

Optimization of a microwave-assisted extraction method for the analysis of polychlorinated biphenyls in ash samples

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Abstract

An alternative method for the extraction of polychlorinated biphenyls (PCBs) in ash samples, which is less time and solvent consuming than Soxhlet extraction, is presented. A study was carried out to evaluate the possibilities of microwave-assisted extraction (MAE) to determine exactly which parameters affect the efficiency of the process, since direct extrapolation of extraction conditions for PCBs in other solid matrices, failed when applied to coplanar congeners in ash samples. Influence of the organic solvent on the yield of the extraction was first evaluated using two ash samples with different percentages of carbon. Once the extraction solvent was fixed, the effects of solvent volume, extraction temperature and extraction time were investigated using an experimental design. It was found that the volume of organic solvent played a more important role in the extraction efficiency than the other factors. In the optimal conditions microwave extractions were performed at 110 °C, for 10 min and using 30 ml of toluene. Recoveries higher than 80% were obtained for all the highly chlorinated congeners, including coplanar species, in a spiked ash sample containing a relatively high concentration of carbon. The proposed method was also applied to the determination of PCBs in a reference material of urban dust. Recoveries were similar to those obtained for spiked ash samples.

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1. Introduction

Polychlorinated biphenyls (PCBs) are very stable ubiquitous contaminants. Due to their toxicity and persistence in the environment their production has decreased gradually since 1970s. However, apart from anthropogenic sources, these compounds can also be introduced into the environment unintentionally as byproducts of a wide variety of chemical processes in which hydrocarbons and chlorine are

used as raw materials; especially, in noncontrolled incineration processes. Furthermore PCBs can also escape into the environment in accidental fires where electric equipment and other materials containing these compounds are burnt. From these sources PCBs are released to the atmospheric environment in the gas phase and also associated with suspended particles [1–4].

The high surface area and adsorptivity of these particles combined with low temperatures, can mean that more than half of penta- and higher chlorinated biphenyls present in atmospheric samples, are associated with particulate matter and fly ash. The study of particles (ash) derived from industrial processes, incineration, etc. has been the aim of several works

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focused in the determination of several persistent organic pollutants including PCBs [5–7].

The analysis of PCBs in this type of sample is a multistep process, due to their low concentration level, the presence of interfering analytes and the high surface area of ash particles. Therefore, extraction, clean-up and concentration processes are necessary before analysis, which is normally performed using GC in combination with ECD or MS detection [8,9]. Soxhlet and sonication have been the classic approaches for the extraction of PCBs from solid samples such as soils, sludge, food, ashes, etc. [6,10,11]. Normally, both techniques present very high recoveries; however, they also have some inherent drawbacks: the Soxhlet technique is time and solvent consuming, as is sonication which often requires a number of successive extractions and a high volume of an organic solvent [12]. Microwave-assisted extraction (MAE) using closed vessels can overcome most of these disadvantages achieving quantitative extraction yields using a moderate volume of an appropriate organic solvent and relatively short extraction times [13]. This technique has already been successfully used in the extraction of PCBs and other semivolatile pollutants from solid matrices such as sediments, soils and sludge [14–18]. However, its usefulness in the extraction of PCBs from ash has not been deeply investigated yet. Only, Takaoka et al. used this technique for the extraction of PCBs in ash samples from an urban solid waste incinerator. They found that the yield of the extraction was heavily affected by the nature of the matrix [19].

The aim of this work is the optimization of the experimental parameters for the microwave extraction of PCBs from ash matrices. Several preliminary assays were carried out to determine the effect of the organic solvent in the yield of the process, and the influence of the carbon content of the sample in the efficiency of the extraction. After that, the influence of the solvent volume, extraction time and temperature were evaluated using a surface response factorial design. Obtained recoveries were compared to those corresponding to Soxhlet extraction using the same solvent and matrix, and the proposed procedure was also applied to the determination of PCBs in a certified reference material of urban dust.

