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Determination of chlorophenols by solid-phase microextraction and liquid chromatography with electrochemical detection

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Abstract

A solid-phase microextraction method has been developed for the determination of 19 chlorophenols (CPs) in environmental samples. The analytical procedure involves direct sampling of CPs from water using solid-phase microextraction (SPME) and determination by liquid chromatography with electrochemical detection (LC–ED). Three kinds of fibre [50 μm carbowax-templated resin (CW-TPR), 60 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 85 μm polyacrylate (PA)] were evaluated for the analysis of CPs. Of these fibres, CW-TPR is the most suitable for the determination of CPs in water. Optimal conditions for both desorption and absorption SPME processes, such as composition of the desorption solvent (water–acetonitrile–methanol, 20:30:50) and desorption time (5 min), extraction time (50 min) and temperature (40 °C) as well as pH (3.5) and ionic strength (6 g NaCl) were established. The precision of the SPME–LC–ED method gave relative standard deviations (RSDs) of between 4 and 11%. The method was linear over three to four orders of magnitude and the detection limits, from 3 to 8 ng l^{-1}, were lower than the European Community legislation limits for drinking water. The method was applied to the analysis of CPs in drinking water and wood samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase microextraction; Water analysis; Environmental analysis; Wood; Chlorophenols; Pentachlorophenol

1. Introduction

Chlorophenols (CPs) are prevalent in environmental waters and soils due to their widespread use in industrial processes [1]. CPs have been used as preservative agents, pesticides and disinfectants and are also used as intermediates in many industrial processes. CPs are considered to be carcinogenic and they are quite persistent compounds in the environment. Some of them, such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol, have been included in the U.S. Environmental Protection Agency (EPA) list of the 11 priority pollutant phenols in waters [2]. Pentachlorophenol has also been widely used for the protection of wood and wood-based products, and its analysis has received special attention with regard to the removal or recycling of waste-wood, the contamination of indoor air and the use of consumer products.

Most of the methods used for the analysis of CPs are based on separation techniques such as liquid chromatography [3–6], gas chromatography [6–10] and capillary electrophoresis [11,12]. These methods offer a successful separation and detection of CPs in

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a single run. The conventional extraction methods used for the analysis of CPs in water involve liquid–liquid [7–9] and solid-phase extraction [3–6,13,14], whereas for the analysis of pentachlorophenol in wood, sonication and Soxhlet are mainly employed [10].

Solid-phase microextraction (SPME) [15] coupled to GC analysis has been successfully used for the analysis of phenolic compounds in environmental matrices, such as water [16–22] and soil samples [23,24]. The methods proposed for the analysis of water samples basically used direct SPME of phenols [16–18,20,22] with a polyacrylate fibre in both direct SPME [16–18,22] and headspace SPME [17,20]. SPME coupled to GC achieved limits of detection for phenols at the ng l^{-1} concentration level. SPME coupled to LC [25–27] or automatic in-tube SPME–LC [28,29] have been employed for the analysis of environmental pollutants. To our knowledge, only one study has been reported on the determination of (nine) phenols in water by SPME–LC [27], but the limits of detection are not low enough to analyse these compounds in natural waters.

In this paper, a method for the analysis of 19 CPs in water and pentachlorophenol in wood samples using SPME–LC–ED is proposed. Three kinds of commercially available fibres [50 μm carbowax-templated resin (CW-TPR), 60 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 85 μm polyacrylate (PA)] were evaluated to determine the extraction efficiency of CPs. Parameters affecting the desorption process, such as composition of the desorption solvent and desorption time, were studied. Moreover, time and temperature of absorption and the effect of pH and ionic strength were also investigated. The optimised procedure was applied to the analysis of CPs in spiked drinking water and pentachlorophenol in wood samples. The results for wood samples using SPME were compared with the results using Soxhlet extraction and with those obtained in two inter-laboratory exercises.

