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Optimization of Large-Volume Injection for the Determination of Polychlorinated Biphenyls in Children's Fast-Food Menus by Low-Resolution Mass Spectrometry

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This study includes the determination of five indicator polychlorinated biphenyls (PCBs) (52, 101, 153, 138, and 180), six non-ortho PCBs (35, 80, 81, 77, 126, and 169), and two mono-ortho PCBs (28 and 118) in fast food for children. A freeze-dried sample of 10 g is extracted by using pressurized n-hexane in two 5 min cycles at 120 °C and 100 mbar. Fatty extracts were cleaned up by means of acetonitrile/n-hexane partitioning and gel-permeation chromatography. The fractionation of non-ortho, mono-ortho, and indicator PCBs was made on graphitized carbon solid-phase extraction cartridges by using n-hexane, n-hexane/toluene (99:1, v/v), and toluene as elution solvents. Gas chromatography coupled to tandem mass spectrometry and large-volume injections with a programmed-temperature vaporizer (PTV-LV) were used to increase sensitivity and selectivity of the PCB determination. The PTV-LV injection settings, that is, vaporizing temperature, vaporizing time, and purge flow, were optimized by using a central composite design. A 15−40 times increased sensitivity was reached as compared with that obtained with the conventional 1 μL splitless injection. The limits of detection achieved were between 0.3 and 1.2 pg/g, and repeatability data, as relative standard deviation varied, ranged from 2 to 9% for the 0.05 ng/mL PCB level.

KEYWORDS: polychlorinated biphenyls; children fast-food menu; PVT−CG−MS−MS; large-volume injection

INTRODUCTION

Polychlorinated biphenyls (PCBs) are widespread contaminants in the environment because of their persistence and resistance to chemical transformation. PCBs have become truly ubiquitous and have been detected even in the most remote species and places, for example, in deep-sea fish or in Antarctic air (*1, 2*). Because of their lipophilicity, PCBs are typical compounds accumulated in the food chain above all in fatty food, which is a significant route of dietary exposure. In fact, this is the most important source of non-occupational human exposure to PCBs.

PCBs consist of 209 different congeners, but the World Health Organization recommends the systematic consideration of 7 PCB congeners (28, 52, 101, 118, 138, 153, and 180) for monitoring purposes (*3*). However, the high toxicity of PCB mixtures is mainly due to only a few congeners, the non-ortho-substituted and the mono-ortho-substituted so-called coplanar PCBs (*4, 5*). These coplanar PCBs are more toxic because their molecular configuration is very close to that of the highly toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). For these aforementioned reasons, toxic equivalent factors (TEFs) for 2,3,7,8-TCDD have been estimated by the World Health Organization for the coplanar PCB congeners (*6, 7*). Maximum residue levels (MRL) for food, expressed as toxic equivalents (TEQ) and defined by the European Community, are 4 pg/g for fresh fish and 3 pg/g for milk and egg fat and range from 1 to 6 pg/g for meat fat and from 0.75 to 3 pg/g for oils and other fats (*8*). The contribution of PCB compounds to the total TEQ dietary intake has been estimated to be 30% (*9*).

PCBs have been found at ultra-trace levels (ng/g or less) in food samples; so, there is a need for specific and sensitive measurements of these compounds, mainly for the coplanar congeners which are present in concentrations 50–100 times lower than those of noncoplanar PCBs (*10, 11*).

Tandem mass spectrometry (MS−MS) using a low-resolution ion-trap mass spectrometer is a very selective technique which is widely employed for pollutant analysis in food. However, its sensitivity cannot be compared with that of high-resolution mass spectrometry (HRMS) instruments (*12, 13*).

There are two common ways for increasing sensitivity of chromatography determinations: one involves the increase of