2. Experimental

2.1. Apparatus

Analyses of PCBs were performed using two gas chromatographic systems equipped, with ECD and MS detection. The GC–ECD system was a HP 5890 series II gas chromatograph (Hewlett-Packard, Avondale, MA, USA) with a ^{63}Ni electron capture detector and a split/splitless injection port. Injections were done using an autosampler device. Separations were carried out using a Hewlett-Packard BP-1 type capillary column (30 m \times 0.25 mm I.D., d_f : 0.25 μm). Nitrogen was employed as column carrier gas (45 kPa) and also as auxiliary gas in the detector. The GC–MS system consisted of a Varian CP 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a split–splitless injector and connected to an ion-trap mass spectrometer (Varian Saturn 2000). Separations were carried out using a BP-1 type capillary column (25 m \times 0.32 mm I.D., d_f : 0.17 μm). Helium (99.999%) was used as carrier gas at constant column flow of 1.4 ml/min. Mass spectra were obtained in the electron impact mode (70 eV) in the range from 100 to 550 m/z .

In both apparatus 1 μl of a standard mixture or sample extract was injected in the splitless mode (purge time 1 min), using the following GC oven program: 2 min at 90 $^\circ\text{C}$, first ramp at 20 $^\circ\text{C}/\text{min}$ to 170 $^\circ\text{C}$ (held for 7.5 min), second ramp at 3 $^\circ\text{C}/\text{min}$ to 250 $^\circ\text{C}$ (held for 5 min).

Microwave extractions of PCBs from ash samples were performed in a MES-1000 microwave extraction system (CEM, Matthews, NC, USA) equipped with PTFE-lined 100 ml extraction vessels. Numerical analysis of data resulting from the experimental design was carried out by means of the statistical package STATGRAPHICS PLUS for Windows, version 3.3 (Manugistics, USA).

2.2. Reagents and materials

All the trace analysis organic solvents were purchased from Merck (Darmstadt, Germany). Glass wool, anhydrous sodium sulphate, florisil (60–80 mesh) and alumina grade I (150 mesh) were obtained from Aldrich (Milwaukee, WI, USA). Sodium sul-

phate, florisil and alumina were stored at 105 °C. Alumina was deactivated with water until grade II before use.

2.3. Standards and samples

A mixture containing several PCB congeners in isooctane (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). In addition, individual standards of 2,3',4,4',5-pentachlorobiphenyl PCB 118, 3,3',4,4'-tetrachlorobiphenyl PCB 77, 3,3',4,4',5-pentachlorobiphenyl PCB 126, 3,3',4,4',5,5'-hexachlorobiphenyl PCB 169 and decachlorobiphenyl PCB 209, were purchased from Dr. Ehrendorfer (Augsburg, Germany). A mixture of the ten PCBs congeners was prepared in isooctane. Calibration solutions were prepared by dilution of this mixture with the different solvents evaluated during the optimization of the extraction process. All PCBs solutions were conserved in the dark and refrigerated at 4 °C.

A standard of 4,4'-dibromobiphenyl (PBB 15) was obtained from Dr. Ehrendorfer and considered as a possible internal standard. A BP-MS test solution containing a mixture of 62 PCBs congeners (2 µg/ml) in isooctane was obtained from Wellington Labs. (Ontario, Canada) and used to evaluate the efficiency of the chromatographic column.

Two ash samples (fraction under 60 µm) containing 2.8 and 8.7% of carbon (samples A and B) were obtained from the combustion of coal (sample A) and lignocellulosic materials (sample B). In preliminary experiments direct spikes of known amounts (100 ng) of all PCBs were performed over 1 g of each sample just 1 h before their extraction. In further experiments only the sample containing the highest percentage of carbon (sample B) was used. In order to achieve a better simulation of the interaction between the PCBs and the matrix, a mixture was prepared spiking a known amount of this sample with a solution of the ten studied PCB congeners in *n*-hexane. The slurry was left in the dark, and allowed to air-dry for 2 weeks until

constant mass was achieved. It was then stored at 4 °C for 1 month before analysis. Theoretical concentrations of each congener in this sample were 49.8 ng/g (PCB 28), 49.8 ng/g (PCB 52), 62.2 ng/g (PCB 77), 50.6 ng/g (PCB 118), 49.8 ng/g (PCB 153), 49.8 ng/g (PCB 138), 52.5 ng/g (PCB 126), 49.8 ng/g (PCB 180), 56.0 ng/g (PCB 169) and 47.6 ng/g (PCB 209).

A reference material of urban dust (SRM 1649a) with certified concentrations of several PCB congeners and a total carbon content of 17.7% was obtained from the National Institute of Standards & Technology and used to verify the efficiency of the extraction method with a real polluted sample.

