

1 **Sampling and analysis of polychlorinated biphenyls in indoor air by sorbent**
2 **enrichment followed by headspace solid-phase microextraction and gas**
3 **chromatography- tandem mass spectrometry**

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1 Abstract

2 In this study, a combination of solid-phase extraction (SPE) and solid-phase
3 microextraction (SPME) techniques has been used to determine polychlorinated
4 biphenyls in air. Using a vacuum pump, a known volume of air was forced to pass
5 through a porous polymer (Tenax TA) where the target analytes were retained and
6 headspace SPME was carried out. The quantification was performed using gas
7 chromatography coupled to mass spectrometry in tandem. Some parameters that could
8 affect SPE and SPME steps were studied and a screening factorial design was used to
9 evaluate the influence of the addition of solvents to the adsorbent and the type of fibre
10 coating. Performance of the method was evaluated demonstrating that external
11 calibration, which does not require performing the complete determination procedure,
12 was suitable. The correlation coefficients were calculated and a lack-of-fit test was run
13 within the calibration data. Repeatability of the method was found adequate
14 ($RSD \leq 12\%$). Limits of quantification were found below 0.100 ng/m^3 when only 2.5 m^3
15 air were sampled, well lower than recommended exposure levels given by different US
16 health organizations. In addition, more sensitivity could be attained by increasing the
17 volume of air sampled (decrease in retention efficiency was not detected for sample
18 volumes up to 25 m^3), and/or extending the extraction time in the SPME step.

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21 Key words

22 Air analysis, polychlorinated biphenyls, gas chromatography-mass spectrometry, solid-
23 phase microextraction, solid-phase extraction, factorial design, chlorinated compounds.

1 Introduction

2 Polychlorinated biphenyls (PCBs) are compounds with high lipid solubility and high
3 stability and persistence in the environment. They have been manufactured in
4 substantial amounts since the 1920s for being used in the electrical, paint, pigments,
5 paper, and cardboard industries; so, they were spread to the remotest areas of the world
6 before any control on use or disposals was implemented. The application of PCBs can
7 cause potential adverse health effects to humans by contaminating soil, water, air, plants
8 and animal life. Due to their stable, low volatility and lipophilic chemical nature, PCBs
9 exhibit bio-accumulative, chronic health effects; therefore, monitoring the presence of
10 these compounds in ambient air is of great importance [1-3].

11 The International Agency for Research of Cancer (IARC) has determined that PCBs are
12 probably carcinogenic to humans. US Environmental Protection Agency (US EPA) has
13 classified PCBs as a Group B2, probable human carcinogen. The National Institute for
14 Occupational Safety and Health (NIOSH) recommends workers not breathe air with
15 more than 0.001 milligrams of PCBs per cubic meter of air (0.001 mg/m^3) for a 10-hour
16 workday, 40-hour workweek. The Occupational Safety and Health Administration
17 (OSHA) requires workplace exposure limits of 0.5 mg/m^3 (54 percent chlorine) or 1
18 mg/m^3 (42 percent chlorine) for a 8-hour workday to protect workers from non cancer
19 harmful health effects [4-7].

20 Due to their low concentration in air, polychlorinated biphenyls have been extensively
21 sampled by solid phase extraction (SPE), pumping air through a solid sorbent or
22 mixtures of solid sorbents, where the compounds are retained. Florisil [8], silica gel [9],
23 polyurethane foam (PUF) [10, 11], XAD-2 resin [12], Carbosphere activated carbon
24 [13], functionalized styrene-divinylbenzene [14], are sorbents used to retain PCBs from
25 air. Tenax, a 2,6-dipheyl-p-phenylene oxide porous polymer, presents hydrophobic

1 nature and low interference by moisture adsorption for sampling humid air.

2 Consequently, Tenax has been extensively used for the recovery of volatile organic
3 compounds from contaminated air [15-18]. Its hydrophobic nature is an advantage over
4 some common hydrophilic sorbents, such as charcoal and silica gel, because air
5 humidity may reduce the sorption efficiency. [19].

