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Determination of polychlorinated biphenyl compounds in indoor air samples

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Abstract

A simple procedure for the determination of six non-coplanar polychlorinated biphenyls (PCBs) in medium volumes of indoor air is described. Samples are forced at $6 \text{ m}^3/\text{h}$ through a device consisting of a quartz filter connected to the end of a conventional solid-phase extraction cartridge containing 60 mg of functionalized styrene–divinylbenzene. PCBs retained on the sorbent are directly eluted with 2 ml of hexane. Those associated to airborne particulate matter are microwave extracted in 10 min using 15 ml hexane–acetone (1:1). The proposed procedure is favorably compared to the use of polyurethane cylinders for the concentration of PCBs in terms of solvent consumption and rapidity of the desorption step. Furthermore, the functionalized sorbent showed higher breakthrough volumes than Amberlite XAD-2 for PCBs in gas phase. Quantification limits between 2 and $40 \text{ pg}/\text{m}^3$ were obtained for six PCBs (from di- to heptachlorobiphenyls) using GC–electron-capture detection. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polychlorinated biphenyls (PCBs) have been recognized as environmental contaminants since the mid-1960s when they were widely used as transformer and capacitor oils, cutting oils, hydraulic oils, heat transfer fluids, paints or pesticides. The accumulation of these compounds in different environmental matrices, such as soil or living organisms, is due to their stable and lipophilic chemical nature [1].

Because of their low volatility, levels of PCBs in atmospheric samples are much lower than in soils and fat tissues. However, air plays an important role

in the global distribution of these contaminants, which can be present in the gas phase and also associated to suspended particles. Indoor air is also a potential source of human exposition to PCBs in polluted closed environments [2–5]. Thus, the quality of indoor air needs to be specially controlled since long exposure periods to these compounds cause known toxic effects [6–9]. Typical concentrations of PCB compounds in indoor air are in the high pg/m^3 or even the low ng/m^3 range, much higher than in outdoor open atmospheres [6]. However, a pre-concentration step is still necessary prior to their analytical determination. Nowadays, in most of the sampling systems for PCBs air is pumped through different kinds of solid traps where the gaseous analytes are retained, such as silica gel [3], Florisil [10], active charcoal [17], Amberlite XAD-2

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[11,12], Tenax [13] or polyurethane foam [14]. The particulate matter is usually collected on a quartz or glass fiber filter. The polyurethane foam (PUF) has been extensively used in monitoring of air contaminants, and it is recommended in some official methods [US Environmental Protection Agency (EPA TO-10A)] [15–19]. This porous polymer allows high sampling flow-rates, making possible the concentration of several hundreds or even thousands of cubic meters of air. However, its elution involves the traditional time- and solvent-consuming Soxhlet extraction. In fact, with the exception of Tenax, most of the solid sorbents used in the pre-concentration of PCBs in air samples are eluted using this method, which requires several hours to perform, uses relatively large volumes of organic solvents and results in a diluted sample that needs to be concentrated before the chromatographic analysis.

Regarding the determination technique, GC–electron-capture detection (ECD) and GC–MS with electron impact or chemical ionization are the most widely used techniques to carry out PCB analysis. GC–ECD requires a previous extensive clean-up procedure while the main advantage of GC–MS is the structural information provided joined to the possibility of a library search [20–24]. If a higher selectivity in the determination is necessary, tandem GC–MS/MS and GC–high resolution (HR) MS are valuable alternatives to GC–MS.

The aim of this study is the development of an alternative to the EPA TO-10A method, allowing the sampling of medium volumes of air and fastening and simplifying the desorption of the gaseous PCBs trapped on a sorbent, as well as those associated to the particulate matter retained on the filters. A solid sorbent, consisting of a polymer of styrene–divinylbenzene functionalized with N-vinylpyrrolidone groups has been evaluated to carry out the concentration of these analytes in indoor air samples (until 50 m³). Because of the small amount of sorbent used, only 2 ml of hexane are required to recover the compounds successfully. Moreover, microwave-assisted extraction, which has been used in the last years to extract organic contaminants from different environmental matrices like soil or sludge [25–31], was evaluated for the desorption of PCBs from fly ashes retained on the quartz filters of the sampling unit.

