

Original Paper

# A simple and fast micromethod for the analysis of polychlorinated biphenyls in air by sorbent enrichment and ultrasound-assisted solvent extraction

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**Abstract** A combination of sorbent enrichment and ultrasound-assisted solvent extraction has been used to determine polychlorinated biphenyls in air. Analytes were sampled by pumping a known volume of air through a porous polymer (Tenax TA). The enriched adsorbent was transferred into a glass vial, and ultrasound-assisted extraction of the analytes was then performed in *n*-hexane. Quantification was carried out by using gas chromatography coupled to tandem mass spectrometry. Breakthrough volume of the sampling step was studied, indicating that 10 m<sup>-3</sup> of air could be processed without losses of the most volatile compounds. Good recoveries (75–86%) were obtained, and limits of detection at the sub ng m<sup>-3</sup> were achieved for all the analytes. The proposed method is very simple and fast, avoiding the use of large solvent volumes and time-consuming preconcentration steps.

**Keywords** Air analysis · Polychlorinated biphenyls · Gas chromatography–mass spectrometry · Ultrasound-assisted extraction

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# Introduction

The term polychlorinated biphenyls (PCBs) refers to a class of synthetic organic chemicals in which the biphenyl structure has been chlorinated to varying degrees. The group of PCBs contains 209 individual compounds (known as congeners) with varying toxic effects. Known sources of PCBs in the environment are always anthropogenic. PCBs enter the environment as trade name mixtures Arochlor containing a variety of individual components and mixtures. Because they do not burn easily and are good insulating materials, PCBs have been widely used as coolants and lubricants in transformers, capacitors and other electrical equipment. The manufacture of PCBs stopped in the USA in October 1977 because of evidence that PCBs caused harmful effects. Before 1977, waste that contained PCBs was generated during the manufacture and use of PCBs, and such waste was placed in poorly maintained sites. Today, PCBs can be released into the environment from these sites; PCBs can also be released into the environment by municipal and industrial incinerators from the burning of organic wastes [1, 2].

Polychlorinated biphenyls in air can be present in aerosols and as vapours that eventually return to the land and water by settling or washout by snow and rain. PCBs may remain in the air for an average of more than 10 days depending on the type of PCB. Once in the air, PCBs can be carried over large distances. They have been found in areas far away from where they were released into the environment. People who live near hazardous waste sites that contain PCBs may be exposed primarily by breathing air that contains PCBs. Breathing indoor air in buildings that have electrical parts that contain PCBs may also be a source of human exposure [3]. The Department of Health and Human Services has determined that PCBs may reasonably be anticipated to be carcinogens. The International Agency for Research of Cancer has determined that PCBs are probably carcinogenic to humans [4]. EPA has classified PCBs as a Group B2, probable human carcinogen. No reports of effects in humans following acute (short-term) exposure to PCBs are available, but chronic inhalation exposure of workers to PCBs has been reported to result in respiratory tract symptoms [5]. The National Institute for Occupational Safety and Health (NIOSH) recommends workers do not breathe air with more than 0.001 mg of PCBs per cubic metre of air ( $0.001 \text{ mg m}^{-3}$ ) for a 10 h workday, 40 h work week. The Occupational Safety and Health Administration (OSHA) requires workplace exposure limits of  $0.5 \text{ mg m}^{-3}$  (54% chlorine) or  $1 \text{ mg m}^{-3}$  (42% chlorine) for an 8-h workday to protect workers from non-cancer harmful health effects [4].

Due to their low concentrations in air, PCBs are usually sampled by pumping a known volume of air through a solid adsorbent where the compounds are retained. Silica gel, Florisil, active

charcoal, XAD-2 resin, styrene–divinylbenzene functionalised with *N*-vinylpyrrolidone, Tenax, or polyurethane foam [6–12] are some of the adsorbents used. Most of these adsorbents are usually extracted by using Soxhlet solvent extraction, which is very time-consuming and requires large volumes of organic solvents, resulting in diluted extracts that need to be concentrated before the chromatographic analysis.

Gas chromatography (GC) is the technique selected for the analysis of PCBs using an electron capture detector (ECD) with low-resolution mass spectrometry (MS) working either in the electron ionisation or chemical ionisation mode. When higher selectivity is required, tandem mass spectrometry (MS-MS) [10] or high-resolution mass spectrometry can be used for the analysis.