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Table 1. Detector Parameters for GC−MS−MS Determinations of PCBs and 2,3,7,8-TCDD TEF for Each Compound[a]

compound	retention time (min)	precursor ion (*m*/*z*)	excitation energy (eV)	maximum excitation energy (Q value)	measurement range (*m*/*z*)	product ions (*m*/*z*)	TEF[c]
PCB 28	11.38	256	1.40	0.45	170–200	186	NC
PCB 52	12.57	292	1.35	0.45	205–235	220,222	NC
PCB 35	13.19	256	1.45	0.45	170–200	186	NC
PCB 80	14.85	292	1.60	0.45	205–235	220,222	NC
PCB 101	15.68	326	1.50	0.45	240–270	254,256	NC
PCB 81	16.63	292	1.60	0.45	205–235	220,222	0.0001
PCB 77	16.98	292	1.60	0.45	205–235	220,222	0.0001
PCB 118	17.94	326	1.50	0.45	240–270	254,256	0.0001
PCB 153	18.74	360	1.40	0.45	270–300	288,290	NC
PCB 138	19.68	360	1.40	0.45	270–300	288,290	NC
PCB 126	20.03	326	1.60	0.45	240–270	254,256	0.1
PCB 180	22.11	394	1.40	0.45	310–340	322,324	NC
PCB 169	22.53	360	1.70	0.45	270–300	288,290	0.01
PCB 209[b]	28.68	499	1.45	0.45	410–440	428,430	NC

[a] These determinations were carried out by using an isolation time of 12 ms, an excitation time of 15 ms, three microscans, and a maximum ion time of 25 ms, which provide a scan event time of 0.32 s. [b] Internal standard. [c] TEF values were obtained from World Health Organization and Official Journal of the European Community (*6, 7*). NC: no contribution from this PCB.

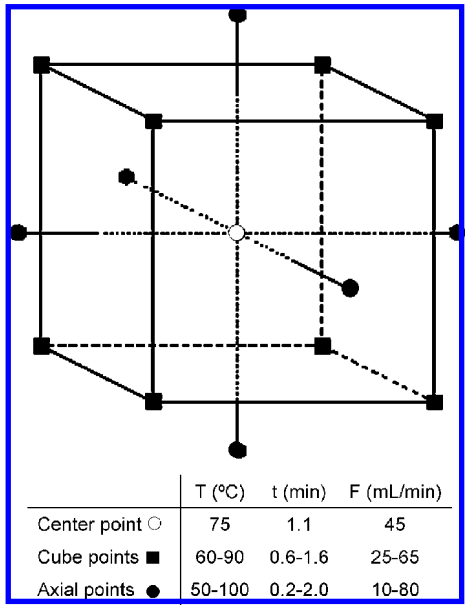

Figure 1. CCD model scheme and PTV variables employed for center, cube, and axial points.

the sample size used for analysis, and the other one consists in injecting large volumes of sample extracts into the gas chromatography (GC) column. Both ways require an extensive extract cleanup.

Large-volume injection with a programmed-temperature vaporizer (PTV-LV) combined with GC coupled to MS−MS (GC−MS−MS) has been previously employed for the determination of polycyclic hydrocarbons in airborne particles (*14*), polybrominated diphenyl ethers, polybrominated biphenyls, and polychlorinated naphthalenes in sediments (*15*), or dioxins in foods and feeds (*16*). This technique has the advantage of increasing sensitivity considerably compared to the use of conventional split/splitless (S/SL) injectors. So, PTV-LV coupled to GC−MS−MS appears to be a good alternative for HRMS equipments, offering a compromise between sensitivity, versatility, and cost.

Some authors have found considerable levels of PCBs in various fast foods, for example, burgers, pizzas, and fried chicken (*17–19*), and one of the reasons for this observation is that these meals present a high content of fat. The abuse in the intake of fast foods may pose a risk to human health, above all in the specific case of children's menus.

The main goal of this paper has been the optimization of the injection parameters of PTV-LV coupled to GC−MS−MS for monitoring PCBs in foods in order to reach enough sensitivity for the MRL defined by the legislation. The proposed methodol-

Table 2. Experimental Conditions of the Central Composite Design Used for Optimization of PTV-LV Injection

run order	*T* (°C)	*t* (min)	*F* (mL/min)
1	90	1.6	66
2	75	1.1	45
3	60	0.6	66
4	50	1.1	45
5	75	1.1	45
6	90	0.6	66
7	60	1.6	66
8	60	0.6	24
9	75	1.1	45
10	75	1.1	45
11	75	1.1	10
12	75	2	45
13	50	1.1	45
14	60	1.6	24
15	100	1.1	45
16	75	1.1	45
17	75	0.2	45
18	75	1.1	80
19	90	0.6	66
20	60	1.6	66
21	90	1.6	66
22	75	0.2	45
23	100	1.1	45
24	60	0.6	24
25	75	1.1	10
26	75	1.1	80
27	75	1.1	45
28	75	1.1	45
29	60	1.6	24
30	90	1.6	24
31	60	0.6	66
32	90	1.6	24
33	90	0.6	24
34	90	0.6	24
35	75	1.1	45
36	75	2	45
37	75	1.1	45
38	75	1.1	45
39	75	1.1	45
40	75	1.1	45

