literature and the results of the present study.

Column	Final Oven Temperature (°C)	Run Time (min)	Minutes at Temperature ≥295 °C	Elution Temperature (°C)	Reference
12m x 0.25mm, 0.1µm, DB-1MS	325	13	2.2	325	Björklund et al., 2003
15m x 0.25mm, 0.25µm, DB-5MS	325	29.5	9.35	325	Eljarrat et al., 2004
12.5m x 0.15mm, 0.1µm, BPX5	315	55	5.1	310	Peterman, 2006
15m x 0.25mm, 0.25µm, DB-5MS	280	55	-[a]	280	Stapleton et al., 2004, 2006c
15m x 0.25mm, 0.25µm, DB-5MS	315	39.4	7.6	315	Kierkegaard et al., 1999
12m x 0.18mm, 0.10µm, AT-5	300	25.8	-[b]	275	Covaci and Voorspoels, 2005
30m x 0.25mm, 0.25µm, DB-5MS	330	100	-[c]	285	Ahn et al., 2004
15m x 0.25mm, 0.1µm, DB-5MS	**295**	**25.2**	**13.1**	**295**	**present study**
LP-GC 0.25µm	**295**	**17.7**	**6.6**	**295**	**present study**
LP-GC 0.15µm	**295**	**12.0**	**2.6**	**295**	**present study**

[a] – 14.4 min at 280 °C; [b] – 5.1 min at 275 °C; [c] – 58.2 min at 285 °C

Table 4. Validation parameters (linearity: the slope (*a*) and correlation coefficient (r^2); instrumental and method LODs and LOQs) for selected PBDEs obtained using LP-GC and conventional GC.

Compound	Method	*a*	r^2	LOD		LOQ	
				Instrumental (pg injected)	Method (ng/g)	Instrumental (pg injected)	Method (ng/g)
BDE-28	**LPGC, 0.15 µm FT**	0.722	0.999	0.08	0.4	0.27	0.7
	LPGC, 0.25 µm FT	0.833	0.999	0.08	0.2	0.27	0.5
	Conventional GC	0.766	0.997	0.04	0.2	0.13	0.5
BDE-47	**LPGC, 0.15 µm FT**	0.721	1.000	0.05	0.4	0.17	0.8
	LPGC, 0.25 µm FT	0.784	0.997	0.02	0.4	0.07	0.8
	Conventional GC	0.695	0.999	0.04	0.5	0.15	1.1
BDE-99	**LPGC, 0.15 µm FT**	0.803	1.000	0.07	0.6	0.25	1.4
	LPGC, 0.25 µm FT	0.794	0.997	0.05	0.6	0.18	1.6
	Conventional GC	0.780	0.999	0.03	0.7	0.13	1.6
BDE-100	**LPGC, 0.15 µm FT**	0.897	1.000	0.07	0.2	0.22	0.3
	LPGC, 0.25 µm FT	0.927	0.997	0.11	0.1	0.36	0.3
	Conventional GC	0.864	1.000	0.03	0.1	0.11	0.2
BDE-153	**LPGC, 0.15 µm FT**	0.829	1.000	0.06	0.3	0.19	0.7
	LPGC, 0.25 µm FT	0.784	0.997	0.07	0.2	0.24	0.5
	Conventional GC	1.470	0.997	0.05	0.1	0.16	0.3
BDE-183	**LPGC, 0.15 µm FT**	0.791	1.000	0.05	0.3	0.17	0.7
	LPGC, 0.25 µm FT	0.698	1.000	0.30	1.8	0.98	5.4
	Conventional GC	1.360	0.998	0.04	0.1	0.13	0.3
BDE-209	**LPGC, 0.15 µm FT**	1.120	1.000	0.06	3.3	0.18	6.9
	LPGC, 0.25 µm FT	1.150	1.000	0.10	4.1	0.34	8.8
	Conventional GC	1.100	1.000	0.09	4.3	0.31	9.0