6 Analytes retained by Tenax can be desorbed using an organic solvent or by thermal
7 desorption, prior to gas chromatographic analysis. Tenax is incompatible with many
8 solvent systems and then, it is rarely used for the retention of PCBs, which are mostly
9 extracted from the sorbents using Soxhlet extractors. On the other hand, thermal
10 desorption is more indicated for volatile analytes. Desorption of some low volatility
11 PCBs would require the application of high temperatures to the Tenax, and regardless of
12 its relatively inert nature, thermal desorption can cause drawbacks, as thermally,
13 mechanically and chemically degradation of the sorbent, as well as carryover problems
14 coming from poorly desorptions [20]. Some authors have noted changes in Tenax TA
15 from re-used thermal desorption tubes [21] and a few degradation products from Tenax
16 GC, such as benzaldehyde and acetophenone are well known [22].

17 Saba and co-workers have proposed the use of SPME following a preconcentration step
18 on Tenax to determine benzene and toluene in air [23,24], and recently, the authors have
19 optimized the experimental conditions to analyze volatile and semivolatile
20 chlorobenzenes in indoor air [25].

21 Solid-phase microextraction (SPME) provides some advantages over traditional
22 extraction methods. It offers solvent-free operation, and in spite of the limited amount
23 of analyte extracted, all is introduced into the GC injection port, allowing for good
24 sensitivity, with cost effectiveness and operational simplicity [26-28]. In addition,
25 SPME quantitative analysis is feasible in non-equilibrium situations once experimental

1 parameters are held constant, so a much shorter sampling time can be used for
2 quantitative analysis [29].
3 The aim of the present paper is to demonstrate that the combination of SPE-SPME
4 using Tenax as adsorbent can be useful to develop a method for the analysis of
5 polychlorinated biphenyls in indoor air samples. Thus, a study of the parameters
6 influencing SPME was carried out with the help of an experimental design strategy,
7 which reduces the experimental work required and allows accounting for possible factor
8 interactions. The performance of the method was also studied, demonstrating that limits
9 of detection in the low-medium pg/m^3 can be achieved. In addition, the method was
10 applied to a real contaminated air sample.

11

12 Experimental

13 Reagents

14 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-
15 pentachlorobiphenyl (PCB-101), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-138),
16 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-153), 2,3,3',4,4',5'-hexachlorobiphenyl (PCB-
17 156), 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180) were supplied by Ultra Scientific
18 (North Kingston, RI). All organic solvents used (isooctane, acetone, methanol and n-
19 hexane) were of pesticide grade and were obtained from Merck (Mollet del Vallés,
20 Barcelona, Spain).

21 Standard stock solutions of 800-1000 $\mu\text{g}/\text{mL}$ of individuals were prepared in isooctane,
22 and a stock solution containing a mixture of the seven target PCBs at 50 mg/L was
23 prepared in acetone. Working solutions were obtained by appropriate dilution in
24 isooctane, n-hexane or acetone. All solutions were stored in amber colored vials and
25 stored at -20°C .

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2 Air sampling and extraction of PCBs
3 Using a vacuum pump working at 100 L/min, a known volume of air was pumped
4 through a glass tube containing 25 mg Tenax TA adsorbent (mesh size 60/80) (Aldrich,
5 Madrid, Spain). A schematic view of the sampling device is shown in Figure 1. Only
6 Teflon (PTFE) tubing was used for connections. The adsorbent was then poured into a
7 10-mL glass vial and sealed with an aluminium cap furnished with a PTFE-faced
8 septum. As it will be discussed later, a known volume of organic solvent (n-hexane,
9 acetone or a mixture of both solvents) is added to the adsorbent. Then, solid phase
10 microextraction was carried out immersing the vial into a water bath maintained at 50 or
11 100°C and exposing a SPME fiber to the headspace of the vial (HSSPME). Experiments
12 at 150°C were carried out inside a conventional GC oven. The extraction time was fixed
13 at 30 or 60 minutes. To achieve good repeatability, vials should be immersed up to the
14 neck into the thermostated water bath. Once finished the SPME process, the fiber was
15 immediately inserted into the injection port of the gas chromatograph during 4 minutes
16 at 260°C.

17 To study the retention of PCBs on Tenax, 100 µL of standard mixtures of the target
18 PCBs in n-hexane were directly spiked on 25 mg of the adsorbent. The spike was left to
19 homogenize with the adsorbent for several hours. Then, the spiked Tenax was treated as
20 described above. In some experiments performed to detect the possible breakthrough of
21 the adsorbent, a second glass tube containing 25 mg of non-spiked Tenax was
22 connected in series with the first spiked one, and both portions of adsorbent were
23 individually extracted using the SPME procedure.