2. Experimental

2.1. Chemicals

The CPs studied were obtained from the following sources: 4-chlorophenol (4-CP, 99%) from Carlo Erba (Milan, Italy); 2-chlorophenol (2-CP, 98%) from Merck (Darmstadt, Germany); 3-chlorophenol (3-CP, 99%), 2,3-dichlorophenol (2,3-DCP, 98%), 2,4-dichlorophenol (2,4-DCP, 99%), 2,5-dichlorophenol (2,5-DCP, 98%), 3,4-dichlorophenol (3,4-DCP, 99%), 3,5-dichlorophenol (3,5-DCP, 99%), 2,3,4-trichlorophenol (2,3,4-TCP, 99%), 2,3,5-trichlorophenol (2,3,5-TCP, 99%), 2,3,6-trichlorophenol (2,3,6-TCP, 99%), 2,4,5-trichlorophenol (2,4,5-TCP, 99%) and 2,4,6-trichlorophenol (2,4,6-TCP, 98%) from Sigma–Aldrich (Milwaukee, WI, USA); 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP, 98%) and 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP, 96%) from Chem Service (West Chester, PA, USA); 3,4,5-trichlorophenol (3,4,5-TCP, 98.9%) and 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP, 99%) from Supelco (Bellefonte, PA, USA); and, finally, 2,6-dichlorophenol (2,6-DCP, 99%) and pentachlorophenol (PCP, 99%) from Fluka (Buchs, Switzerland). The compounds 3-bromophenol (3-BP, 97%, Sigma–Aldrich), 4-bromophenol (4-BP, 98%, Merck) and pentabromophenol (PBP, 99%, Aldrich) were tested as internal standards.

Anhydrous sodium acetate was obtained from Fluka at high purity (≥99%). Methanol and acetonitrile of HPLC grade, *n*-hexane and acetone for residue analysis as well as acetic acid and chlorhydric acid of analysis grade were supplied by Merck. Anhydrous sodium sulfate was supplied by Panreac (Barcelona, Spain), and sodium chloride and potassium chloride were purchased from Merck. Water from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used.

Individual stock standard solutions of each CP (2 mg ml^{-1}) were prepared by weight in methanol. A standard stock solution (50 μg ml^{-1}) containing all the compounds was prepared from individual CP standard solutions by dilution with methanol. For optimisation of the SPME procedure, water standards containing 100 μg l^{-1} of each CP were prepared by adding 40 μl of the stock standard solution of 50 μg ml^{-1} to 20 ml Milli-Q water, and then sealed in a 30-ml screw-capped vial.

2.2. Chromatographic conditions

LC was carried out on a Hewlett-Packard (Palo Alto, CA, USA) Series 1050 liquid chromatograph

with an isocratic pump and an automatic injector. A Hypersil Green C_8 250×4.6 mm I.D. (5 μm particle size) HPLC column (Shandon Scientific, Cheshire, UK) and a Pelliguard LC-18 20×4.6 mm I.D. (20 μm particle size) pre-column (Supelco) were used. An isocratic ternary mobile phase of [sodium acetate–acetic acid (30 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) at 1.5 ml min^{-1} was used [30]. For detection, an electrochemical amperometric detector (HP 1049 A, Hewlett-Packard) was used. The working potential was set at +1100 mV between the glassy carbon working electrode and the Ag/AgCl reference electrode with internal electrolyte (KCl). The surface of the working electrode was cleaned electrochemically after each injection by cycling the applied potential 10 times between −600 and +1400 mV for 300 ms, and the working glassy carbon electrode was polished daily.

2.3. Solid-phase microextraction procedure

SPME experiments were performed with a manual fibre holder supplied by Supelco. Three commercially available fibres, 85 μm PA, 60 μm PDMS–DVB and 50 μm CW-TPR, were purchased from Supelco. Before use, each fibre was conditioned by immersion in acetonitrile with stirring for 1 h, followed by methanol for 1 h.