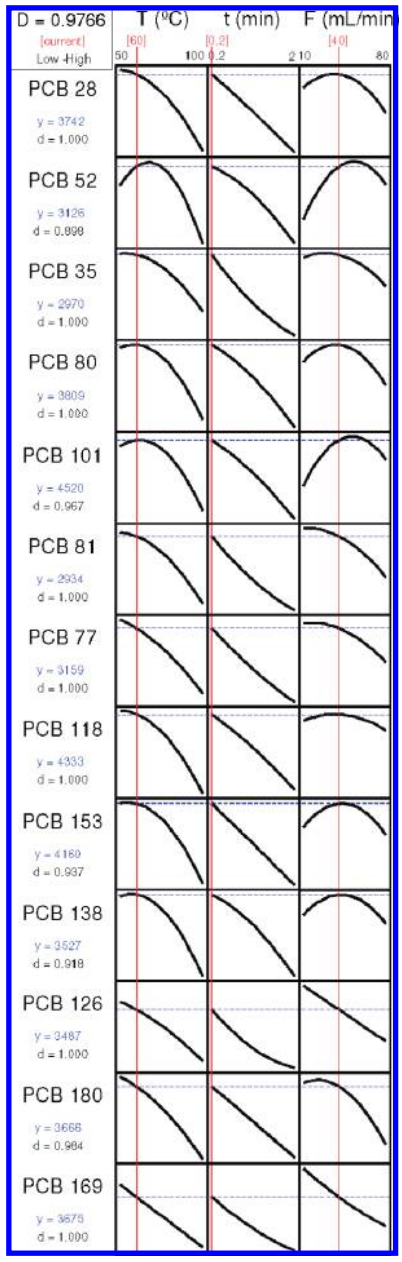

Figure 2. Variability of peak area vs vaporization temperature (*T*), time (*t*), and flow (*F*) for each PCB considered. *D* means composite desirability, and *d* means individual desirability.

ogy has been employed for the determination of PCBs, including coplanar congeners, in several fast-food menus for children.

MATERIALS AND METHODS

Apparatus and Reagents. A fast-pressurized solvent extractor (PSE) from Applied Separations (Allentown, PA) was used for PCB extraction of samples. The system allows a parallel extraction of up to six samples in extraction cells of 11, 22, or 33 mL. Otawa sand, also provided by Applied Separations, was employed to fill the reactor cells completely.

Cleanup of the extracts was carried out by using a Hewlett-Packard (Palo Alto, CA) HP1050 liquid chromatograph and two Envirogel gel-permeation chromatography (GPC) columns (19 mm × 150 mm and 19 mm × 300 mm), employing UV detection at 254 nm. Dichloromethane was employed as mobile phase.

Fractionation of PCBs was performed with Supelclean Envicarb (0.25 g graphitized carbon) solid-phase extraction (SPE) cartridges provided by Supelco (Bellefonte, PA).

A Thermo Finnigan (Waltham, MS) Trace GC , combined with a PolarisQ ion-trap mass spectrometer detector, was used for detection of PCB congeners. PTV-LV was carried out by using a Best PTV injector and an AS2000 autosampler, both from Thermo Finnigan. A low-bleed Hewlett-Packard HP-5MS capillary column (30 m × 0.32 mm, 0.25 μm) was used for compound separation, and high-purity helium (99.999%) was selected as carrier gas.

Individual solutions of 10 μg/mL for each PCB were supplied by Dr. Ehrenstorfer GmbH (Augbsburg, Germany). PCB 209 was employed as internal standard, and all the standard solutions were prepared in isooctane. Analytical grade acetone, dichloromethane, n-hexane, toluene, isooctane, and acetonitrile were purchased from Scharlau (Barcelona, Spain), and the anhydrous sodium sulfate was purchased from J. T. Baker (Deventer, Holland).

Different samples of children's menus were obtained from a fast-food restaurant in the city of Valencia (Spain), and they were composed of burger (meat, bread, and complements), french fries, ketchup, sweet drink, and dairy product.