2.4. Extraction and clean-up procedure

MAEs of PCBs from ash samples were carried out using different solvents such as *n*-hexane–acetone (1:1), dichloromethane and toluene; Soxhlet extractions were also performed with 90 ml of toluene during 24 h (4–5 cycles per hour). All the extracts were centrifuged and the organic phase concentrated on a Turbo Vap II workstation (Zymark) by means of a 55-kPa nitrogen current at 25 °C until a final volume of ~2 ml. Once concentrated, organic extracts were passed through a Pasteur pipette filled with 0.25 g of anhydrous sodium sulphate, 0.25 g of florisil and 0.5 g of basic alumina grade II, previously conditioned with 10 ml of *n*-hexane [20]. PCBs were eluted with 5 ml of *n*-hexane and then this extract concentrated to 1 ml before injection into the chromatographic system.

3. Results and discussion

3.1. Preliminary experiments: choice of the extraction solvent

Recoveries of PCBs after direct addition over both samples described in the Experimental section are given in Table 1. Microwave extractions were performed using 15 ml of *n*-hexane–acetone (1:1), dichloromethane, or toluene. The extraction time was 10 min and the temperature 115 °C for toluene and *n*-hexane–acetone, and 90 °C in the case of dichloro-

Table 1
Influence of the extraction solvent and ash sample, on the yield of the MAE of the selected PCB congeners

E. solvent Ash sample	Recovery (%) 1-g samples ($n=1$)			
	Hexane–acetone (1:1)		Dichloromethane	Toluene
	A	B	B	B
PCB 28	63.2	63.7	75.5	52.8
PCB 52	70.4	67.7	77.8	48.6
PCB 77	61.0	0.0	15.4	59.9
PCB 118	80.1	33.7	73.1	62.2
PCB 153	75.4	62.7	90.9	69.4
PCB 138	80.0	63.7	83.6	64.4
PCB 126	70.2	0.0	18.5	62.6
PCB 180	60.1	63.5	83.4	66.0
PCB 169	71.0	3.8	15.4	67.2
PCB 209	65.0	67.1	84.4	69.3

methane. In these assays 1 g of ash was taken and GC–ECD was used as detection technique. Non-spiked samples were also extracted using the same solvents, in order to detect any possible contribution from native pollutants to PCB signals in the spiked samples. As shown in the first two columns of Table 1, the recovery of coplanar PCBs (congeners 77, 126 and 169), using hexane–acetone, depends strongly on the type of ash. In the case of sample A, recoveries of the coplanar congeners were similar to those obtained for the noncoplanar species. However, in sample B (which presents the highest level of carbon) congeners 77, 126 and 169 could not be recovered to a significant extent; moreover, the mono–ortho congener 118 was also recovered to a lower extent in comparison to sample A. Therefore, previous published microwave-assisted methods, developed for the extraction of PCBs from solid matrices, soil, sediments and sludge, which normally use hexane–acetone as extraction solvent, are not directly transferable to the extraction of coplanar PCBs from ash samples. Probably, the carbonaceous structure of this matrix is responsible for this behavior. This observation is in agreement with previous results reported for the extraction of coplanar PCBs from dust samples containing moderate percentages of carbon [21]. In fact, it has been demonstrated that carbonaceous materials can be used for the fractionation of noncoplanar and coplanar pollutants because of the stronger interaction of the latter compounds with the sorbent [22]. Further assays

were carried out with sample B, using dichloromethane and toluene as extraction solvents. The latter was the only tested solvent able to recover the spiked coplanar compounds and the rest of congeners to a similar extent (Table 1). The higher extraction efficiency of toluene was probably related to its capacity to produce π – π interactions with the aromatic rings of PCBs, breaking the analyte–sample interaction; therefore this solvent was used in further experiments. The recoveries given in Table 1 are only an indication of the best PCBs extractant for different carbon content ash samples; the values are not really representative of the efficiency of the extraction since analytes were added to ash samples just 1 h before their extraction, and therefore, the analyte–matrix interaction is probably weaker than in a real polluted sample.