The sample (20 ml) was introduced into a 30-ml screw-cap glass vial and the pH was then adjusted to 3.5 with HCl (2% w/v). After addition of sodium chloride (6 g) the vial was closed and clamped inside a water-thermostated bath, which was placed on a hot plate/stirrer. After 5 min, a 50 μm CW-TPR fibre was exposed to the aqueous solution for 50 min at 40 °C. Magnetic stirring at 1200 rpm was applied during both stabilisation and extraction steps using a

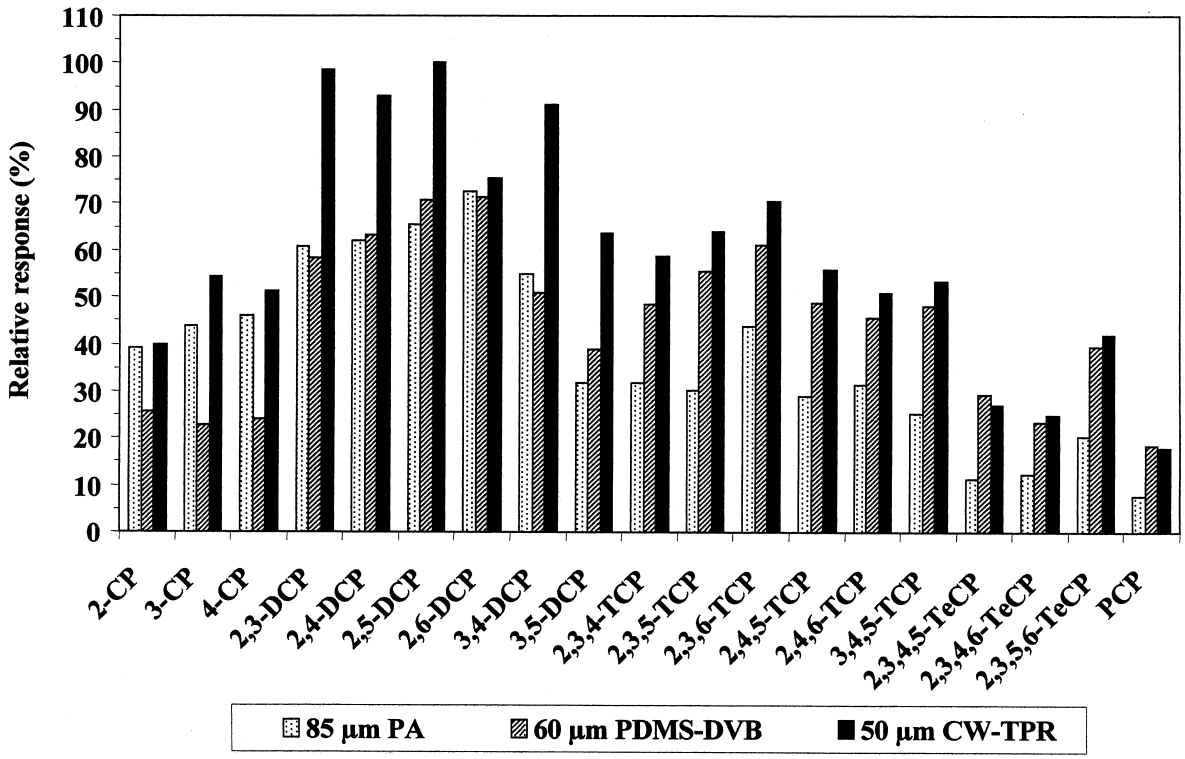

Fig. 1. Extraction efficiency of the SPME fibres. All recoveries are normalised to the maximum area response. Milli-Q water containing 100 μg l^{-1} of each CP; pH 3.5; sodium chloride, 6 g; extraction time, 60 min; extraction temperature, 30 °C; desorption solvent, sodium acetate–acetic acid 30 m*M* pH 4.5–acetonitrile–methanol, 60:30:10 v/v; desorption volume, 40 μl; desorption time, 15 min.

10×5 mm Teflon-coated stir bar. The fibre was immersed in 40 μl desorption solvent (water–acetonitrile–methanol, 20:30:50, v/v), which was placed in a conical glass insert of 0.10 ml contained in a 2-ml crimp vial for 5 min at 30 °C. An aliquot (20 μl) of this final solution was injected into the LC–ED system. Possible carryover was prevented by keeping the fibre first in 4 ml methanol solution for 5 min, and then in 4 ml Milli-Q water for 5 min. Blanks were run periodically during the analysis to confirm the absence of contaminants.