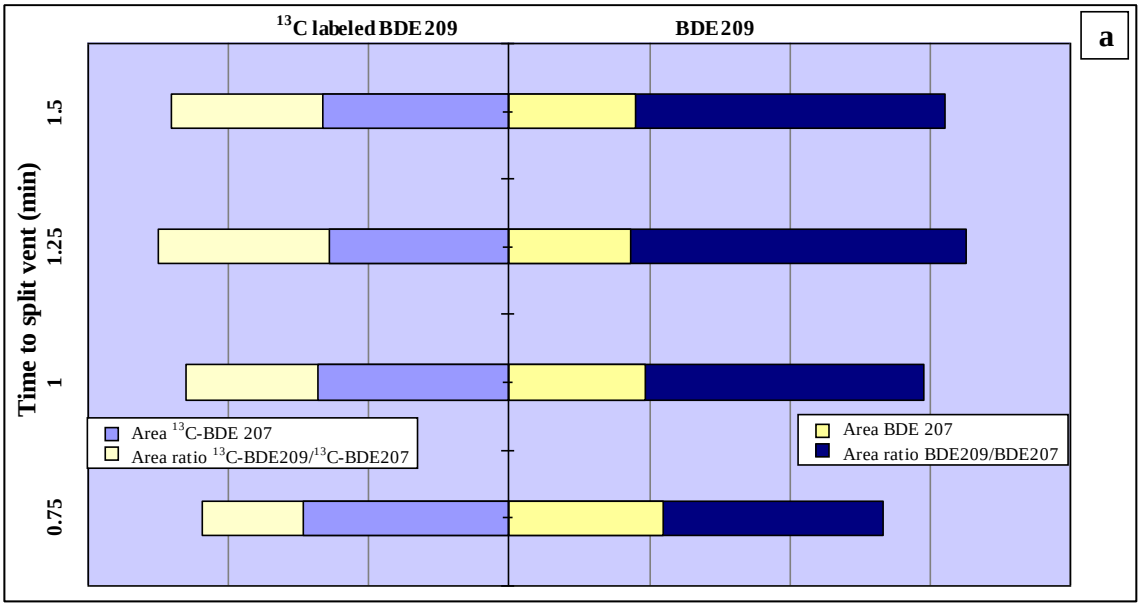
Table 5. Estimation of accuracy (Δ_m – absolute difference between mean measured value and indicative value available for SRM 2584; U_Δ – expanded uncertainty of difference between result and indicative value) – bold-italic values correspond to no significant difference between the measurement result and the indicative value.

Compound	Method	Measured mean (ng/g)	Measured SD (ng/g)	Indicative value (ng/g)	Indicative SD (ng/g)	Δ_m	U_Δ
	LPGC, 0.15 µm FT	18	0.9			***0.6***	***3.35***
BDE-28	**LPGC, 0.25 µm FT**	16	0.7	19	3.3	***2.4***	***3.3***
	Conventional GC	18	0.4			***1.2***	***3.3***
	LPGC, 0.15 µm FT	332	5.1			31.2	25.2
BDE-47	**LPGC, 0.25 µm FT**	282	6.2	363	25	80.5	25.3
	Conventional GC	324	5.4			39.1	25.2
	LPGC, 0.15 µm FT	558	9.6			113	43.5
BDE-99	**LPGC, 0.25 µm FT**	458	9.9	671	43	213	43.5
	Conventional GC	520	9.9			151	43.5
	LPGC, 0.15 µm FT	89	6.0			19.2	7.5
BDE-100	**LPGC, 0.25 µm FT**	79	1.8	108	6.3	29.4	6.4
	Conventional GC	90	1.6			17.8	6.4
	LPGC, 0.15 µm FT	80	2.9			***5.9***	***6.0***
BDE-153	**LPGC, 0.25 µm FT**	85	5.6	86	5.7	***1.0***	***6.8***
	Conventional GC	81	5.5			***5.2***	***6.8***
	LPGC, 0.15 µm FT	36.6	2.8			***4.7***	***4.7***
BDE-183	**LPGC, 0.25 µm FT**	19	3.1	32	4.2	13.1	4.7
	Conventional GC	33	3.1			***1.0***	***4.7***
	LPGC, 0.15 µm FT	2077	209			***252***	***252***
BDE-209	**LPGC, 0.25 µm FT**	2149	237	2330	210	***181***	***263***
	Conventional GC	2188	226			***142***	***259***

Table 6. BDE 209 concentrations (ng/g) in Belgian indoor dust samples compared between LP-GC systems and conventional GC.

Sample code	BDE 209 (ng/g)		
	LP-GC 0.15 µm FT	**LP-GC 0.25 µm FT**	**Conventional GC 0.10 µm FT**
BE-01	21	21	21
BE-02	8	8	8
BE-03	157	157	165
BE-04	151	148	156
BE-05	74	75	76
BE-06	136	135	141
BE-07	292	295	307
BE-08	176	180	184
RO-01	27	27	27
ESP-01	138	139	140

Figure 1. Influence of the split time (a) and final injector's temperature (b) on the response of the instrument (peak area of BDE 209 and/or area ratio of BDE 209 and BDE 207 corresponding peaks) of 1.25 ng injected BDE 209 and ^{13}C-labeled BDE 209.



