

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

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Abstract

In this study, a combination of solid-phase extraction (SPE) and solid-phase microextraction (SPME) techniques has been used to determine polychlorinated biphenyls (PCBs) in air. Using a vacuum pump, a known volume of air was pulled through a porous polymer (Tenax TA) where the target analytes were retained and then headspace SPME was carried out. The quantification was performed using gas chromatography coupled to tandem mass spectrometry. Certain factors, such as temperature and the addition of solvents to the adsorbent, were found to be very important for the transfer of the target PCBs from the Tenax to the SPME fiber. Some of these factors were studied using an experimental design strategy. Performance of the method was evaluated demonstrating that external calibration, which does not require performing the complete sampling process, was suitable. The coefficients of determination were calculated and a lack-of-fit test was run within the calibration data, demonstrating linearity of the method. Repeatability was found adequate ($RSD \leq 12\%$). Limits of detection (LODs) were found below 0.100 ng/m^3 when only 2.5 m^3 air were sampled. These LODs were low enough to check for harmful levels of PCBs in indoor air, and are well below the most restrictive limits established by countries regulations. In addition, more sensitivity could be attained by increasing the volume of air sampled (decrease in retention efficiency was not detected for sample volumes up to 25 m^3), and/or extending the extraction time in the SPME step.

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1. Introduction

Polychlorinated biphenyls (PCBs) are compounds with high lipid solubility and high stability and persistence in the environment. They have been manufactured in substantial amounts since the 1920s for use in the electrical, paint, pigments, paper, and cardboard industries; so, they were spread to the remotest areas of the world before any control on use or disposals was implemented. The application of PCBs can cause potential adverse health effects to humans by contaminating soil, water, air, plants, and animal life. Due to their stable, low volatility, and lipophilic chemical nature, PCBs

exhibit bio-accumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance [1–3].

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

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Due to their low concentration in air, polychlorinated biphenyls have been extensively sampled by solid-phase extraction (SPE), pumping air through a solid sorbent or mixtures of solid sorbents, where the compounds are retained. Florisil [8], silica gel [9], polyurethane foam (PUF) [10,11], XAD-2 resin [12], Carbosphere activated carbon [13], functionalized styrene–divinylbenzene [14], are sorbents used to retain PCBs from air. Tenax, a 2,6-diphenyl-*p*-phenylene oxide porous polymer, presents hydrophobic nature and low interference by moisture adsorption for sampling humid air. Consequently, Tenax has been extensively used for the recovery of volatile organic compounds from contaminated air [15–18]. Its hydrophobic nature is an advantage over some common hydrophilic sorbents, such as charcoal and silica gel, because air humidity may reduce the sorption efficiency [19].

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

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

Solid-phase microextraction (SPME) provides some advantages over traditional extraction methods. It offers solvent-free operation, and in spite of the limited amount of analyte extracted, all is introduced into the GC injection port, allowing for good sensitivity, with cost effectiveness and operational simplicity [26–28]. In addition, SPME quantitative analysis is feasible in non-equilibrium situations once experimental parameters are held constant, so a much shorter sampling time can be used for quantitative analysis [29].

The aim of the present paper is to demonstrate that the combination of SPE–SPME using Tenax as adsorbent can be useful to develop a method for the analysis of polychlorinated biphenyls in indoor air samples. Thus, a study of the parameters influencing SPME was carried out with the help of an experimental design strategy, which reduces the experimental work required and allows accounting for possible factor interactions. The performance of the method was also studied, demonstrating that limits of detection in the low-medium pg/m^3 can be achieved. In addition, the method was applied to a real contaminated air sample.

2. Experimental

2.1. Reagents

2,4,4'-Trichlorobiphenyl (PCB-28); 2,2',5,5'-tetrachlorobiphenyl (PCB-52); 2,2',4,5,5'-pentachlorobiphenyl (PCB-101); 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-138); 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153); 2,3,3',4,4',5'-hexachlorobiphenyl (PCB-156); 2,3,3',4,4',5-heptachlorobiphenyl (PCB-180) were supplied by Ultra Scientific (North Kingston, RI, USA). All organic solvents used (isooctane, acetone, methanol, and *n*-hexane) were of pesticide grade and were obtained from Merck (Darmstadt, Germany).