1 SPME manual holders and fibers were obtained from Supelco. Fibers used in this work
2 were: 100 μm polydimethylsiloxane (PDMS) or 65 μm polydimethylsiloxane-
3 divinylbenzene (PDMS/DVB).

4

5 Gas Chromatography-In tandem Mass Spectrometry

6 Analyses were performed in a Varian 3800 gas chromatograph (Varian Chromatography
7 systems, Walnut Creek, CA, USA) equipped with a 1079 split/splitless injector and an
8 ion trap mass detector Varian Saturn 2000 with a waveboard for MS^n analysis. The
9 system was operated by Saturn GC-MS WorkStation v5.4 software. The target
10 compounds were separated on a 25 μm length x 0.25 mm i.d., Varian CP-Sil8 CB Low
11 bleed/MS column coated with a 0.25 μm film. The GC oven temperature program was:
12 60°C hold 3 min, rate 20°C/min to 180°C hold 7.5 min, rate 5°C/min to 260°C hold 2
13 min with a total acquisition program of 34.5 min. Helium was employed as carrier gas,
14 with a constant column flow of 1.2 mL/min. The injector was operated in the splitless
15 mode and programmed to return to the split mode after 2 min from the beginning of a
16 run. Split flow was set at 50 mL/min. Injector temperature was held constant at 270°C.
17 The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. The
18 mass range was scanned from 40 to 650 m/z at 1 s/scan for the full scan mode. For
19 MS/MS, all compounds were analyzed using a resonant waveform type. Each segment
20 included an ion preparation method (IPM) that defines MS-MS parameters and m/z scan
21 range [30]. Trap, manifold and transfer line temperatures were maintained at 250°C,
22 50°C and 280°C, respectively.

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2 Results and discussion

3 The SPME process was studied before optimization of the sampling step because the
4 transfer of the polychlorinated biphenyls from the adsorbent to the fiber might seriously
5 affect the sensitivity of the whole extraction method, and the amount of PCBs retained
6 by the fiber greatly depends on the experimental conditions used to carry out the
7 microextraction.

8 Initial experiments were performed using dry Tenax (no solvent addition). The amount
9 of adsorbent was selected according to previous results [25]. Portions of 25 mg
10 adsorbent were spiked with the target analytes, and SPME was conducted at different
11 extraction temperatures (50, 100 and 150°C). Similar results (a factor 0.9-1.2 for all
12 compounds) were obtained working at 100°C and 150°C, while an important detriment
13 in response (a factor of 15-100) was observed when temperature was maintained at
14 50°C. Then, an extraction temperature of 100°C was chosen to carry out next studies.

15 To improve extraction of target analytes from Tenax and their transfer to the fiber, the
16 addition of a small volume (100 µL) of different solvents (hexane, acetone, water,
17 methanol) and solvent mixtures (hexane/acetone and methanol/acetone) previously to
18 SPME step was also investigated. A considerable improvement of the chromatographic
19 response was observed when hexane or acetone was used to wet the adsorbent. The
20 responses obtained were 20-70-fold higher than those obtained when no solvent was
21 added. Therefore, the addition of these solvents was considered for further study using
22 an experimental design approach.

23 A multifactor screening 3×2^2 mixed level factorial experimental design (type V
24 resolution), was carried out to study in 12 runs the influence of three main factors in the
25 SPME process [31]. The advantage of this design is that it allows the study of main

1 effects, as well as two-factor interactions. The factors considered in this design were:
2 percentage of acetone:hexane mixture and volume of solvent added to Tenax, both as
3 continuous factors; and type of fiber coating as discontinuous factor. The fiber included
4 in this study, PDMS and PDMS/DVB, were selected considering previous experience in
5 SPME of PCBS [32] In Table 1, the upper and lower levels given to each factor, as well
6 as the factor key, are presented.

7 The results of the experimental design indicated the statistical significance of some of
8 the main factors. Table 2 summarizes the analysis of variance for main factors.