General Procedure. *PSE Extraction.* A sample of 10 g was mixed with Ottawa sand and divided over two PSE cells of 33 mL internal volume each. Sets of six PSE cells were extracted simultaneously with n-hexane by employing two cycles of a program with a temperature of 150 °C, a pressure of 100 bar, a static time of 5 min, a solvent purge of 1 min, and a gas purge of 2 min (*20*). Extracts corresponding to each sample were collected in glass tubes, mixed, accurately weighted, and evaporated until dryness to determine the percentage of fat extracted.

Cleanup of Extracts. Fat was dissolved in 2 mL of n-hexane, and it was extracted three times with 10 mL of acetonitrile; PCBs were transferred to the acetonitrile phase. The whole acetonitrile extract was evaporated almost to dryness in a rotary evaporator and finally to dryness by employing a nitrogen flow. Then, the solid residue was dissolved in 2 mL of dichlorometane.

The reconstituted extract (2 mL) was injected in a GPC system by employing dichloromethane as mobile phase at a flow rate of 5 mL/min. The collected fraction for PCBs corresponded to the volume collected between 14 and 19 min. This fraction was completely separated from the fat fraction obtained between 8 and 12 min. The collected fractions were evaporated almost to dryness in a rotary evaporator and finally to dryness by employing a nitrogen flow. Then, the residue was dissolved in 0.5 mL of n-hexane.

Fractionation of Coplanar PCBs. Fractionation of PCBs was performed by SPE with graphitized carbon cartridges which were conditioned with 10 mL of toluene and 10 mL of n-hexane. Fat-free extract, which contained the noncoplanar PCBs eluted with 15 mL of n-hexane, was added to the cartridge. Then, a second fraction was eluted with 20 mL of n-hexane/toluene (99:1 v/v), eluting the mono-ortho PCBs. Finally, 20 mL of toluene was added, eluting the coplanar PCBs (*21*). All independent fractions were evaporated almost to dryness in a rotary evaporator and finally to dryness by employing a nitrogen flow. The residue was dissolved in 0.2 mL of 10 μg/L PCB-209 internal standard solution in isooctane.

S/SL−GC−MS−MS Determination of PCBs. A total of 1 μL of isooctane extract containing the internal standard was injected in splitless mode at 300 °C by employing helium as carrier with a constant flow of 1 mL/min. The oven temperature program was 110 °C held for 1 min, increased at a rate of 15 °C/min up to 150 °C and at a rate of 5 °C/min up to 280 °C, and finally held at 280 °C for 5 min. The transfer line and source temperatures were 280 and 250 °C, respectively.

Electron impact ionization was performed with an electron energy of 70 eV and a rate of 0.3 mL/min. Helium was employed as damping gas. Excitation energy and precursor and product ions for each compound in tandem mass determinations are shown in **Table 1**, together with the retention time corresponding to each compound studied. The methodology employed to select the tandem mass parameters for each compound was similar to that used before for other compounds (*22*). Ion-trap tests and mass calibration were performed weekly with perfluorotributylamine.

PTV-LV−GC−MS−MS Determination of PCBs. PTV injections can be divided into four steps: injection, solvent evaporation, analyte transfer, and cleaning. In the injection step, the split valve was open, and 80 μL samples were introduced into the liner at a temperature of 50 °C. During the evaporation step, the temperature was raised