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

2.2. Air sampling and extraction of PCBs

Using a vacuum pump working at 100 L/min (Telstar model S-8, Tarrasa, Spain), a known volume of air was pumped through a glass tube containing 25 mg Tenax TA adsorbent (mesh size 60–80) (Supelco, Bellefonte, PA, USA). A schematic view of the sampling device is shown in Fig. 1. Only PTFE tubing was used for connections. The adsorbent was then poured into a 10-mL glass vial and sealed with an aluminium cap furnished with a PTFE-faced septum. As it will be discussed later, a known volume of organic solvent (*n*-hexane, acetone or a mixture of both solvents) is added to the adsorbent. Then, solid-phase microextraction was carried out immersing the vial into a water bath maintained at 50 or 100 $^\circ\text{C}$ and exposing a SPME fiber to the headspace of the

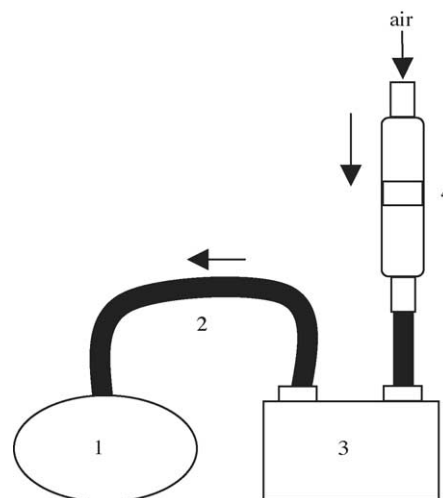


Fig. 1. Schematic plot of the air-sampling device. (1) Vacuum pump, (2) PTFE connectors, (3) flow meter, (4) glass tube containing Tenax TA.

vial (HS-SPME). Experiments at 150 °C were carried out inside a conventional GC oven. The extraction time was fixed at 30 or 60 min. To achieve good repeatability, vials should be immersed up to the neck into the thermostated water bath. Once finished the SPME process, the fiber was immediately inserted into the injection port of the gas chromatograph during 4 min at 260 °C.

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

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

2.3. Gas chromatography–mass spectrometry

Analyses were performed in a Varian 3800 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a 1079 split/splitless injector and an ion trap mass detector Varian Saturn 2000 with a waveboard for multiple MS (MS^n) analysis. The system was operated by Saturn GC–MS WorkStation v5.4 software. The target compounds were separated on a 25 µm × 0.25 mm i.d., Varian CP–Sil8 CB Low bleed/MS column coated with a 0.25 µm film. The GC oven temperature program was: 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 min with a total acquisition program of 34.5 min. Helium was employed as carrier gas, with a constant column flow of 1.2 mL/min. The injector was operated in the splitless mode and programmed to return to the split mode after 2 min from the beginning of a run. Split flow was set at 50 mL/min. Injector temperature was held constant at 260 °C. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. The mass range was scanned from 40 to 650 m/z at 1 s/scan for the full scan mode. For MS/MS, all compounds were analyzed us-

ing a resonant waveform type. Each segment included an ion preparation method (IPM) that defines MS/MS parameters and m/z scan range [30]. In Table 1, the most representative IPM parameters for the segments of the GC–MS/MS method are presented. Trap, manifold and transfer line temperatures were maintained at 250, 50, and 280 °C, respectively.

3. Results and discussion

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

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

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

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

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	13.0	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	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

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

The results of the experimental design indicated the statistical significance of some of the main factors. Table 3 sum-

Table 3
ANOVA results showing the significance of main effects

Compound	% Hexane		Solvent volume		Fiber coating	
	<i>F</i> -ratio	<i>p</i> -value	<i>F</i> -ratio	<i>p</i> -value	<i>F</i> -ratio	<i>p</i> -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

marizes the analysis of variance for main factors. Interactions were not included in this table since they were not significant with the exception of BC (extraction volume and fiber coating) for PCB-52 and PCB-101. This interaction will be discussed later. A factor is significant when its *p*-value is lower than 0.05 (95% confidence level). As can be seen in this table,