The aim of this work is to present a simple and fast method for the determination of PCB in air based on the combination of sorbent enrichment on Tenax TA and ultrasound-assisted solvent extraction. Tenax TA is selected as the polymeric phase owing to its fast desorption kinetics [13]. As such, using a small amount of sorbent, a solvent volume of less than 1 mL can be used to desorb the target PCBs.

## Experimental

### Reagents

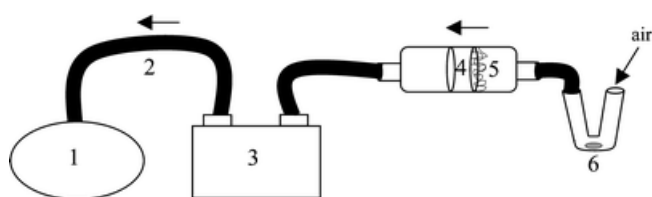
The PCB congeners, 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-pentachlorobiphenyl (PCB-101), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-138), 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-153), 2,3,3',4,4',5'-hexachlorobiphenyl (PCB-156) and 2,2',3,4,4',5,5'-heptachlorobiphenyl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

Standard stock solutions of 2,000–4,000  $\mu\text{g mL}^{-1}$  of individuals were prepared in isooctane, and working mixture solutions were obtained by appropriate dilution in isooctane or *n*-hexane. All solutions were stored in amber-coloured vials at  $-20^{\circ}\text{C}$ .

### Air sampling and extraction of PCBs

By using a vacuum pump working at  $100\text{ L min}^{-1}$ , a known volume of air was pumped through a glass tube containing 25 mg of Tenax TA adsorbent (mesh size 60/80) retained by a little plug of glass wool (Aldrich, Madrid, Spain) (Fig. 1). Only Teflon (PTFE) tubing was used for connections.

The adsorbent was then poured into a glass vial, and the analytes were extracted into 0.50-mL *n*-hexane using an ultrasound bath (model P-Selecta) for 10 min. A 2- $\mu$ L aliquot of the extract was injected into the chromatographic port.



**Fig. 1** Schematic diagram of the air-sampling device: 1 vacuum pump, 2 PTFE connectors, 3 flow meter, 4 Tenax TA, 5 glass wool, 6 glass tube containing analytes

To study the retention of PCBs on Tenax, 100  $\mu$ L of a standard mixture of the target PCBs in *n*-hexane was directly spiked on 25 mg of the adsorbent to achieve a concentration of 4 ng mg<sup>-1</sup> for each congener. The spike was left to homogenise with the adsorbent for several hours. The spiked Tenax was then treated as described above. In some preliminary experiments, 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 ultrasound-extracted with 0.5 mL *n*-hexane.

## Gas chromatography–tandem mass spectrometry

Analyses were performed on a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA) equipped with a 1079 split-splitless injector and an ion trap mass detector Varian Saturn 2000 (Varian Chromatography Systems, Walnut Creek, CA, USA) with a waveboard for MS-MS analysis. The system was operated by Saturn GC-MS WorkStation v5.4 software. The target compounds were separated on a 25-m length $\times$ 0.25-mm id, CP-Sil8 CB Low bleed/MS column coated with a 0.25- $\mu$ m film. The GC oven temperature program was: 130°C hold 2 min, rate 30°C min<sup>-1</sup> to 170°C, hold for 10 min, rate 3°C min<sup>-1</sup> to 250°C, rate 20°C min<sup>-1</sup> to a final temperature of 280°C, hold for 10 min. Helium (purity 99,999%) was employed as carrier gas with a constant column flow of 1.2 mL min<sup>-1</sup>. 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<sup>-1</sup>. Injector temperature was held constant at 270°C. The mass spectrometer was operated in electron ionisation (EI) mode at 70 eV. The mass range was scanned from *m/z* 40 to 650 at 1 s/scan for the full scan mode. Trap, manifold and transfer line temperatures were maintained

at 250, 50 and 280°C, respectively. For MS-MS, all compounds were analysed by using a resonant waveform type.