3.2. Optimization of microwave extraction conditions: factorial design

Once toluene was selected as the extraction solvent, the effect of time, temperature and volume of solvent in the yield of the extraction were evaluated using a factorial design type 2^3 plus star with a total of 18 randomized experiments divided in two blocks. The extractions corresponding to each block were carried out on 2 consecutive days. In all cases 1.5 g of ash (sample B, 8.7% of carbon) spiked with the ten PCB congeners, and allowed to stabilize for 1 month before extraction, were used. After clean-up

Table 2
Design matrix and found PCB concentrations (ng/ml) for the experiments of the central composite design

Exp.	Block	Time (min)	Temperature (°C)	Volume (ml)	PCB	PCB	PCB	PCB	PCB	PCB	PCB	PCB	PCB	PCB
					28	52	77	118	153	138	126	180	169	209
1	1	10	120	20	51.5	51.8	62.2	51.5	53.3	50.6	53.6	50.8	63.1	51.0
2	1	15	135	25	48.2	55.2	52.2	45.5	48.8	47.7	50.7	47.4	58.1	47.4
3	1	15	135	25	57.2	61.2	67.0	56.8	59.0	56.5	59.0	55.9	67.4	55.1
4	1	20	120	30	72.6	81.7	70.2	61.3	63.5	60.2	63.6	60.9	75.4	61.8
5	1	20	150	30	65.0	60.8	55.7	52.6	54.7	58.0	60.5	50.6	60.5	48.6
6	1	10	150	30	59.3	64.8	64.3	57.6	52.6	56.6	61.4	60.1	69.8	59.2
7	1	10	150	20	48.7	52.3	61.6	52.3	55.6	55.5	53.8	52.6	60.8	52.2
8	1	20	150	20	47.5	88.7	50.6	49.6	52.9	51.9	53.0	52.3	60.3	52.7
9	1	10	120	30	53.1	57.5	67.7	59.5	63.6	60.9	59.5	60.5	70.4	62.0
10	1	20	120	20	47.8	49.5	60.1	51.8	53.9	57.2	53.0	48.9	56.2	46.3
11	2	24	135	25	41.4	42.2	55.0	48.8	52.0	56.4	54.3	51.3	60.9	50.1
12	2	6	135	25	44.5	48.3	60.4	51.1	55.9	52.5	52.8	53.4	62.0	55.5
13	2	15	135	25	53.0	54.5	52.5	46.8	50.7	58.5	52.1	50.5	57.4	53.3
14	2	15	162	25	48.9	52.1	53.0	51.3	52.7	55.4	51.3	49.4	56.8	49.4
15	2	15	135	25	47.4	48.0	55.8	53.2	56.4	56.9	55.2	53.7	63.2	58.3
16	2	15	108	25	44.6	45.0	54.0	47.2	50.9	48.4	49.4	51.5	60.6	54.7
17	2	15	135	34	57.7	61.7	65.7	58.4	64.7	57.5	61.1	59.6	69.9	62.8
18	2	15	135	16	63.3	57.4	49.5	50.9	54.4	53.5	53.1	49.5	56.7	49.2

the final extracts (1 ml) were analyzed by GC–ECD. Concentrations of each congener in these extracts were determined against a calibration curve obtained for standards prepared in toluene. Extraction conditions and found concentrations of PCB congeners in each experiment of the factorial design are given in Table 2.

Table 3 presents the standardized values for the main effects of time, temperature and volume of

Table 3
Standardized values for the main effects of time, temperature and volume of toluene in the efficiency of the microwave-assisted extraction of PCBs from ash (sample B)

Compound	Time (min)	<i>T</i> (°C)	Volume toluene (ml)
PCB 28	0.60	0.13	1.80
PCB 52	0.94	0.84	0.59
PCB 77	−1.59	−1.61	2.86*
PCB 118	−0.74	−0.36	2.96*
PCB 153	−1.38	−0.44	3.79*
PCB 138	0.62	0.33	1.60
PCB 126	0.41	0.21	4.17*
PCB 180	−1.28	−0.80	3.87*
PCB 169	−0.86	−1.29	3.73*
PCB 209	−1.77	−1.3	3.85*

*, Statistically significant factors at the 95% confidence level.

toluene in the efficiency of the microwave extraction of each PCB. Statistically significant factors, for a confidence level of 95%, are those with an absolute value higher than 2.36. Thus, the volume of solvent had a positive and significant influence on the extraction of most PCBs, especially for coplanar congeners and those containing more than four atoms of chlorine in their molecules. For this group of congeners the extraction time and temperature showed a negative influence on the yield of the extraction (except for PCB 126 and PCB 138), but without achieving the statistically significance boundary. For the most volatile species, PCB 28 and 52, the main effects associated with the three considered factors were not statistically significant. First order interactions and quadratic terms did not achieve the statistical significance level for any compound (data not given).