2. Experimental

2.1. Apparatus

Analysis of PCBs was performed on an HP 5890 series II gas chromatograph (Hewlett-Packard, Avondale, MA, USA) equipped with a ⁶³Ni electron-capture detector and a split/splitless injection port. Injections were done using an automatic autosampler device. A Hewlett-Packard BP-1 (30 m×0.25 mm) poly(dimethylsiloxane) capillary column, 0.25 μm film thickness, was used for the separation of the PCB congeners. Nitrogen was employed as carrier gas at a constant head pressure of 41 kPa and also as make-up gas in the ECD system (45 ml/min). Injections were performed in the splitless mode (purge time 1 min), and the injection volume was 1 μl. The split flow was adjusted to 50 ml/min.

The GC oven was programed as follows: 2 min at 90 °C, first ramp at 20 °C/min to 170 °C (held for 7.5 min), second ramp at 3 °C/min to 250 °C (held for 5 min). Injection port and detector temperatures were adjusted to 250 °C and 280 °C, respectively.

Microwave extractions of PCB compounds associated to particulate matter were performed in a MES-1000 microwave extraction system (CEM, Matthews, NC, USA). This system can perform 12 simultaneous extractions in PTFE closed vessels with a volume of 100 ml. It controls the temperature and the pressure in one vessel and assumes the same values for the others.

2.2. Reagents and materials

HPLC-grade acetone and diethyl ether were obtained from Merck (Darmstadt, Germany), hexane and isooctane for trace analysis were also purchased from Merck. Glass wool, anhydrous sodium sulfate, Florisil (60–100 mesh), alumina grade I (150 mesh), and Amberlite XAD-2 (60–80 mesh) were obtained from Aldrich (Milwaukee, WI, USA). Sodium sulfate, Florisil and alumina were stored at 105 °C. Alumina was deactivated with water until grade II before use.

Commercial polyurethane foam Orbo-1000 cylinders (76 mm×2 mm I.D.) (Supelco), Oasis HLB Vac RC cartridges containing 60 mg of styrene–divinylbenzene functionalized with N-vinylpyrrolidone

(Waters, Milford, MA, USA) and laboratory-filled Amberlite XAD-2 Vac RC cartridges (60 mg) were used to concentrate PCB compounds from air samples. Amberlite and Oasis HLB sorbents were pre-cleaned using 10 ml of methanol, PUF cylinders were Soxhlet extracted with 90 ml of hexane–diethyl ether (95:5) for 24 h. After that, all sorbents were dried with a flow of nitrogen and stored wrapped in aluminum foil pre-cleaned with hexane. Commercial cartridges assemblies (Supelco) furnished with quartz filters (I.D. 32 mm) were directly connected to the body of the PUF holder or the Vac RC cartridges (containing Amberlite or functionalized styrene–divinylbenzene) after cutting the top edge of the polypropylene syringe.

2.3. Standards and samples

A mixture containing six PCB congeners in iso-octane (2,6-dichlorobiphenyl PCB 10, 2,4,4'-trichlorobiphenyl PCB 28, 2,2',5,5'-tetrachlorobiphenyl PCB 52, 2,2',3,4,4',5'-hexachlorobiphenyl PCB 138, 2,2',4,4',5,5'-hexachlorobiphenyl PCB 153, and 2,2',3,4,4',5,5'-heptachlorobiphenyl PCB 180, 10 µg/ml of each one) was obtained from Supelco (Bellefonte, PA, USA). Calibration solutions containing the six PCBs at different concentrations between 10 and 200 ng/ml and working mixtures used to spike ash samples were prepared in hexane. All PCB solutions were conserved in the dark and refrigerated at 4 °C.

A sample of ash from the combustion of lignocellulosic material (fraction under 60 µm, total carbon 6.8%) was spiked with a standard of the six PCB congeners in hexane. The slurry was manually mixed, allowed to air-dry for 2 weeks and then stored at 4 °C for 1 month before analysis.

In order to study the retention of PCBs in the sorbent materials (PUF, Amberlite XAD-2 and the functionalized styrene–divinylbenzene), 80 µl of a PCB standard in hexane were spiked well directly over the sorbent (retention efficiency experiments), well over ca. 100 mg of pre-cleaned (Soxhlet extracted with hexane:diethyl ether, 95:5) glass wool placed inside the solid-phase extraction syringe, over the sorbent (collection efficiency experiments). After allowing the evaporation of the solvent, the open edge of the cartridge was connected to a quartz filter

to avoid airborne particulate matter deposition on the sorbent material. A second cartridge containing the same sorbent was serially connected to the first one, in order to detect the breakthrough of the sorbent and to prevent human exposition to PCBs. Indoor air was forced through the sampling system at 6 m³/h using a vacuum pump. A gas counter was placed before the pump to measure the volume of air passed through the sampling system.