## Results and discussion

In addition to the common MS parameters listed in Table 1, each segment included a previously optimised ion preparation method (IPM) which defines MS-MS parameters and  $m/z$  can range (Table 2). Instrumental linearity was evaluated in the range 10–500 ng mL<sup>-1</sup>, obtaining correlation coefficients ( $R^2$ ) higher than 0.99 [14].

**[Table 1 will appear here. See end of document.]**

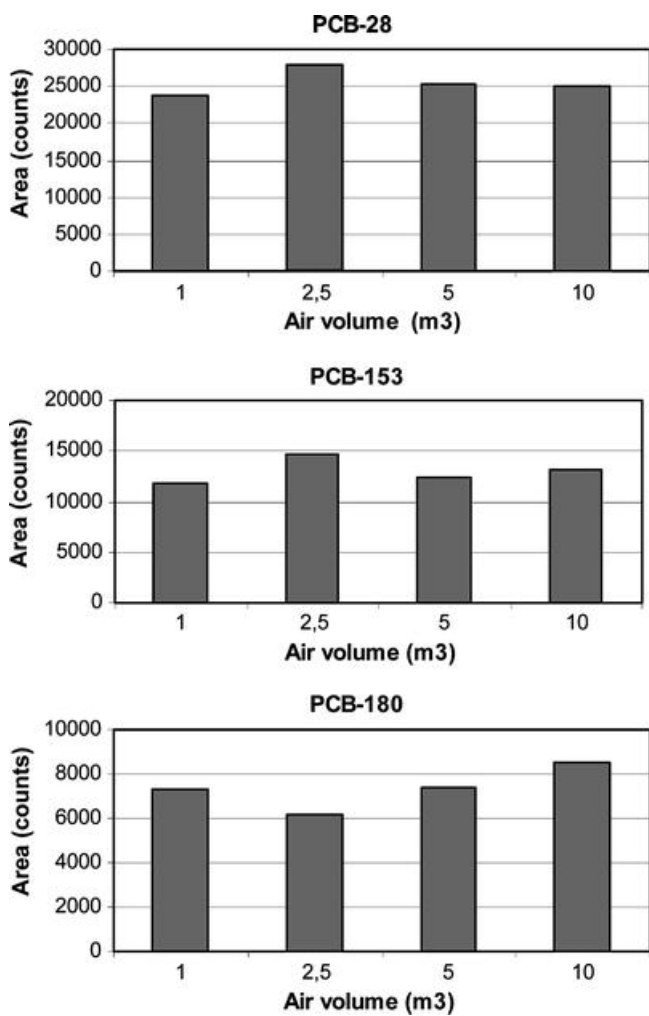
**[Table 2 will appear here. See end of document.]**

Tenax TA was the adsorbent selected for the sampling step. Owing to its fast desorption kinetics it is advantageous over other sorbents such as PUF to be combined with a rapid ultrasonic solvent desorption. Under the experimental conditions selected, extraction recoveries from spiked Tenax (100 ng of each congener) ranged from 72.3 to 97.9% (%RSD=8.0–14.3), and are shown in Table 3.