9 Interactions were not included in this table since they were not significant with the
10 exception of BC (extraction volume and fiber coating) for PCB-52 and PCB-101. This
11 interaction will be discussed later. A factor is significant when its p-value is lower than
12 0.05 (95% confidence level). As can be seen in this table, solvent volume was
13 significant for the extraction of PCBs 52, 101 and 180. The percentage of hexane in the
14 solvent (acetone) was significant for PCBs 28, 52 and 138. In addition, fiber coating
15 was a significant factor for the extraction of the most chlorinated PCBs (PCB-156 and
16 PCB-180).

17 Figure 2 shows the main effects graphs for the target PCBs excluding PCB-153 since,
18 for this compound, none of the factors was statically significant (see Table 2). In these
19 plots, obtained by drawing a line between the low and the high levels of main factors, we
20 can see the magnitude of the effect of each factor on the microextraction process, as
21 well as the level of the factor that produces the highest response. The influence of each
22 factor is clearly appreciated in this figure. The fiber coating is an important factor in the
23 extraction of the most chlorinated PCBs. For these compounds, higher response is
24 achieved by PDMS coating. For the other compounds, responses obtained were
25 independent on the fiber used. So, PDMS can be selected as the most suitable coating

1 for the extraction of the target analytes. Regarding solvent volume, PCBs 28, 52 and
2 101 show higher analytical response when they are extracted using 200 μL solvent,
3 while the remaining compounds show better responses using 100 μL solvent.
4 Nevertheless, this factor was only significant for PCB-52, 101 and 180 (see Table 2).
5 An adequate selection of the level of this factor requires a deeper insight in the
6 experimental design results since the interaction between the factors solvent volume and
7 fiber coating (BC) was significant for PCB-52 and PCB-101. This interaction effect is
8 clearly appreciated in Figure 3. This figure shows the interaction plot for PCB-52; (-)
9 sign represents the low level of the second factor considered in each interaction, and (+)
10 sign represents the corresponding high level (see Table 1 for factor key). For
11 PDMS/DVB coating, a volume of 200 μL of solvent produces a significant increase in
12 response; nevertheless, when PDMS is used, response is not affected by solvent volume.
13 In consequence, and taken into account that low solvent volume benefits the extraction
14 of the most chlorinated PCBs, 100 μL was selected as the most convenient solvent
15 volume. Finally, the percentage of hexane in the solvent (acetone) presents a negative
16 effect for the less chlorinated PCBs (see Figure 2). On the other hand, the addition of
17 hexane appears favourable for the most chlorinated compounds. This factor was only
18 significant for PCBs 28, 52 and 138 (see Table 2). In this case, a compromise solution
19 has to be taken. It must also be mentioned here that some of the experiments in which
20 200 μL of acetone:hexane (1:1) mixture were used led to damage of the PDMS fibers.
21 Nevertheless, using 100 μL acetone to wet the Tenax, up to one hundred SPME
22 determinations were performed using the same PDMS fiber. Therefore, 100 % acetone
23 was the solvent selected.
24 In summary, the experimental conditions selected after this study involve the addition of
25 100 μL acetone and the use of PDMS fiber.

1 To evaluate the efficiency of SPME with the extraction time, exposition times of 30 and
2 60 minutes were studied. Results demonstrate that analytical response for all
3 compounds can be improved using longer extraction times, which indicates that the
4 system has not reached equilibrium within 60 minutes. However, an extraction time of
5 30 min is considered satisfactory to obtain adequate responses for all PCBs, and it was
6 the time selected for further studies. Nevertheless, if higher sensitivity is required larger
7 extraction times could be employed.

8 After proving that chlorinated biphenyls could be transferred from the adsorbent to a
9 SPME fiber, the SPE sampling step was studied. Breakthrough of the adsorbent was
10 studied sampling rising volumes of air from 1 to 25 m³ containing the same total
11 amount of PCBs (100 ng of each congener). Responses obtained for the different
12 volumes were equivalent, which indicates that no breakthrough occurs even for 25 m³.
13 Nevertheless, as sensitivity of the method is adequate sampling lower volumes, 2.5 m³
14 air, which are collected in only 25 min, this volume was selected for next studies, in
15 spite of the fact that larger sampling volumes would allow improving sensitivity.

16

17 Performance of the method

18 Blank air samples as well as adsorbent blanks were obtained in a clean room provided
19 with a laminar flow system and analyzed before every set of experiments.