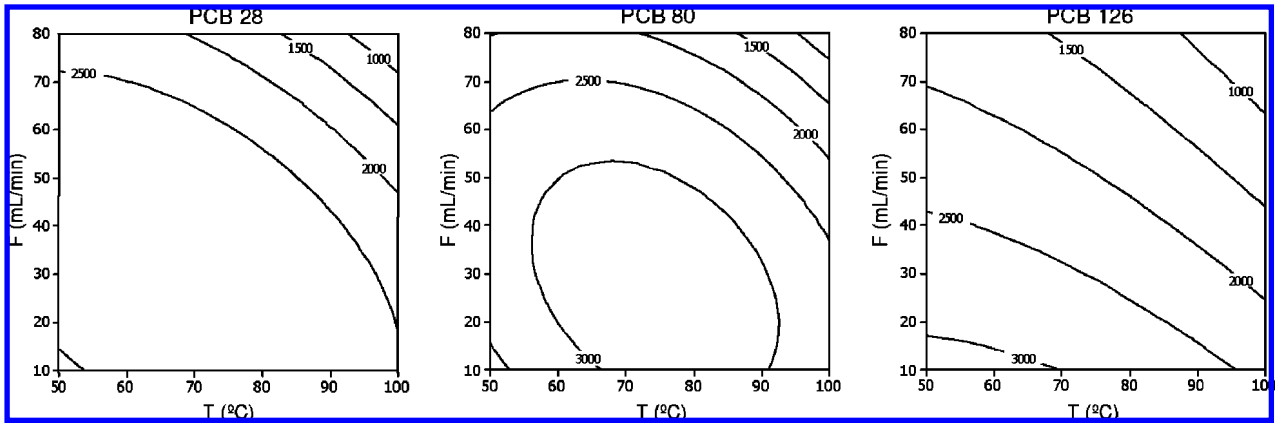

Figure 3. Contour surfaces for PCB 28, PCB 80, and PCB 126 at a fixed value of 0.2 min for the evaporation time.

Table 3. Analytical Features of GC−MS−MS Determination of PCBs by Using 1 μL (S/SL) and 80 μL (PTV) Injections

	S/SL (1 μL)[a]				PTV (80 μL)[b]			
compound	slope (mL/pg)	RSD (%)	LOD (pg/mL)	LOD (pg/g)[c]	slope (mL/pg)	RSD (%)	LOD (pg/mL)	LOD (pg/g)[c]
PCB 28	69	8	600	12	156	4	30	0.6
PCB 52	63	9	900	18	145	9	60	1.2
PCB 35	57	5	700	14	110	7	50	1.1
PCB 80	84	9	600	12	160	3	21	0.3
PCB 101	80	7	900	18	170	8	30	0.6
PCB 81	66	3	600	12	129	4	60	1.2
PCB 77	61	7	900	18	128	2	30	0.6
PCB 118	82	8	900	18	155	2	27	0.5
PCB 153	77	10	600	12	157	4	30	0.6
PCB 138	70	9	600	12	142	6	60	0.9
PCB 126	74	6	600	12	149	7	30	0.8
PCB 180	81	5	900	18	129	5	60	1.2
PCB 169	86	8	900	18	159	7	60	0.9
TEQ LOD (pg/$g_{raw\ sample}$)			11	0.2			0.6	0.01
TEQ LOD (pg/$g_{freeze\text{-}dried\ sample}$)			35	0.7			1.8	0.05
TEQ LOD (pg/$g_{fat\ extract}$)			250	4.9			13.0	0.32

[a] RSD and LOD were established by using a 1 ng/mL PCB standard. [b] RSD and LOD were established by using a 0.05 ng/mL PCB standard. [c] LOD refers to 10 g freeze-dried sample from a children's menu.

to 60 °C at a rate of 14 °C/s for 20 s to eliminate the solvent, which was vented through the split valve at a flow of 40 mL/min. In the transfer step, the split valve was closed, and the temperature quickly increased to 250 °C at a rate of 14 °C/s in splitless mode for 1 min. The injector was kept at 300 °C for 5 min, with a purge flow of 100 mL/min for cleaning purposes. The rest of GC and MS−MS parameters were maintained as for S/SL injections.

RESULTS

Optimization of PTV-LV Injection. Large-volume introduction into a PTV injector can be done in three different modes: (i) at-once, (ii) with speed control, and (iii) with multiple injections (*23*). The first two modes are used with the Thermo Finnigan Best PTV. In mode (i), the sample is introduced at relatively high speed, whereas the sample is introduced at a rate that is theoretically equal to that of evaporation in mode (ii). To simplify the optimization process, we used mode (i) injection at a speed of 100 μL/s.