In a second set of experiments, the sampling unit was placed inside a closed box containing a glass beaker with 10 g of ashes previously spiked with PCBs (1 µg/g). The sample was magnetically stirred during the experiment to increase the amount of suspended particles inside the box, and thus the amount of ashes trapped in the quartz filter. Once the sampling step was finished, the quartz filter and each one of the sequential sorbent cartridges were individually extracted.

2.4. Extraction procedure

PCBs retained in the Amberlite XAD-2 or the Oasis cartridges were eluted using 2 ml of hexane. Desorption of PCBs from the PUF cylinders was carried out by Soxhlet extraction for 24 h using 90 ml of a mixture hexane:diethyl ether (95:5) according to the EPA TO-10A method. This extract was concentrated on a Turbo Vap II workstation (Zymark) by means of a 55 kPa nitrogen current at 25 °C until it reached a final volume of ca. 2 ml.

The amount of ashes collected in the quartz filter was determined by mass. The full filter or a part of it were Soxhlet extracted using the procedure already described for the PUF cylinders. Alternatively microwave extractions with 15 ml hexane:acetone (1:1) at 115 °C for 10 min, according to a procedure described in the bibliography for sediment samples were also performed [25]. Extracts were concentrated to ca. 2 ml and then subjected to the clean-up procedure.

2.5. Clean-up

Extracts from the polymeric materials (Amberlite, Oasis HLB or PUF after volume reduction) and from quartz filters, were passed through a Pasteur pipette filled with 0.25 g of anhydrous sodium sulfate, 0.25

g of Florisil and 0.5 g of alumina grade II, previously conditioned with 10 ml of hexane [32]. PCBs were eluted with 5 ml of hexane and this eluate reduced to 1 ml before injection in the chromatographic system.

3. Results and discussion

3.1. PCBs in gas phase

3.1.1. Retention efficiency

Table 1 compares the recoveries for PCB compounds directly spiked over Oasis and Amberlite XAD-2 cartridges containing the same amount of sorbent. After passing 5 m³ of air through the system, both materials allowed the quantitative recovery of the studied PCBs. However when 50 m³ of air were sampled, the recoveries for PCB 10 were significantly lower for Amberlite than for Oasis, which suggested the breakthrough of the first material for this compound. The presence of the most volatile compounds in the extract of the Amberlite back cartridge confirmed this supposition (ca. 10% of the PCB 10 amount spiked over the first syringe, and traces of PCB 28 and PCB 52). Recoveries using the Oasis sorbent for 5 and 50 m³, were similar to those obtained for the same PCB compounds spiked over PUF cylinders, which were Soxhlet extracted for 24 h according to the EPA TO-10A method. Moreover, the extract from the PUF cylinders needs to be concentrated to ca. 2 ml prior to the clean-up step. The pre-cleaning of the Oasis HLB sorbent is also faster and it uses a smaller volume of solvent than the Soxhlet extraction, which should be performed in

Table 2

Collection efficiency for PCB compounds using Oasis cartridges

Compound	Recovery (%)	SD
PCB 10	86.1	4.3
PCB 28	87.8	4.6
PCB 52	85.5	4.8
PCB 153	98.7	3.7
PCB 138	95.0	4.1
PCB 180	90.2	6.9

Percentages of recovery correspond to the PCBs remaining in the glass wool plus those retained in the polymeric sorbent ($n=3$ samples).

the pre-cleaning of the PUF plugs. Thus, Oasis cartridges were selected for the following experiments.

3.1.2. Collection efficiency

Table 2 shows the recoveries for PCB congeners in gas phase using an Oasis HLB sorbent. These values corresponded to the sum of PCBs trapped in the first sorbent cartridge plus those remaining in the glass wool after sampling 5 m³ of air. After disconnecting the vacuum source from the sampling device, the plug of glass wool was sonicated with 6 ml of hexane for 5 min, concentrated to 1 ml and directly analyzed without a clean-up step of the organic extract. The sorbent was eluted and the extract purified according to the Experimental section. Global recoveries are similar to those given in Table 1 and clearly show the capacity of the Oasis HLB sorbent to retain PCBs in gas phase. Distribution of PCB congeners between the sorbent and the glass wool was not the same for all the samples, however the amount of each congener remaining in

Table 1
Comparison of retention efficiencies with different sorbents ($n=3$ samples)