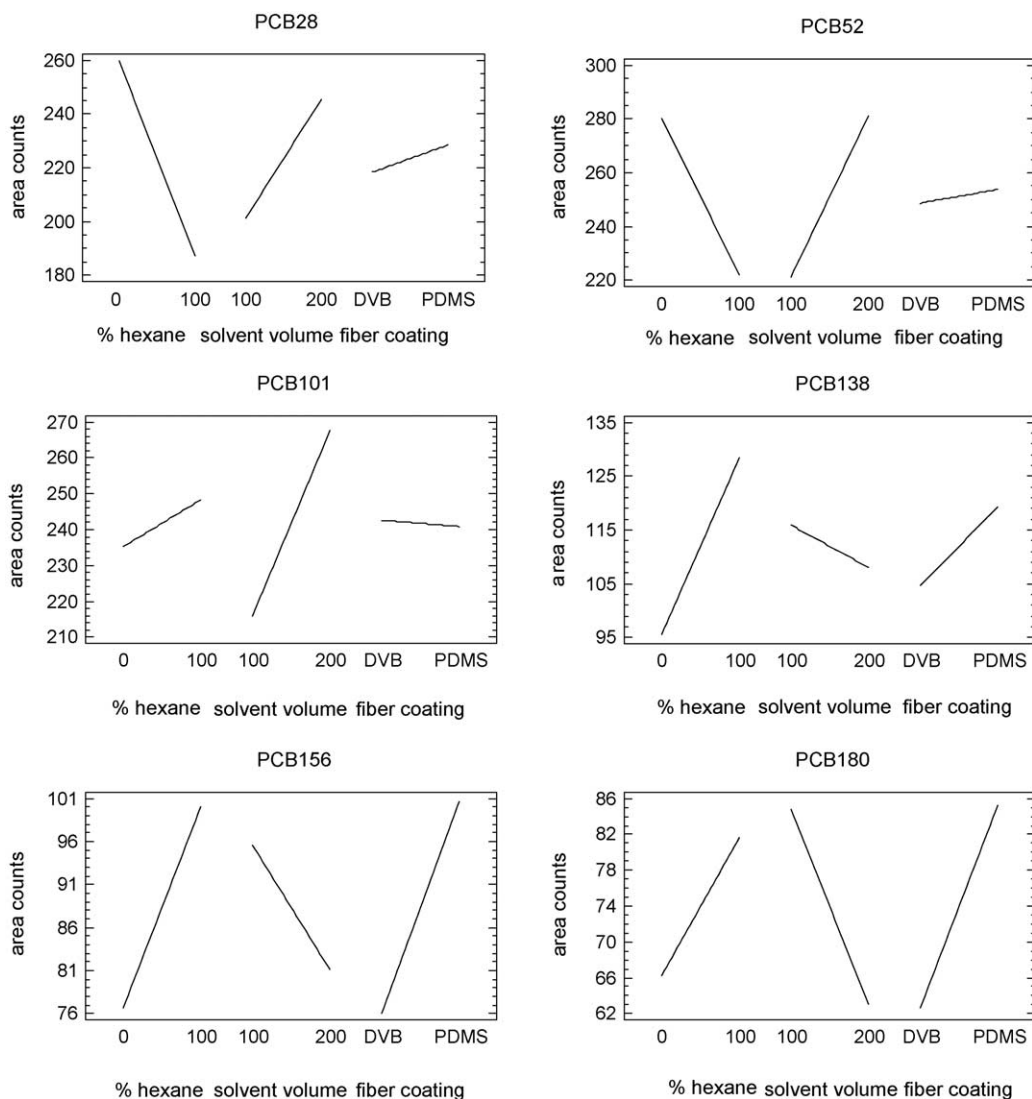


Fig. 2. Graphics showing the influence of main effects on the extraction of the target PCBs.

solvent volume was significant for the extraction of PCBs 52, 101, and 180. The percentage of hexane in the solvent (acetone) was significant for PCBs 28, 52, and 138. In addition, fiber coating was a significant factor for the extraction of the most chlorinated PCBs (PCB-156 and PCB-180).

Fig. 2 shows the main effects graphs for the target PCBs excluding PCB-153 since, for this compound, none of the factors was statically significant (see Table 3). In these plots, obtained by drawing a line between the low and the high levels of main factors, we can see the magnitude of the effect of each factor on the microextraction process, as well as the level of the factor that produces the highest response. The influence of each factor is clearly appreciated in this figure. The fiber coating is an important factor in the extraction of the most chlorinated PCBs. For these compounds, higher response is achieved by PDMS coating. For the other compounds, responses obtained were independent on the fiber used. So, PDMS can be selected as the most suitable coating for the extraction of the target analytes. Regarding solvent volume, PCBs 28, 52, and 101 show higher analytical response when they are extracted using 200 μL solvent, while the remaining compounds show better responses using 100 μL solvent. Nevertheless, this factor was only significant for PCB-52, 101, and 180 (see Table 3). An adequate selection of the level of this factor requires a deeper insight in the experimental design results since the interaction between the factors solvent volume and fiber coating (BC) was significant for PCB-52 and PCB-101. This interaction effect is clearly appreciated in Fig. 3. This figure shows the interaction plot for PCB-52; (–) sign represents the low level of the second factor considered in each interaction, and (+) sign represents the corresponding high level (see Table 2 for factor key). For PDMS–DVB coating, a volume of 200 μL of solvent produces a significant increase in response; nevertheless, when PDMS is used, response is not affected by solvent volume. In consequence, and taken into account that low solvent volume benefits the extraction of the most chlorinated PCBs, 100 μL was selected as the most convenient solvent volume. Finally, the percentage of hexane in the solvent (acetone) presents a negative effect for the less chlorinated PCBs (see Fig. 2). On the other hand, the addition of hexane appears favourable for the most chlorinated compounds. This factor was only significant for PCBs