The optimization of the PTV injection parameters involves a big number of experimental variables that can be simplified by using an experimental design. Central composite designs (CCD) have been used and preferred to one-factor-at-a-time to optimize the injection process. Taking into account preliminary studies carried out in our group (*13, 14*), three factors were selected as significant in the injection efficiency: vaporization temperature (T), vaporization time (t), and flow during the evaporation step (F). For all the experiments, the transfer temperature was fixed at 250 °C in splitless mode for 1 min,

Table 4. PCB Recoveries Obtained for a Clean Sample Spiked with 200 pg/g of Each Compound by Using PTV Injections and the SPE-GCB Fraction Where Each Compound Was Separated

compound	recovery (% ± s, $n = 3$)	elution fraction[a]
PCB 28	107 ± 4	A
PCB 52	86 ± 8	A
PCB 35	84 ± 7	B
PCB 80	96 ± 8	B
PCB 101	91 ± 7	A
PCB 81	72 ± 2	B + C
PCB 77	84 ± 4	B + C
PCB 118	99 ± 9	A
PCB 153	86 ± 7	A
PCB 138	94 ± 6	A
PCB 126	97 ± 6	B + C
PCB 180	92 ± 4	A
PCB 169	103 ± 4	B + C

[a] A, 15 mL of n-hexane; B, 20 mL of n-hexane/toluene 99:1 (v/v); and C, 20 mL of toluene.

the cleaning temperature was kept at 300 °C for 5 min, the split valve was open, and the purge flow was 100 mL/min.

Optimization of the significant PTV factors was carried out by a CCD composed of a full factorial 2^3 design that includes eight cube points to which six axial points and six central points were added, with two replicates, involving a total of 40 randomized chromatographic runs. **Figure 1** shows a scheme and the experimental values employed for each variable for the

Table 5. PCB Concentrations Found in Fast-Food Menus for Children

	PCB concentration (pg/g ± s, $n = 3$)[a]				
compound	sample 1	sample 2	sample 3	sample 4	sample 5
PCB 28	10 ± 3	12 ± 6	13 ± 1	11.1 ± 0.7	23 ± 2
PCB 52	ND	ND	ND	ND	ND
PCB 35	ND	ND	ND	ND	ND
PCB 80	ND	ND	5.2 ± 0.3	4.2 ± 0.1	6.8 ± 0.2
PCB 101	ND	ND	2.6 ± 0.1	5.1 ± 0.6	9.2 ± 0.8
PCB 81	ND	ND	ND	ND	ND
PCB 77	ND	ND	ND	ND	ND
PCB 118	15 ± 1	5.2 ± 0.1	13.0 ± 0.5	15 ± 1	17 ± 2
PCB 153	39 ± 1	47 ± 1	28.1 ± 0.6	48 ± 3	58 ± 4
PCB 138	30 ± 6	30 ± 2	18 ± 6	31 ± 6	46 ± 1
PCB 126	ND	ND	ND	ND	ND
PCB 180	11 ± 4	19 ± 1	17 ± 1	14.3 ± 0.7	79 ± 2
PCB 169	ND	ND	ND	ND	ND
TEQ ($pg/g_{raw\ sample}$)	0,015	0,013	0,015	0,014	0,014
TEQ ($pg/g_{freeze\text{-}dried\ sample}$)	0,045	0,045	0,045	0,045	0,045
TEQ ($pg/g_{fat\ extract}$)	0,32	0,35	0,28	0,34	0,32

[a] Concentration refers to freeze-dried sample. ND, less than the limit of detection.