	Recovery (%)±SD				
	Amberlite XAD-2		Oasis HLB		PUF
	5 m ³	50 m ³	5 m ³	50 m ³	5 m ³
PCB 10	85.2±4.6	74.1±4.2	89.0±3.5	90.9±4.9	88.2±2.6
PCB 28	93.5±5.1	79.9±4.4	94.7±3.1	90.3±6.8	86.1±1.9
PCB 52	95.5±2.1	76.9±8.2	91.3±4.4	90.1±3.8	90.4±2.3
PCB 153	105.1±3.2	92.2±10.1	97.3±5.4	93.0±5.9	104.1±2.0
PCB 138	103.5±2.0	88.6±11.2	96.9±6.2	92.1±6.0	102.9±2.2
PCB 180	100.8±2.8	88.1±11.7	98.2±7.2	93.6±7.2	104.6±3.0

Table 3
Distribution of PCB congeners between the glass wool plug and the Oasis HLB sorbent in a collection experiment ($n=1$)

Compound	Recovery (%) in the sorbent	% Remaining in the glass wool plug
PCB 10	87.8	2.3
PCB 28	87.0	3.9
PCB 52	88.0	2.1
PCB 153	74.0	23.0
PCB 138	62.2	30.5
PCB 180	22.0	64.0

Sampled air volume 5 m³.

the glass wool increased with the decrease of its vapor pressure (from 1.1 Pa for PCB 10 to $1.3 \cdot 10^{-4}$ Pa for PCB 180 at 25 °C), Table 3.

3.2. PCBs associated to ash samples

A preliminary comparison between Soxhlet and microwave extraction to recover PCB compounds from fly ashes was performed directly, using 100 mg of the bulk spiked sample prepared as described in the Experimental section (this sample had been Soxhlet extracted previously to the spike to confirm the absence of PCBs contamination). Only in the case of PCB 10, slightly higher recoveries were obtained with Soxhlet than with microwave extraction, Table 4. Anyway, with both methods the concentrations found were in reasonable agreement with the spiked level, showing that not-significant PCB losses occurred during sample preparation and storage.

After that, 10 g of the spiked ash sample were placed in a 250 ml glass beaker and stirred magnetically. The sampling device was situated (upside down) 15 cm over the beaker, and 5 m³ of air were passed through the system. The amount of ash retained over the filter (ca. from 30 to 80 mg) was

Table 4
Direct extraction of PCB compounds from ashes ($n=3$ samples)

Compound	Recovery (%) \pm SD	
	Soxhlet extraction	Microwave extraction
PCB 10	90.2 \pm 8.2	75.6 \pm 6.7
PCB 28	87.8 \pm 3.3	84.8 \pm 8.7
PCB 52	103.3 \pm 7.3	87.3 \pm 9.2
PCB 153	100.4 \pm 6.9	91.8 \pm 8.2
PCB 138	97.7 \pm 6.7	93.0 \pm 8.7
PCB 180	92.7 \pm 7.4	97.3 \pm 9.5

determined by the increase of its mass. After finishing the sampling step, the filter and the first sorbent cartridge were individually extracted. PCBs were not detected in the extract of the polymeric sorbent, showing the expected strong interaction of these compounds with the ash sample.

In the first approach, the whole filter was Soxhlet extracted. Concentrations found (ng of each congener per g of ash retained over the quartz filter) were normally higher than the PCB concentrations in the bulk of the spiked ash sample (results not shown). As PCB compounds were not detected in particulate matter suspended in the laboratory indoor air (blank samples), we assumed that the ash trapped in the quartz filter was not representative of the bulk sample. Probably, ash particles retained on the filter have a smaller average diameter than those particles in the sample, therefore they present a higher superficial area per unit of mass and a higher concentration in PCBs than the bulk of the ash material.

In further experiments each filter was weighed and divided in four equal parts. Two of them were Soxhlet extracted and the other ones subjected to microwave extraction with hexane:acetone (1:1). Table 5 shows the results for three samples extracted using both methods, assuming that the same amount of ash is present in each half of the filter. Differences between results obtained with both methods for each congener, were statistically evaluated with the t -test ($t_{\text{exp}} = (\bar{x}_d/s_d) \sqrt{n}$). For a confidence limit of 95% the t -experimental values (0.01 for PCB 10, 1.03 for PCB 28, 0.83 for PCB 52, 2.99 for PCB 153, 2.66 for PCB 138 and 1.54 for PCB 180) were always lower than the tabulated one (4.36). Therefore, not significant differences were found between the efficiency of both extraction techniques. However, this statement should be confirmed with the analysis of a

Table 5

Comparison of Soxhlet vs. microwave for the extraction of PCBs from ashes retained on the quartz filters