**[Table 3 will appear here. See end of document.]**

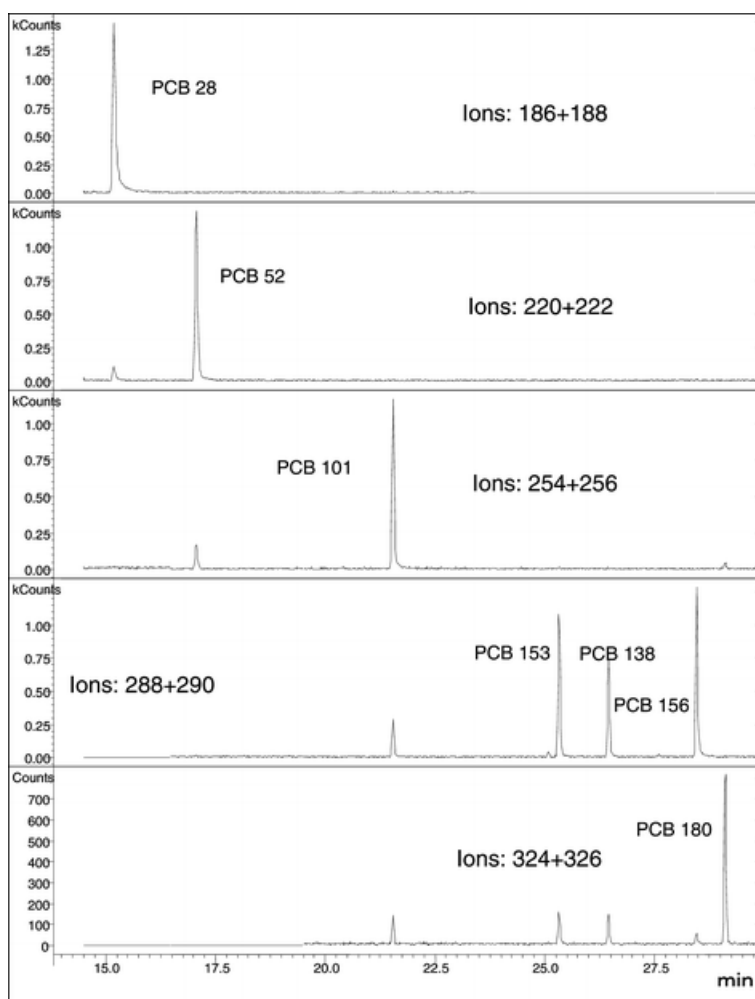
Air analysis was carried out by following the experimental procedure described in the “Experimental” section. To ensure blank air samples, sampling was carried out in a clean room provided with a laminar flow system. Air blanks and adsorbent blanks were analysed for every set of experiments.

In order to evaluate the possible breakthrough of the adsorbent, experiments were initially performed by sampling 1 m<sup>-3</sup> of air through a system of two consecutive tubes each containing a portion of adsorbent (see “Experimental” section). Each portion was extracted by ultrasound-assisted solvent extraction, and the analysis of both extracts showed that analytes were not recovered in the second Tenax portion. Thus, to evaluate if larger air volumes could be collected without breakthrough of the adsorbent, volumes of air from 1 to 10 m<sup>-3</sup> were sampled. The results obtained are shown in Fig. 2 for three selected PCBs (PCB-28, PCB-153 and PCB-180). As can be seen in the figure, breakthrough did not occur for any polychlorinated biphenyl even when volumes of air sampled were as large as 10 m<sup>-3</sup>. Figure 3 shows the mass chromatograms obtained by using the proposed method for the analysis of an air sample which was forced to pass through Tenax TA spiked with the target polychlorinated biphenyls (40 ng m<sup>-3</sup>).



**Fig. 2** Variation of the chromatographic response (expressed as area counts) for three selected polychlorinated biphenyls (PCB-28, PCB-153 and PCB-180) with the volume of air sampled

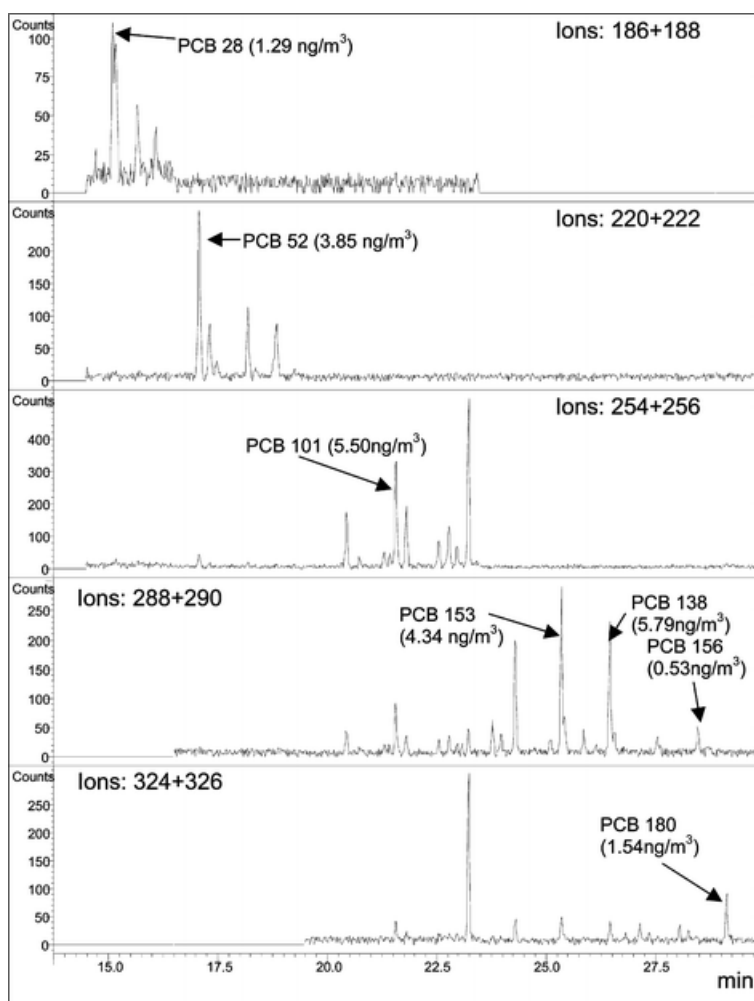
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**Fig. 3** Mass chromatograms obtained using the proposed method for the analysis of an air sample contaminated with the target polychlorinated biphenyls ( $40 \text{ ng m}^{-3}$ )