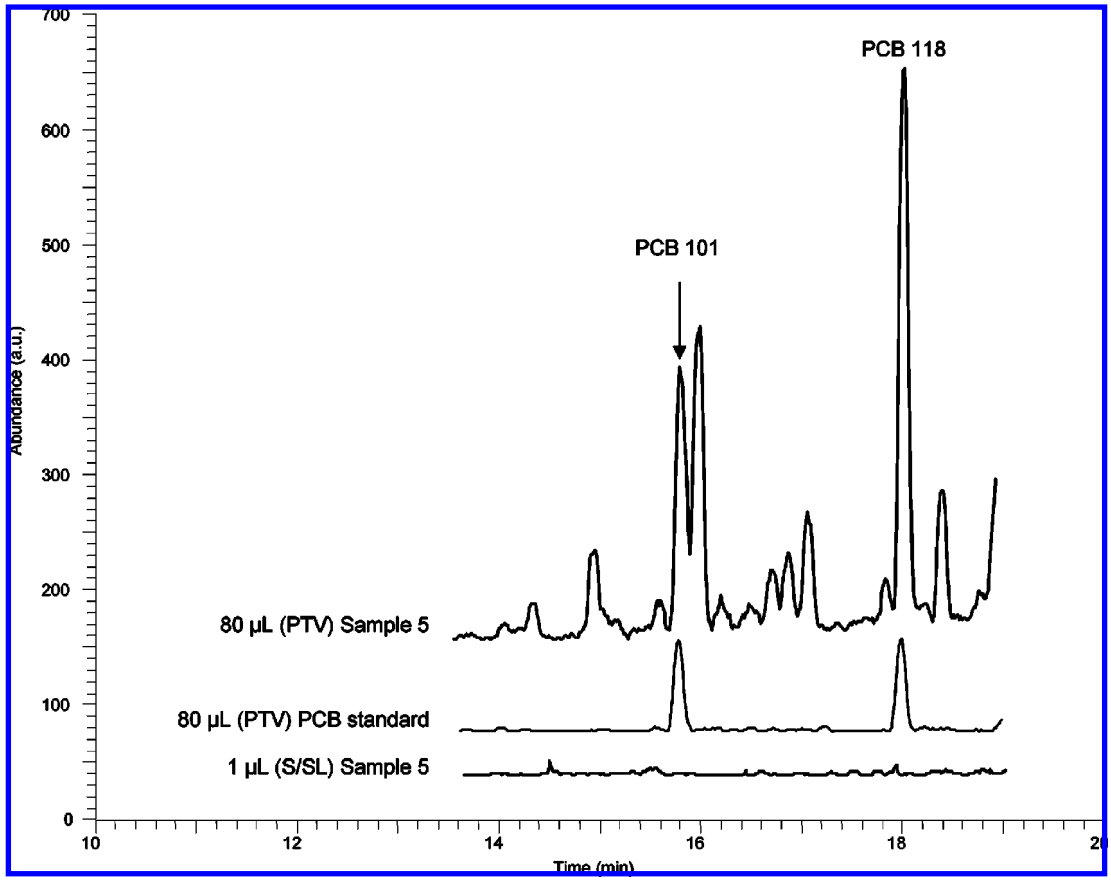

Figure 4. Chromatograms obtained for PCB 101 and PCB 118 in sample 5 by using 1 and 80 μL injections and for a 100 pg/mL PCB standard (80 μL injection). In all cases, GC−MS−MS measurements were made.

center, cube, and axial points. The values corresponding to every factor in each experiment are shown in **Table 2**.

The responses were fitted by a multiple regression equation, including curvature and interaction terms. As we have multiple responses for the 13 PCBs studied, there is no factor setting that simultaneously maximizes the desirability for each dependent variable. So, the selection of the factor settings that optimize the PCB responses was done by using the response optimizer (see **Figure 2**) from the response surface design in MINITAB 14 software from Minitab Inc. (State College, PA). It must be noticed that the desirability is 0.0 for the lowest values obtained in the CCD, increases as response values increase, and is 1.0 for the highest response obtained in the experiments. For this reason, we maximized the composite desirability (D) that combines the individual desirability (d) of all the response variables into a single measure, taking into account that all the response variables have the same importance. Thus, the optimized factor settings were $T = 60$ °C, $t = 0.2$ min, and $F = 40$ mL/min, with $D = 0.9766$.

As it can be seen in **Figure 2**, a minimum vaporization time of 0.2 min provides the maximum area signal for all studied PCBs, whereas the effect of temperature and flow during the solvent vaporization is different for each compound tested. It can be also noticed that the peak area values are highly

influenced by the evaporation flow, making it the most critical factor during the large-volume injection of PCB compounds.

Contour plots may show the effect of two independent variables on a given response, at a constant value of the other independent variables. **Figure 3** shows, as an example, the contour plot obtained for the PCB congeners 28, 80, and 126 for the temperature and flow variables at a constant value of the evaporation time of 0.2 min.

In order to confirm the correct solvent evaporation, volumes from 10 to 100 μL of a 0.1 ng/mL PCB standard were injected by using the optimized factors. A linear relationship of absolute peak area vs injection volume was found with a correlation coefficient R^2 higher than 0.994 for all the considered compounds. This means that an increase in the injection volume will supply an improved sensitivity. Finally, an injection volume of 80 μL was selected in order to use a complementary volume of 10 μL of air during the injection, which improves the repeatability of measurements.