28, 52, and 138 (see Table 3). In this case, a compromise solution has to be taken. It must also be mentioned here that some of the experiments in which 200 μL of acetone–hexane (1:1) mixture were used led to damage of the PDMS fibers. Nevertheless, using 100 μL acetone to wet the Tenax, up to 100 SPME determinations were performed using the same PDMS fiber. Therefore, 100% acetone was the solvent selected.

In summary, the experimental conditions selected after this study involve the addition of 100 μL acetone and the use of PDMS fiber.

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

After proving that chlorinated biphenyls could be transferred from the adsorbent to an SPME fiber, the SPE sampling step was studied. Breakthrough of the adsorbent was studied sampling rising volumes of air from 1 to 25 m^3 containing the same total amount of PCBs (100 ng of each congener). Responses obtained for the different volumes were equivalent, which indicates that no breakthrough occurs even for 25 m^3 . Nevertheless, as sensitivity of the method is adequate sampling lower volumes, 2.5 m^3 air, which are collected in only 25 min, this volume was selected for next studies, in spite of the fact that larger sampling volumes would allow improving sensitivity.

3.1. Performance of the method

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

Linearity of the method was evaluated by external calibration, performing SPME of PCB spiked Tenax in the range 0.008–4 ng/mg, which are equivalent to 0.08–40 ng/ m^3 (2.5 m^3 air), obtaining good coefficients of determination for all compounds ($R^2 \geq 0.992$) (see Table 4). An analysis of variance (ANOVA) was performed to validate the regression data. The lack-of-fit test is designed to determine whether the selected model is adequate to describe the experimental data obtained, or whether a more complicated model should be used. The test compares the variability of the proposed model residuals to the variability between observations (area counts) at replicate values of the independent variable (known concentration of PCBs in the directly spiked Tenax). Results of the lack-of-fit test for the calibration range considered, at a confidence level of 95% are also shown in Table 4. Since p -values are greater than 0.05, linear regression models are adequate for the obtained data [31].

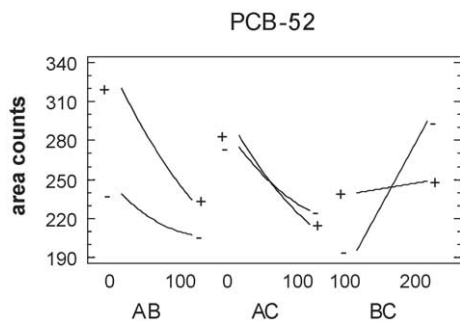


Fig. 3. Interaction plot for PCB-52 (see Table 2 for factor key).

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	$4 \text{ ng}/\text{m}^3$	$40 \text{ ng}/\text{m}^3$	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