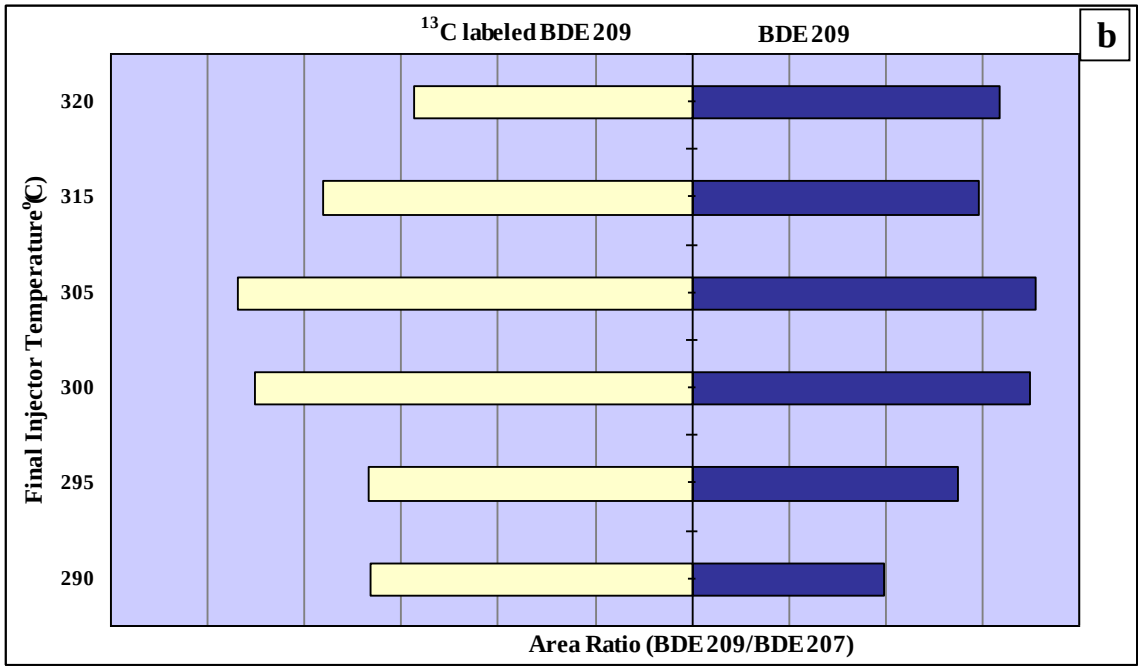
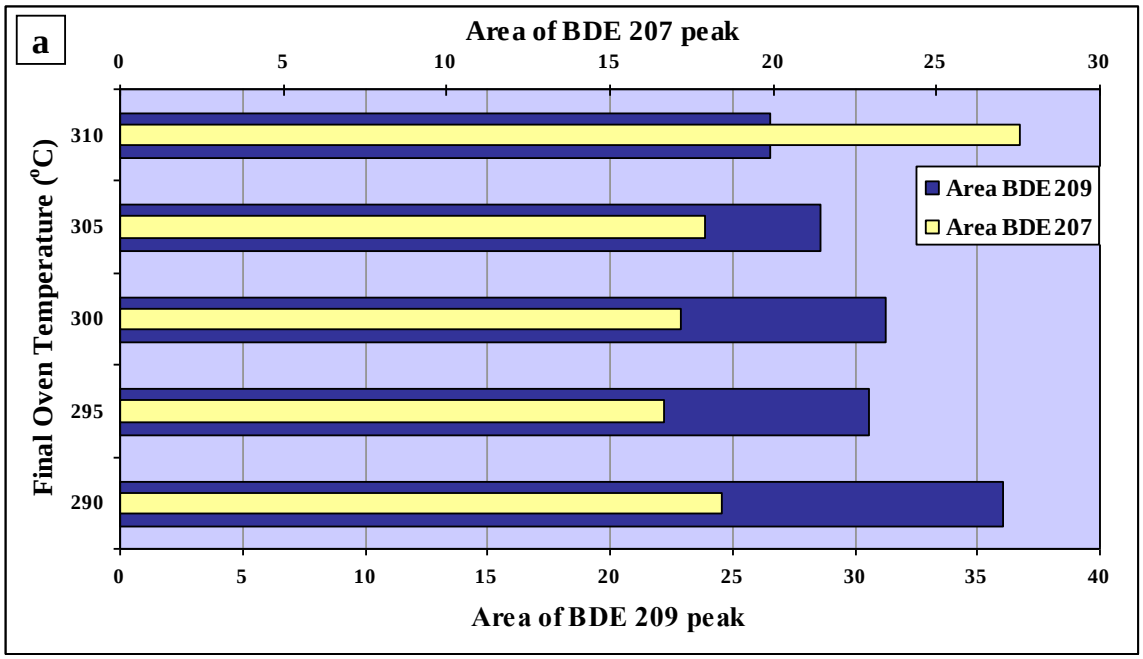


Figure 2. Influence of the final oven temperature on the response of the instrument regarding peak area of BDE 209, BDE 207 (a) and peak width (half height of the peak) and retention time of BDE 209 (b).