From these results it was decided to keep the extraction time at a low level (10 min) and to carry out the process at 110 °C, the lowest explored temperature in the factorial design. The possibility of improving the efficiency of the extraction using volumes of toluene higher than 30 ml was evaluated using a univariant approach. As nonsignificant improvements were achieved when solvent volumes of

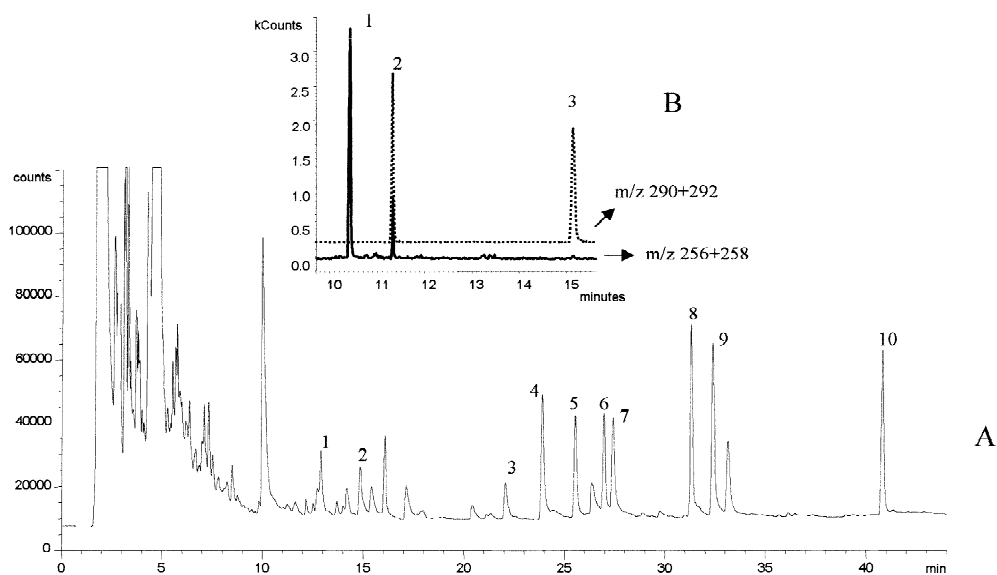


Fig. 1. Chromatogram for the spiked ash sample (sample B). Compounds: 1=PCB 28, 2=PCB 52, 3=PCB 77, 4=PCB 118, 5=PCB 153, 6=PCB 138, 7=PCB 126, 8=PCB 180, 9=PCB 169, 10=PCB 209. (A) GC-ECD chromatogram. (B) GC-MS traces for tri- and tetrachlorobiphenyls.

50 and 70 ml were considered; the extraction volume was limited to 30 ml.

3.3. Choice of the detection technique

Fig. 1 presents a chromatogram corresponding to an extract of the spiked ash sample obtained using the optimized MAE conditions and ECD detection.

In spite of the clean-up step, the presence of potential interference peaks in the earliest region of the chromatogram is evident. As these signals were not observed in GC-MS chromatograms, when the m/z ratios corresponding to the most volatile PCBs congeners were monitored (256+258 for PCB 28 and 290+292 for PCBs 52 and 77), the latter technique was used in further experiments.

Table 4

Linearity, repeatability and estimated quantification limits (S/N 10) of the proposed procedure

Compound	m/z for quantification	Correlation coefficient R^2	Repeatability RSD (%) $n=5$	Instrumental QL (ng/ml)
PCB 28	256+258	0.997	3.2	5
PCB 52	290+292	0.998	3.2	4
PCB 77	290+292	0.995	3.6	5
PCB 118	326+328	0.999	3.3	3
PCB 153	360+362	0.999	2.8	4
PCB 138	360+362	0.999	3.2	4
PCB 126	326+328	0.998	4.5	4
PCB 180	394+396	0.998	4.5	5
PCB 169	360+362	0.997	4.6	4
PCB 209	498+500	0.998	5.0	9

3.4. Performance of the analytical procedure

The linearity of the response in GC–MS was investigated using standard mixtures in toluene containing PCBs concentrations from 10 to 1000 ng/ml. Correlation coefficients higher than 0.995 were obtained for all compounds. Repeatability for consecutive injections of a standard, containing ~100 ng/ml of each congener, ranged from 3 to 5%. Instrumental quantification limits between 3 and 9 ng/ml were obtained for a signal-to-noise ratio of 10, Table 4.