The performance of the method was evaluated for a sampling volume of  $2.5 \text{ m}^{-3}$  air. Recoveries of the target PCBs using the total sampling–extraction procedure ranged from 75.2 to 96.2% with %RSD values of 4.4–12.7% (Table 3). These results indicate that the sampling step do not increase the variability of the method. The detection limits (LODs, signal-to-noise ratio of 3) and the quantification limits (LOQs, signal-to-noise ratio of 10) are also presented in Table 3. LOD values were between  $0.12$  and  $0.40 \text{ ng m}^{-3}$ . Sensitivity of the method could also be improved by sampling  $10 \text{ m}^{-3}$  of air.

Figure 4 shows the mass chromatograms of a real air sample taken in a laboratory area in which a contaminated transformer oil sample was being manipulated. The contamination profile detected in this air sample matched that of Arochlor 1254. Individual congeners could be quantified at concentrations between  $0.5$  and  $5.8 \text{ ng m}^{-3}$ , as shown in fig. 4.



**Fig. 4** Mass chromatograms of an air sample taken in a laboratory area where a real contaminated transformer oil was being manipulated

## Conclusions

A method for the analysis of polychlorinated biphenyls in air samples is proposed. The method is based on the retention of the target compounds on a very small amount of Tenax TA and their rapid desorption using a small volume of *n*-hexane as the extraction solvent. As such, the method is very simple, inexpensive and fast because the use of this adsorbent avoids some problems encountered with more adsorbent polymers, such as expanded polyurethane, which need higher solvent volumes and more tedious operations to quantitatively recover the analytes. With the proposed method, both sampling and analysis are completed in about 60 min, thereby allowing high-throughput analysis of PCBs. The sensitivity of the method was demonstrated, since limits of detection were below  $0.25 \text{ ng m}^{-3}$  for most of the target compounds, and can be improved by

increasing the sample volume. Finally, the method was applied to a real air sample in which some PCBs could be identified and quantified.

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**Table 2** Ion preparation method 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 3** Efficiency of the ultrasound-assisted extraction, efficiency of the total sampling-extraction method, limits of detection and limits of quantification of the proposed method

PCB	Ultrasound extraction recovery, % (%RSD)	Total sampling-extraction recovery, % (%RSD)	Limits of detection (S/N= 3, ng m <sup>-3</sup> )	Limits of quantification (S/N= 10, ng m <sup>-3</sup> )
28	97.9 (8.0)	96.2 (6.6)	0.12	0.39
52	93.2 (8.8)	92.1 (4.4)	0.14	0.46
101	89.1 (12.0)	92.3 (7.6)	0.21	0.70
153	84.9 (14.3)	91.0 (9.4)	0.23	0.75
138	83.2 (13.2)	90.0 (10.4)	0.24	0.80
156	72.3 (13.6)	75.6 (12.7)	0.19	0.65
180	75.0 (11.1)	75.2 (10.3)	0.40	1.35