2.4. Water and wood analysis

A drinking water sample was spiked with CPs at 0.3–0.5 μg l^{-1} and then analysed by SPME using 3-BP as internal standard. Two wood samples containing PAHs and PCP were provided by the Bundesanstalt für Materialforschung und -prüfung (BAM) (Berlin, Germany). Three replicate analyses of each wood sample were carried out by standard addition, spiking the samples with a methanolic solution of PCP (0, 50, 100, 150 and 200%) at the concentration in the wood samples. A methanolic solution of 3-BP (5 μl), used as internal standard, was added and the final volume was made up to 45 μl with methanol. After equilibration of the wood sample overnight at 4 °C, 20 ml of Milli-Q water were added, the pH adjusted to 3.5, and the sample equilibrated with magnetic stirring for 15 min. The SPME analysis of the wood slurry was performed using the conditions established for water samples.

2.5. Soxhlet extraction procedure

Different amounts of each wood sample (4 g for sample 1 and 2 g for sample 2) were Soxhlet extracted with 200 ml of *n*-hexane–acetone (2:3) for 12 h. The organic extract was evaporated (2 ml of acetonitrile was added as a keeper to avoid losses of PCP by evaporation) to ca. 2 ml using a rotary evaporator without heating. The sample was then

Table 1
Relative responses of CPs for different desorption solvent compositions using the CW-TPR fibre[a]

Compound	Relative response (%)					
	Acetate buffer–acetonitrile–methanol			Milli-Q water–acetonitrile–methanol		
	60:30:10	20:70:10	20:30:50	60:30:10	20:70:10	20:30:50
2-CP	39	43	32	48	40	49
3-CP	50	54	42	61	38	57
4-CP	44	51	39	60	36	58
2,3-DCP	67	84	65	77	68	98
2,4-DCP	59	81	61	76	64	96
2,5-DCP	67	87	67	77	69	100
2,6-DCP	55	70	53	77	53	81
3,4-DCP	61	80	62	79	65	92
3,5-DCP	51	62	48	44	51	65
2,3,4-TCP	38	58	41	42	49	66
2,3,5-TCP	43	66	48	45	55	72
2,3,6-TCP	46	70	48	58	58	82
2,4,5-TCP	36	56	41	38	47	63
2,4,6-TCP	31	51	34	43	42	59
3,4,5-TCP	40	61	42	44	51	74
2,3,4,5-TeCP	17	36	21	20	30	38
2,3,4,6-TeCP	15	28	18	18	23	31
2,3,5,6-TeCP	32	48	33	34	40	58
PCP	14	22	14	13	18	26

[a] Concentration, 100 μg l^{-1}; extraction time, 30 min; extraction temperature, 30 °C; desorption volume, 40 μl; desorption time, 15 min.

diluted to a final volume of 5 ml with acetonitrile and passed through a 0.45 μm nylon filter. Aliquots of these extracts were adjusted to 1 ml with the internal standard (2,3,5-TCP for sample 1 and PBP for sample 2) and analysed by LC–ED. For Soxhlet extraction, six replicates of wood were analysed on two different days. The recoveries were calculated from the slope of the addition standard curve obtained by spiking the samples with a solution of PCP in *n*-hexane at the levels described for SPME (between 0 and 200%) for 30 h, and were greater than 98% for both samples.

3. Results and discussion

3.1. Selection of the fibre

The relative extraction efficiencies of CPs using SPME with different stationary phases were evaluated. Three fibres were tested: 85 μm PA, 60 μm PDMS–DVB and 50 μm CW-TPR. Carbowax–divinylbenzene stationary phase (CW–DVB) was not studied because it is not suitable for SPME–LC when acetonitrile–acetate buffers [26] or water–methanol mixtures [31] are used as desorption solvents. The initial conditions were: pH 3.5, 6 g of NaCl, extraction time and temperature 60 min and 30 °C, respectively, and off-line desorption in 40 μl of acetate buffer–acetonitrile–methanol (60:30:10, v/v) at 30 °C for 15 min. The relative responses obtained using the fibres are shown in Fig. 1. The three fibres were suitable for all the analytes, but for monohalogenated compounds, PDMS–DVB fibre gave a worse extraction efficiency than CW-TPR and PA fibres. For tri-, tetra- and pentachlorophenol, the extraction yield for PDMS–DVB and CW-TPR was similar and better than for PA fibre. The most polar fibre, CW-TPR, provided the highest extraction efficiency for all the compounds, especially for