20 Linearity of the method was evaluated by external calibration, performing SPME of
21 PCB spiked Tenax in the range 0.008-4 ng/mg, which are equivalent to 0.08-40 ng/m³
22 (2.5 m³ air), obtaining good correlation coefficients for all compounds ($R^2 \geq 0.992$) (see
23 Table 3). An analysis of variance (ANOVA) was performed to validate the regression
24 data. The lack-of-fit test is designed to determine whether the selected model is
25 adequate to describe the experimental data obtained, or whether a more complicated

1 model should be used. The test compares the variability of the proposed model residuals
2 to the variability between observations (area counts) at replicate values of the
3 independent variable (known concentration of PCBs in the directly spiked Tenax).
4 Results of the lack-of-fit test for the calibration range considered, at a confidence level
5 of 95% are also shown in Table 3. Since p-values are greater than 0.05, linear regression
6 models are adequate for the obtained data [31]
7 To estimate the accuracy of the method air samples containing the analytes at two
8 different concentration levels (4 and 40 ng/ m³) were taken and their concentration were
9 evaluated using external calibration. Accuracy was then estimated as the ratio
10 found/added concentration and expressed as percentage. Table 3 shows that recoveries
11 obtained ranged from 99% to 108% for the lowest concentration level, and from 90% to
12 97% for the highest concentration level. Therefore, accuracy of the method can be
13 considered satisfactory.
14 Precision of the method was evaluated and results can also be seen in Table 3. R.S.D.
15 values ranged from 7.2 to 14% using directly spiked Tenax samples extracted by SPME
16 (n= 4), and from 6.9 to 12% using the complete process of SPE-SPME (n=5), indicating
17 that the sampling step does not increase the variability of the results.
18 Limits of detection (LOD, signal-to-noise ratio of 3) were estimated for the proposed
19 method, considering a sample volume of 2.5m³ air, and are presented in Table 3. LOD
20 values were found at the pg/m³. For most of the target analytes, the proposed method
21 achieves LODs comparable to those recently obtained by Ramil et al. [14], using much
22 higher air volumes (50 m³). For all analytes, limits achieved by the proposed method are
23 low enough to check for harmful levels of PCBs in indoor air, and are well below the
24 most restrictive limits established by countries regulations [4-7]. In addition, more
25 sensitivity could be attained by increasing the volume of air sampled (decrease in

1 retention efficiency was not detected for sample volumes up to 25 m³), and/or extending
2 the extraction time in the SPME step.
3 Finally, the method was applied to a real air sample taken inside a laboratory hood place
4 in which a contaminated transformer oil sample was heated. Figure 4 shows the mass
5 chromatograms for an air sample containing 4 ng/m³ of each PCB analyzed using the
6 combination of SPE-HSSPME techniques. Figure 5 shows the mass chromatograms for
7 the real sample, in which an Arochlor profile can be identified and individual PCB
8 congeners could be quantified. The concentrations found for the target analytes are
9 included in this figure.

10

11 Conclusions

12 A method based on the association of solid-phase extraction and solid-phase
13 microextraction (SPE-SPME) to determine polychlorinated biphenyls in indoor air
14 samples is proposed. External calibration is possible and constitutes an additional
15 advantage, especially for those laboratories that need to perform air monitoring
16 occasionally. Sensitivity of the method is adequate to this type of determinations (limits
17 of detection are below 0.100 ng/m³ for all PCBs tested) and could be improved by
18 increasing sample volume and/or using longer SPME times. The method described is
19 very simple, low-cost and fast, and can constitute an alternative to methods based on
20 thermal or solvent desorption.

21

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Table 1. Ion preparation method (IPM) parameters for each of the six segments of the GC-MS/MS method

Segment	PCB	Start time (min)	Finish time (min)	Parent ions (m/z)	Scan range (m/z)	Quantification ions (m/z)	Excitation storage level (m/z)	Excitation amplitude (V)	Collision induced dissociation frequency offset (Hz)
Solvent delay	-	0.00	13.0	-	-	-	-	-	-
2	28	13.00	16.5	258.0 [M+2]	100-270	186+188	133.0	1.15	600
3	52	16.5	19.5	292.0 [M+2]	140-300	220+222	157.0	1.15	600
4	101	19.5	23.5	325.9 [M+2]	180-330	254+256+289+291	181.0	1.29	700
5	153, 138, 156	23.5	28.7	359.8 [M+2]	180-375	288+290	206.0	1.59	700
6	180	28.7	30.0	395.8 [M+4]	220-400	324+326	231.0	1.71	800

Table 2. Factors and levels considered in the experimental design.