	Extraction technique	Found concentrations (ng/g)					
		PCB 10	PCB 28	PCB 52	PCB 153	PCB 138	PCB 180
Sample 1	Soxhlet	1271.8	1171.2	1617.6	1707.9	1642.2	1651.8
	Microwave	1353.9	1268.5	1567.3	1645.6	1567.8	1510.7
Sample 2	Soxhlet	806.6	948.8	1110.0	1369.2	1347.8	1372.8
	Microwave	822.4	1096.3	1162.2	1307.3	1211.6	1255.1
Sample 3	Soxhlet	954.4	1109.8	1342.9	1467.9	1426.7	1371.5
	Microwavew	854.8	1054.0	1201.3	1452.5	1395.0	1394.0

higher number of ash samples, preferably with different compositions.

3.3. Clean-up

Two protocols were considered to purify the extracts from the polymeric sorbents and also those corresponding to the fly ashes. The first one (recommended in the EPA TO-10A method) uses alumina deactivated to grade IV. The second one combines the use of alumina deactivated to grade II, with Florisil and anhydrous sodium sulfate. In general less interferences were observed in the GC–ECD chromatograms when the second clean-up procedure was used, Fig. 1.

3.4. Quantification limits

Quantification limits for PCBs in gas phase were estimated for a ratio $S/N=10$, assuming that 50 m^3 of air are forced through a 60 mg Oasis HLB sorbent, which corresponds to a sampling period of 8 h. The obtained values (15 pg/m^3 PCB 10; 40 pg/m^3 PCB 28; 30 pg/m^3 PCB 52; 8 pg/m^3 PCB 153; 8 pg/m^3 PCB 138; 3 pg/m^3 PCB 180) are low enough to identify harmful levels of PCB compounds in indoor air working atmospheres. Quantification limits for PCBs associated to suspended particulate matter are very high (over 10 ng/g for each congener) because of the tiny amount of particles collected in each filter. However, in order to control human exposition to PCBs in indoor working areas via respiration, the extracts corresponding to PCBs in

gas phase and those ones corresponding to PCBs associated to particles should be combined before the quantification of these compounds.

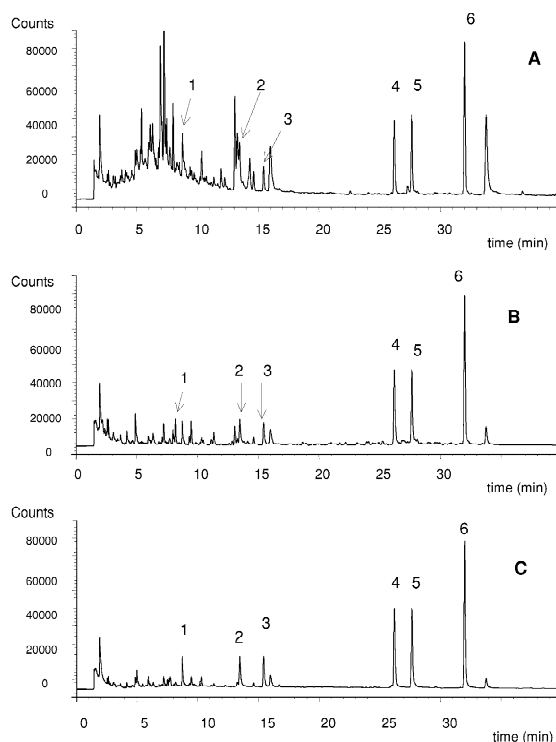


Fig. 1. GC–ECD chromatograms corresponding to the extract of an Oasis cartridge. Sampled air volume 10 m^3 . Spiked amount 80 ng of each congener. 1. PCB 10; 2. PCB 28; 3. PCB 52; 4. PCB 153; 5. PCB 138; 6. PCB 180. (A) Chromatogram before clean-up. (B) Chromatogram after clean-up with alumina grade IV. (C) Chromatogram after clean-up with alumina grade II, Florisil and sodium sulfate.

4. Conclusions

The efficiency of a commercial sorbent for the concentration of six PCB compounds in gas phase has been demonstrated. Because of the high retention of PCBs over the Oasis HLB polymer, 60 mg of this material allowed the concentration of at least 50 m³ of indoor air, at flow-rates of 6 m³/h, achieving detection limits in the pg/m³ region. Sorbent conditioning and analyte elutions are carried out using a few milliliters of an adequate organic solvent without the necessity of performing a Soxhlet extraction. Microwave extraction is proven as a valuable alternative to the Soxhlet method for the extraction of six non-coplanar PCBs associated with fly ashes.

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