Comparison S/SL vs PTV-LV Injection. Calibration curves were established with nine standards with PCB concentrations ranging from 10 pg/mL to 100 ng/mL of each compound. Limit of detection (LOD) values were established by using the expression $3s_{blank}/b$, where s_{blank} is the standard deviation of five measurements of a PCB standard of 0.05 ng/mL, and b is the slope of the calibration curve. The repeatability of the procedure developed was also evaluated as the relative standard deviation (RSD) of five measurements of a PCB standard of 1 ng/mL.

Table 3 shows the curve slopes for PCB standards dissolved in isooctane obtained by using two injection modes: 1 μL by S/SL and 80 μL by PTV injector. RSD and LOD values obtained for each compound are also reported. The detector response was linear over the concentration range studied, with correlation coefficients ranging from 0.996 to 0.9999. LOD ranged from 12 to 18 pg/g for 1μL S/SL injection and from 0.3 to 1.2 pg/g for 80μL PTV. So, the use of PTV-LV provides an increased sensitivity, 15 to 40 times higher than that of the conventional 1 μL S/SL injection.

Repeatability obtained by both assayed methodologies varies from 3 to 10% and from 2 to 9% for S/SL and PTV, respectively. The changes in the slope are not dependent on the injection volume because of the use of an internal standard which compensates the great changes in peak areas.

LOD for the contribution of PCBs in 2,3,7,8-TCDD TEQ was evaluated as the TEQ value obtained in a sample with a PCB concentration equal to half of the LOD value (*19*). So, in the case of PTV injections, TEQ LODs were 0.014 pg/g for the raw diet sample, 0.045 for the freeze-dried sample, and 0.32 pg/g for the fat extract. These LOD values are lower than the maximal values established by the European Community, previously shown in the Introduction.

Levels of PCBs in Children's Fast-Food Menus. The measured children's menus ($n = 5$) were composed of 46 $\pm$ 8 g of burger and complements, 58 $\pm$ 2 g of bread, 91 $\pm$ 9 g of french fries, 12 $\pm$ 1 g of ketchup, 280 $\pm$ 10 g of cola drink, and 51 $\pm$ 2 g of dairy product, for a total weight of 539 $\pm$ 6 g. Water content was established by the weight loss after the freeze-drying step; the average percentage of water in the whole menu was determined to be 69 $\pm$ 2%.

Recovery studies were performed with samples spiked with 200 pg/g of each considered PCB. **Table 4** shows these recoveries; the obtained results range from 72 to 107%, which indicates the accuracy of the proposed methodology. The table also shows the elution fraction of each PCB in the SPE step with graphitized carbon black, and from these data, it can be concluded that each compound was determined in its corresponding extract.

PCBs were determined in five different samples from children's menus from fast-food restaurants. The distribution and concentration of PCB compounds are quite similar for all the evaluated samples, as it can be seen in **Table 5**. Concentrations ranged from 2.6 to 58 pg/g for the PCB congeners 28, 80, 101, 118, 153, 138, and 180, whereas the concentrations of the rest of the compounds were below their LOD.

The corresponding PCB contributions of TEQ, considering half of the LOD concentration for compounds that were not found, are quite similar for all five measured diet samples; the obtained values range from 0.28 to 0.35 pg/g of fat extract. It should be taken into account that some of these values are lower than TEQ-LOD shown in **Table 3**; this is due to the different fat percentage of every measured diet sample. Consequently, we can fortunately conclude that the intake of PCBs by the consumption of fast food from children's menus respects the maximum tolerable levels established by the European Community.

A GC−MS−MS chromatogram of PCB congeners 101 and 118 in a sample is shown as an example in **Figure 4**. When 1 μL of extract was measured, there was not enough sensitivity for PCBs evaluation. However, with the use of 80 μL in a PTV, the signals obtained allowed the right quantification of the considered compounds.

In conclusion, the use of large-volume injections of PCB extracts with a PTV injector coupled to MS−MS improves both sensitivity and selectivity of measurements because of the increase of the analyte signal without an increase of the noise. This methodology involves an extensive cleanup of samples and PTV-GC−MS−MS measurements, which is appropriate for the determination of PCBs at very low levels of concentration. Sensitivity is 20−50 times higher than that of the standard S/SL injection mode. In the case of PCB determination in diets for which S/SL injection does not provide enough sensitivity, the use of PTV injection reaches a LOD value for the contribution of PCBs in TEQ of 0.3 pg/g of fat extract, which is lower than the maximum tolerable levels established by the legislation.

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