Factor	Key	Low level	High level	Continuous
% hexane	A	0	100	yes
solvent volume (μL)	B	100	200	yes
fiber coating	C	PDMS/DVB	PDMS	no

Table 3. ANOVA results showing the significance of main effects

Compound	% hexane		solvent volume		fiber coating	
	F-ratio	p-value	F-ratio	p-value	F-ratio	p-value
PCB-28	9.60	0.02	4.87	0.06	0.26	0.63
PCB-52	5.92	0.04	8.39	0.02	0.06	0.81
PCB-101	0.38	0.56	7.90	0.03	0.01	0.92
PCB-153	3.17	0.12	0.02	0.90	1.32	0.29
PCB-138	5.92	0.04	0.46	0.52	1.63	0.24
PCB-156	3.45	0.11	1.79	0.22	5.17	0.05
PCB-180	2.45	0.16	6.65	0.04	7.16	0.03

Table 4. Linearity, recovery, repeatability (%RSD), and limits of detection of the method.

Compound	Linearity			Recovery (%)		Repeatability (%RSD)		Detection limits (S/N=3, ng/m ³)
	Coefficient of determination (R ²)	F-test	p-value	4ng/m ³	40ng/m ³	SPME	SPE-SPME	
PCB-28	1.000	0.67	0.6402	100	92	14	11	0.011
PCB-52	0.999	4.76	0.0588	101	94	10	10	0.017
PCB-101	0.999	3.64	0.0946	90	90	13	7.8	0.016
PCB-153	0.997	0.64	0.6585	99	95	7.2	6.9	0.018
PCB-138	0.996	1.18	0.4187	108	97	8.8	9.9	0.037
PCB-156	0.993	0.37	0.8206	99	92	8.4	12	0.030
PCB-180	0.992	0.27	0.8859	101	92	8.8	11	0.096

Figure captions

Figure 1. Schematic plot of the air sampling device. 1: vacuum pump, 2: PTFE connectors, 3: flow meter, 4: glass tube containing Tenax TA.

Figure 2. Graphics showing the influence of main effects on the extraction of the target PCBs.

Figure 3. Interaction plot for PCB-52.

Figure 4. Extracted ion current chromatograms for an air sample containing 4 ng/m^3 of the target PCBs.

Figure 5. Extracted ion current chromatograms for a real air sample.

Figure 1

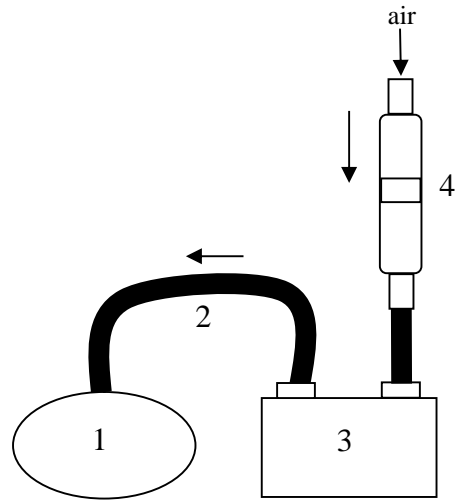


Figure 2.