Efficiency of the chromatographic separation (using the BP1 column 25 m×0.32 mm, 0.17 μm) was evaluated using a BP-MS test mixture of PCBs and also individual congeners in order to detect nonresolved species. From the 62 congeners included in the test mixture, the following species led to overlapped peaks in the TIC GC–MS chromatogram: 10+4, 15+18, 44+37, 118+149, 105+188, 128+167, 156+171 and 202+157, Fig. 2. For the rest of congeners resolution (*R*) factors higher than 1.2 were obtained. Furthermore, it was also verified that working under the conditions given in the Experimental section congeners 28+31 and 138+163+164 led to completely overlapped peaks. Also, it should be taken into account that according to the literature, congeners 126 and 129 (not considered in this study) co-elute using BP-1 type capillary columns [8]. This information must be considered when the proposed method is applied to the analysis of real polluted samples.

Recoveries of the MAE were estimated using external calibration. Obtained values were compared with those corresponding to Soxhlet extraction with 90 ml of toluene. As shown in Table 5, absolute recoveries between 80 and 90% were obtained for all compounds, with the exception of congeners 28 and 52, using microwave extraction. On the other hand, the Soxhlet method led to the quantitative extraction of all congeners spiked over the sample, showing a slightly higher efficiency than MAE and a similar variability in the results. Relative recoveries of microwave extraction were calculated using PBB 15 as internal surrogate added to the ash sample before extraction. In this case, results of 104.3±6.7 and 97.5±4.5% were obtained for PCBs 28 and 52, respectively; however, recoveries for the rest of congeners were higher than 100% (from 110 to

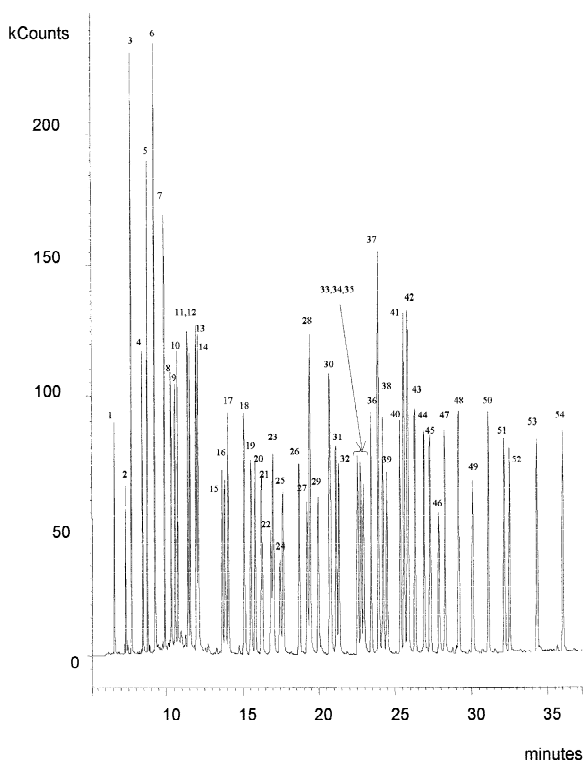


Fig. 2. GC–MS chromatogram for a BP MS test mixture containing 62 PCB congeners. Peak labels: 1=PCB 1, 2=PCB 3, 3=PCB 10+4, 4=PCB 8, 5=PCB 19, 6=PCB 15+18, 7=PCB 54, 8=PCB 28, 9=PCB 33, 10=PCB 22, 11=PCB 52, 12=PCB 49, 13=PCB 104, 14=PCB 44+37, 15=PCB 74, 16=PCB 70, 17=PCB 95, 18=PCB 155, 19=PCB 101, 20=PCB 99, 21=PCB 119, 22=PCB 81, 23=PCB 87, 24=PCB 77, 25=PCB 110, 26=PCB 151, 27=PCB 123, 28=PCB 118+149, 29=PCB 114, 30=PCB 105+188, 31=PCB 153, 32=PCB 168, 33=PCB 138, 34=PCB 158, 35=PCB 126, 36=PCB 178, 37=PCB 187, 38=PCB 183, 39=PCB 128+167, 40=PCB 177, 41=PCB 156+171, 42=PCB 202+157, 43=PCB 201, 44=PCB 180, 45=PCB 191, 46=PCB 169, 47=PCB 170, 48=PCB 199, 49=PCB 189, 50=PCB 208, 51=PCB 194, 52=PCB 205, 53=PCB 206, 54=PCB 209.