Table 2
Effect of sample pH and ionic strength on SPME extraction efficiencies of CPs[a]

Compound	pK_a[b]	Response relative to pH 7 and no salt addition				
		No salt addition		pH 3.5 with salt addition		
		pH 2.5	pH 4.5	NaCl	KCl	Na_2SO_4
2-CP	8.52	1.0	1.0	10	3	4
3-CP	8.97	1.1	1.1	11	4	5
4-CP	9.37	1.1	0.9	11	4	5
2,3-DCP	7.71	1.3	1.2	6	4	3
2,4-DCP	7.90	1.2	1.1	5	4	3
2,5-DCP	7.51	1.4	1.2	6	4	4
2,6-DCP	6.80	2.8	2.4	23	10	16
3,4-DCP	8.60	1.1	1.0	3	3	2
3,5-DCP	8.25	1.2	1.1	3	2	2
2,3,4-TCP	7.00	1.4	1.3	2	2	1
2,3,5-TCP	6.43	2.0	1.9	2	3	1
2,3,6-TCP	5.80	8.8	8.3	22	22	15
2,4,5-TCP	6.72	1.7	1.4	2	3	2
2,4,6-TCP	6.00	5.8	5.4	13	14	10
3,4,5-TCP	7.55	1.3	1.1	1	2	1
2,3,4,5-TeCP	5.64	1.9	1.5	1	2	1
2,3,4,6-TeCP	5.22	8.0	7.0	8	11	5
2,3,5,6-TeCP	5.02	9.9	9.0	11	14	7
PCP	4.74	2.9	2.5	2	2	1

[a] Concentration, 100 μg l^{-1}; extraction time, 30 min; extraction temperature, 30 °C; desorption solvent, Milli-Q water–acetonitrile–methanol (20:30:50, v/v); desorption volume, 40 μl; desorption time, 5 min.
[b] Refs. [32,33].

dichlorophenols, so this coating was selected. For reasons of rapidity, a sampling time of 30 min was used for further optimisation studies.

3.2. Optimisation of desorption

To study the effect of the desorption solvent on the sensitivity, two sets of experiments were performed, one using the LC mobile phase [sodium acetate–acetic acid 30 m*M* pH 4.5, acetonitrile and methanol (60:30:10, v/v)] and the other by changing the acetate buffer with Milli-Q water. In order to optimise the desorption solvent composition, the proportion of one of the organic solvents was changed, while maintaining the other constant. The responses of CPs relative to the maximum area value, which was obtained for 2,5-DCP using Milli-Q water–acetonitrile–methanol (20:30:50), are given in Table 1. In the case of acetate buffer–acetonitrile–methanol, the change in the proportion of acetonitrile from 30 to 70% produced an increase in the desorption from the fibre, which was more effective for polychlorinated phenols. Changes in the methanol percentage up to 50% did not produce any improvement (Table 1). The relative responses obtained with Milli-Q water–acetonitrile–methanol (60:30:10) were slightly higher than those of acetate buffer–acetonitrile–methanol (60:30:10), probably due to a decrease of the ionic strength which favoured the desorption of phenols from the fibre. An increase of the acetonitrile proportion up to 70% did not produce any improvement in the responses. In contrast, a content of 50% methanol in the solution gave high responses for all analytes. Therefore, this composition was chosen for subsequent studies.

The desorption time of the analytes from the fibre was determined at between 1 and 15 min. For monochlorophenols, no significant variation of the