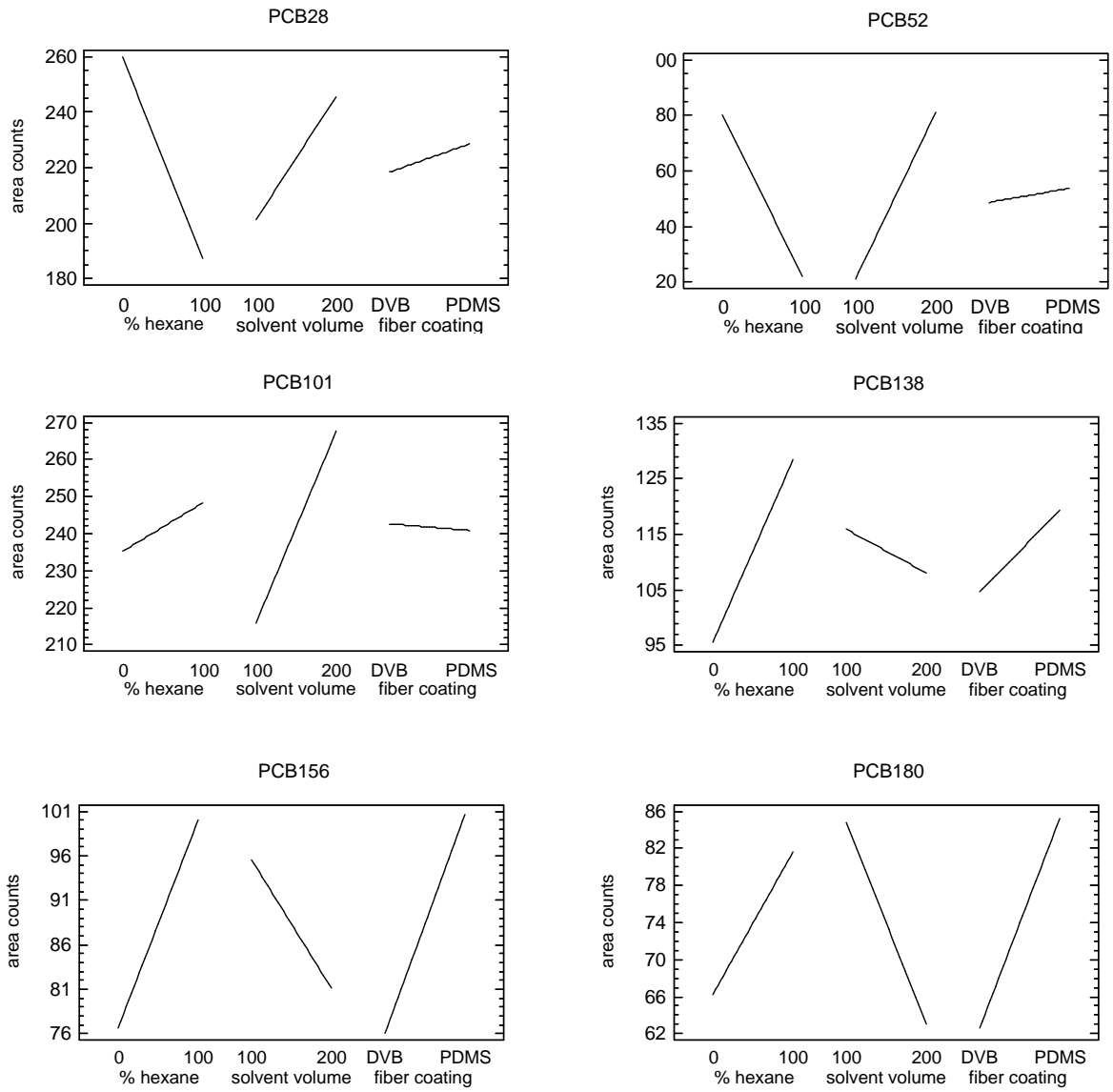


Figure 3

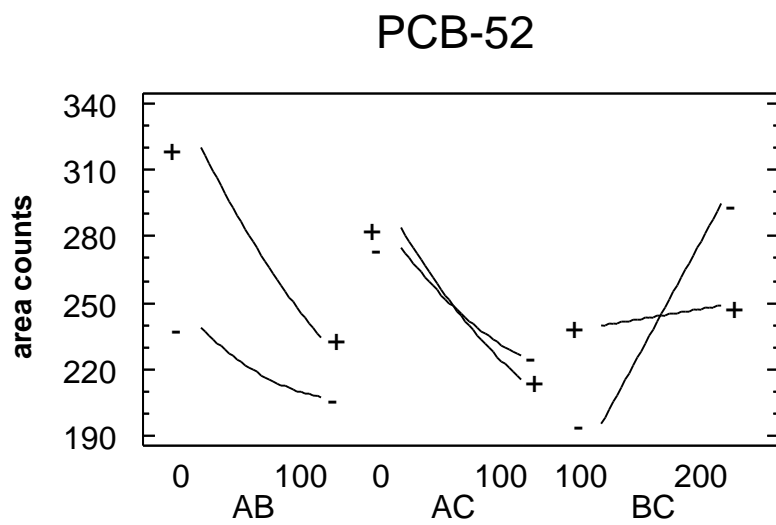