120%). As PCBs congeners were not detected in the nonspiked ash (figure not shown), it was assumed that PBB 15 could be used to compensate extraction losses only for these two congeners (but not for the rest of PCBs) and in further experiments only absolute recoveries were considered.

Quantification limits of the whole procedure were estimated for a sample intake of 1.5 g and an organic extract with a final volume of 1 ml. Obtained values

Table 5

Comparison of microwave ($n=6$) and Soxhlet ($n=3$) extraction efficiencies, using GC–MS detection, for a spiked sample (sample B) with an addition of PCBs at the 50 ng/g level

Compound	Microwave extraction ($n=6$)		Soxhlet extraction ($n=3$)	
	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
PCB 28	77.3	10.1	104.1	9.6
PCB 52	72.0	9.1	88.4	6.9
PCB 77	84.2	7.9	104.3	7.9
PCB 118	82.3	4.6	101.8	6.8
PCB 153	81.8	5.9	105.8	3.7
PCB 138	82.0	11.7	103.9	9.8
PCB 126	87.1	5.0	100.3	4.0
PCB 180	82.3	6.3	104.0	4.5
PCB 169	95.4	7.6	101.9	9.0
PCB 209	81.6	10.0	96.9	7.9

ranged from 2 ng/g for PCB 118 to 6 ng/g for PCB 209.

3.5. Analysis of reference material

The proposed procedure was validated using a certified material of urban dust, SRM 1649a. Since ash reference materials containing certified concentrations of PCBs are not available, this urban dust was selected as a particulate matter sample containing a high level of carbon. However, it should be noted that it does not present the same matrix as the ash samples considered in this study. Microwave extractions were performed under optimized conditions; however, in this case the sample intake was reduced to 0.5 g, in order to avoid yellowish extracts after the clean-up step (the material contains 4.4% of carbon soluble in dichloromethane). Obviously, this reduction in the sample intake increased the quantification limits of the analytical procedure by a factor of 3. The found concentrations for some of the PCBs considered in this study are shown in Table 6. Coplanar congeners were not detected in the urban dust sample and levels of PCB 209 in the final extract were under the quantification limits of the proposed method for this compound (18 ng/g, considering a sample intake of 0.5 g). Moreover, PCB 118 (a pentachlorobiphenyl) was not quantified due to its co-elution with PCB 149 (a hexachlorobiphenyl), which is present at higher levels in the urban dust. Congeners 28+31 and 138+163+164 were quantified using the calibration curves obtained

for PCB 28 and PCB 138, respectively. Comparison of found and certified values lead to similar recoveries to those obtained for the same species in the spiked ash sample (sample B, Table 5) showing an acceptable reliability for the proposed extraction method.

4. Conclusions

A microwave assisted method for the extraction of noncoplanar and coplanar PCBs from ash samples has been optimized. From the obtained results it can be concluded that the yield of the extraction for

Table 6
Results for the determination of PCBs in urban dust SRM 1649a; concentrations given in ng/g, $n=4$ samples

Congener	Certified	Found	Recovery (%) (urban dust)
PCB 28	18.5±1.2	25.3±1.9 ^a	70.7±7.6
PCB 31	17.3±1.4		
PCB 52	24.65±0.97	17.9±1.6	72.6±9.2
PCB 138	69.7±7.5 ^b	68.2±4.1 ^b	97.8±6.1
PCB 163			
PCB 164			
PCB 153	82.5±8.0	65.1±2.6	78.9±4.0
PCB 180	78.7±8.2	68.2±8.9	86.7±13.0
PCB 209	8.04±0.77	N.q.	

N.q., below quantification limits.

^a Found concentration for congeners 28+31.

^b Certified and found concentrations for congeners 138+163+164.

coplanar species is highly dependent on the composition of the ash matrix, and the nature of the extraction solvent: thus *n*-hexane–acetone mixtures and dichloromethane which have been used for the extraction of PCBs from solid samples, failed in the extraction of coplanar congeners from ash samples with high levels of carbon. The main advantages of the proposed procedure are the low consumption of organic solvents and, particularly, the rapidity of the extraction, which was performed in only 10 min achieving absolute recoveries higher than 70% for all investigated congeners.

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