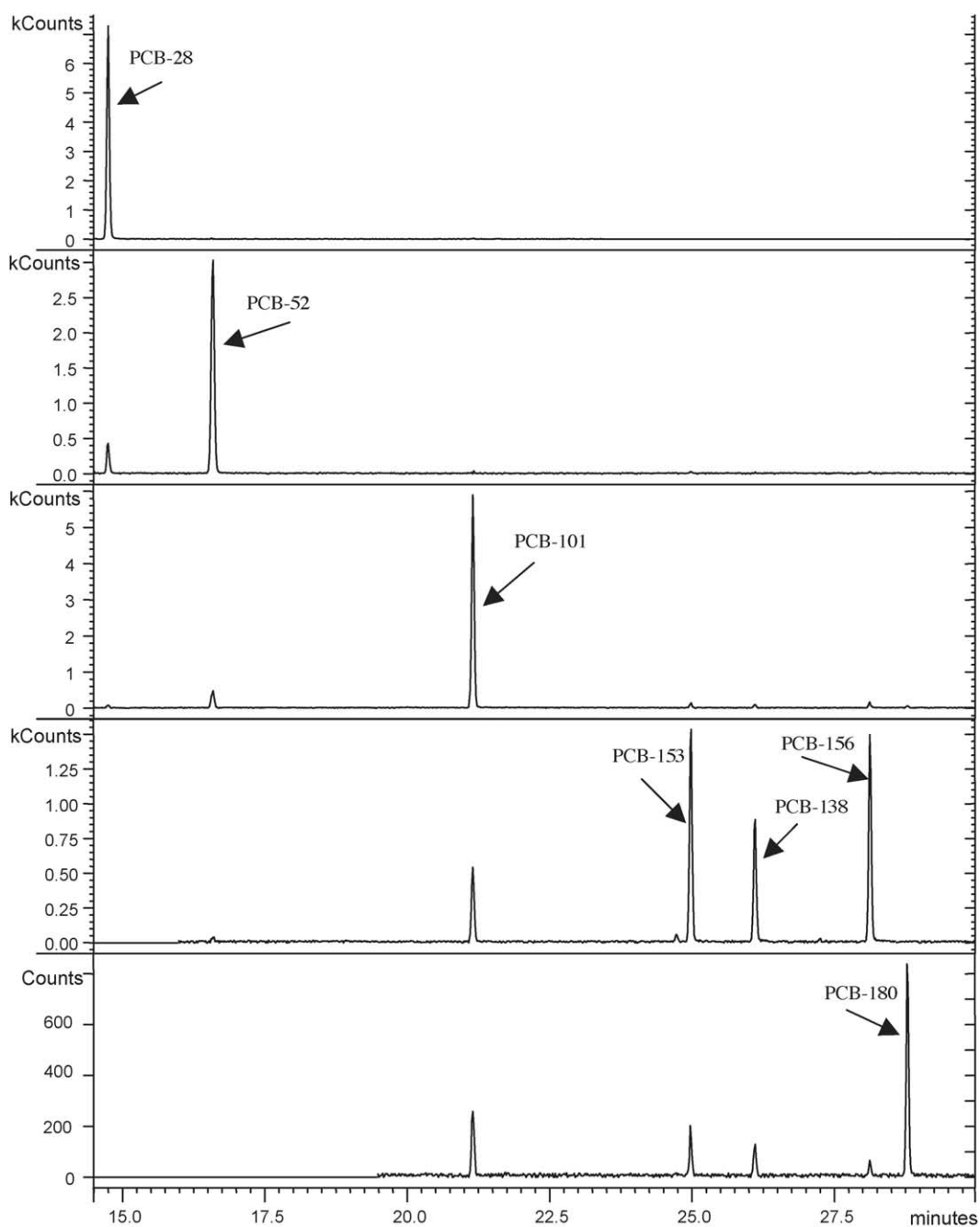


Fig. 4. Extracted ion current chromatograms for an air sample containing $4 \text{ ng}/\text{m}^3$ of the target PCBs.

To estimate the accuracy of the method air samples containing the analytes at two different concentration levels (4 and 40 ng/m³) were taken and their concentration were evaluated using external calibration. Accuracy was then estimated as the ratio found/added concentration and expressed as percentage. Table 4 shows that recoveries obtained ranged from 99 to 108% for the lowest concentration level, and from 90 to 97% for the highest concentration level. Therefore, accuracy of the method can be considered satisfactory.

Precision of the method was evaluated and results can also be seen in Table 4. RSD values ranged from 7.2 to 14%

using directly spiked Tenax samples extracted by SPME, and from 6.9 to 12% using the complete process of SPE–SPME ($n=5$), indicating that the sampling step does not increase the variability of the results.

Limits of detection (LODs, signal-to-noise ratio of 3) were estimated for the proposed method considering a sample volume of 2.5 m³ air, and are presented in Table 4. LOD values were found at the pg/m³. For most of the target analytes, the proposed method achieves LODs comparable to those recently obtained by Ramil et al. [14], using much higher air volumes (50 m³). For all analytes, limits achieved by the pro-