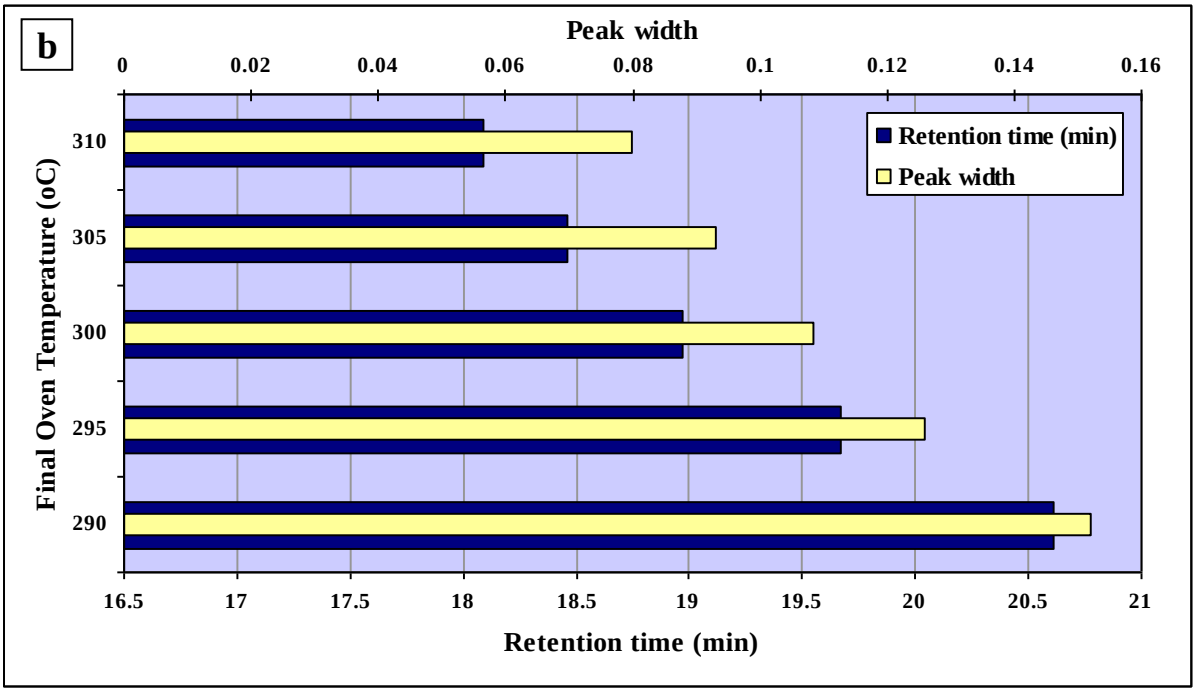


Figure 3. Chromatograms at different column flow (mL/min) for BDE 209 injected on each LP-GC-MS system (0.15 and 0.25 µm FT).