Figure 4

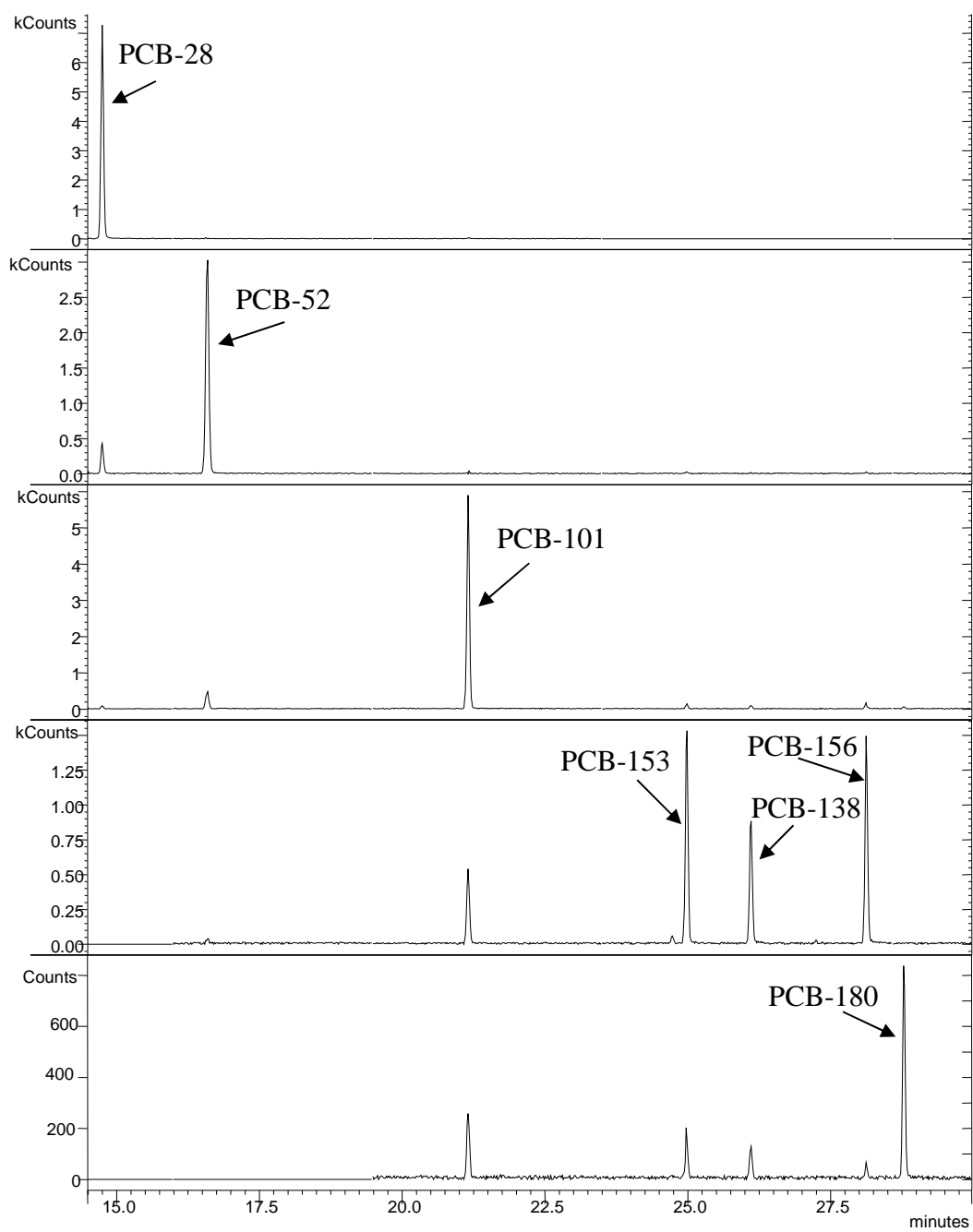


Figure 5