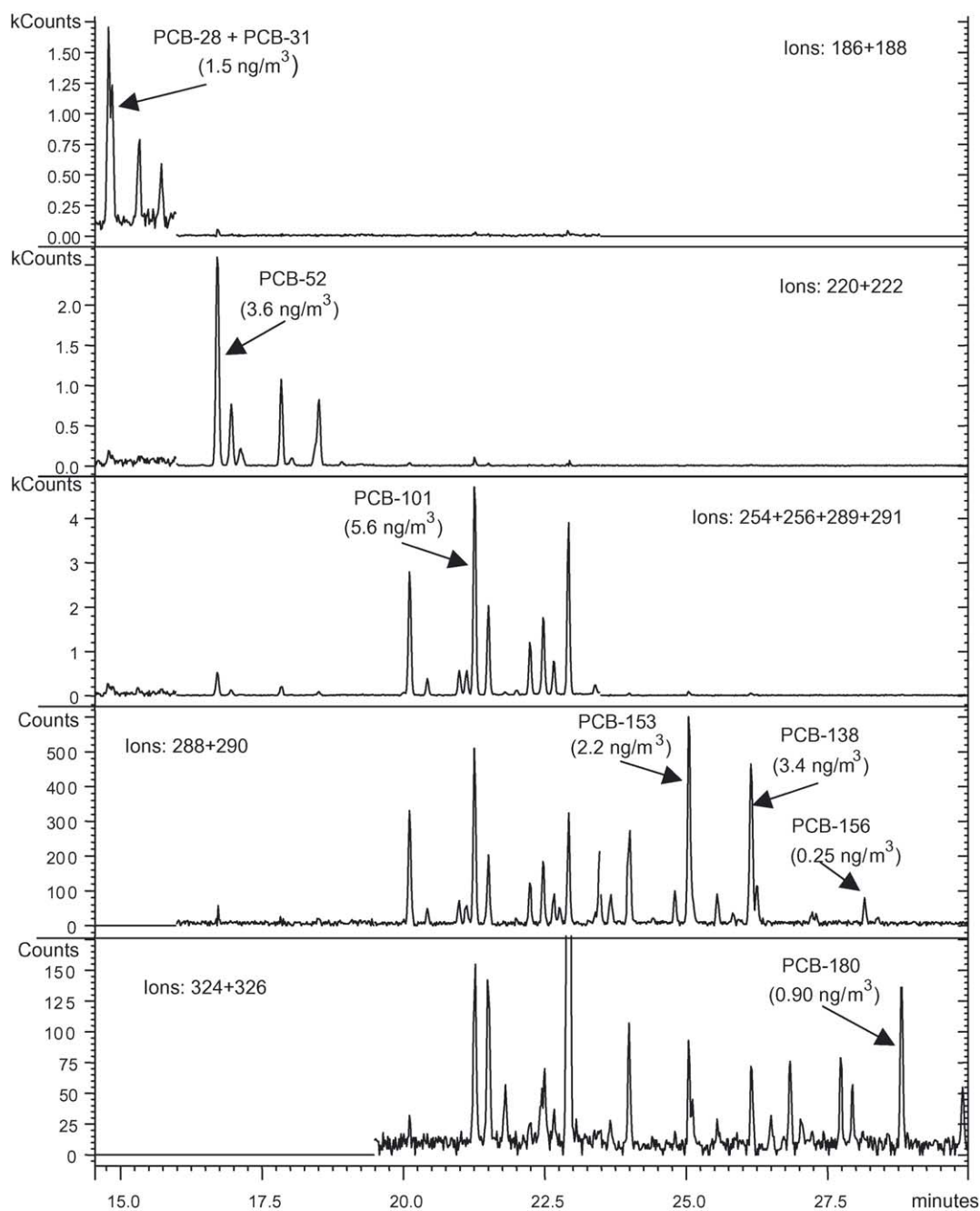


Fig. 5. Extracted ion current chromatograms for a real air sample.

posed method are low enough to check for harmful levels of PCBs in indoor air, and are well below the most restrictive limits established by countries regulations [4–7]. In addition, more sensitivity could be attained by increasing the volume of air sampled (decrease in retention efficiency was not detected for sample volumes up to 25 m³), and/or extending the extraction time in the SPME step.

Finally, the method was applied to a real air sample taken inside a laboratory hood place in which a contaminated transformer oil sample was heated. Fig. 4 shows the extracted ion current chromatograms for an air sample containing 4 ng/m³ of each PCB analyzed using the combination of SPE–HS–SPME techniques. Fig. 5 shows the extracted ion current chromatograms for the real sample, in which an Arochlor profile can be identified and individual PCB congeners could be quantified. The concentrations found for the target analytes are included in this figure.

4. Conclusions

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

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