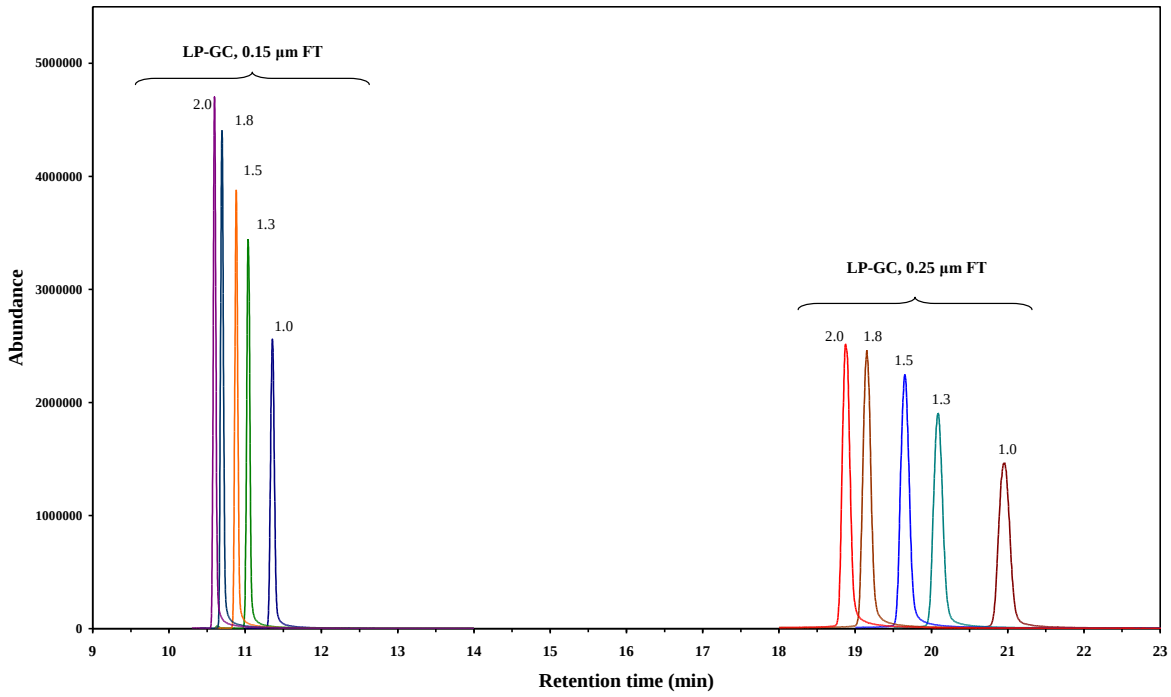


Figure 4. Chromatogram of BDE 209 (1.25 ng) injected in LP-GC systems (0.15 and 0.25 µm FT) and in conventional GC (0.10 µm FT).

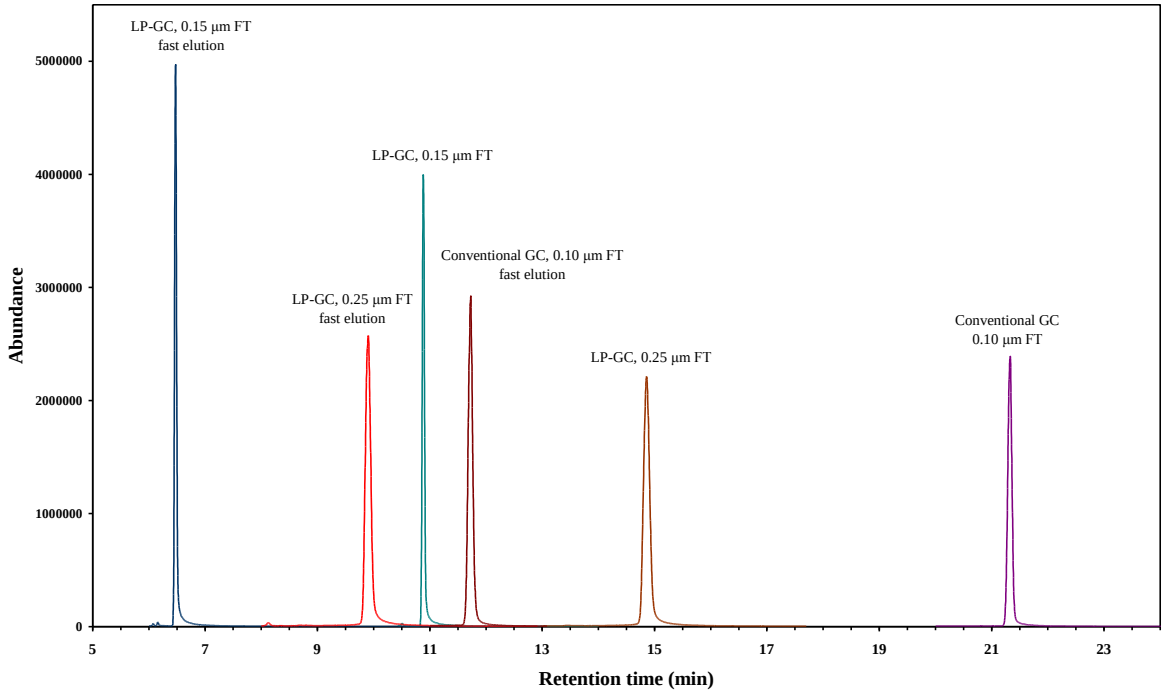


Figure 5. Mass-chromatogram of a PBDE mixture (main components of Penta-, Octa- and Deca-BDE technical mixtures) injected on LP-GC-ECNI-MS system (analytical column – 0.15 μm FT).