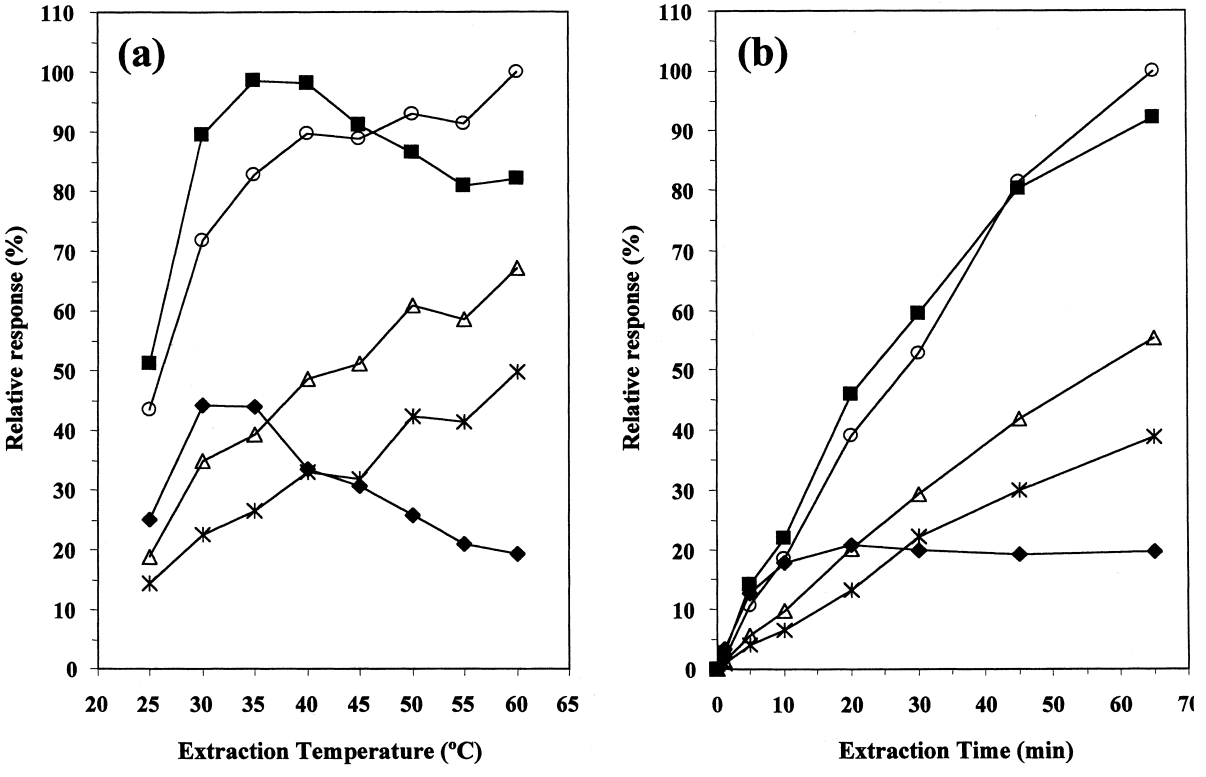

Fig. 2. (a) Extraction temperature and (b) extraction time profiles. Conditions: CW-TPR fibre; pH 3.5; sodium chloride, 6 g; extraction time, 30 min; desorption solvent, water–acetonitrile–methanol (20:30:50); desorption volume, 40 μl; desorption time, 5 min. In (b) the extraction temperature was 40 °C. Compounds: (♦) 2-CP, (■) 2,4-DCP, (○) 2,3,6-TCP, (△) 2,3,4,5-TeCP, (*) PCP.

analyte responses was observed for desorption times longer than 3 min, while for the remaining analytes 5 min were needed. Carryover of all CPs was also tested at two concentrations, 5 and 100 μg l^{-1}, and was found to be between 1.6 and 9.6%.

3.3. Effect of pH and ionic strength

The effect of the acidity of the sample on the extraction efficiency was studied by changing the pH from 2.5 to 7. The relative responses with respect to the area obtained at pH 7 are given in Table 2. The effect of pH on the sorption of CPs is as expected based on their pK_a. For example, compounds with high pK_a values, such as mono- and most of the dichlorophenols, showed no significant change in the amount absorbed when the pH was varied from 7 to 2.5. However, for compounds with pK_a values between 4.7 and 7, the decrease in pH produced a two- to 10-fold increase in the responses. To prevent degradation of the CW-TPR fibre, observed at pH 2.5, a pH of 3.5 was chosen.

The addition of salt was also studied. At pH 3.5, different salts (NaCl, KCl and Na_2SO_4) in the range 0 to 0.4 g ml^{-1} were added to the water. The extraction of CPs was enhanced by the addition of salts and the highest sensitivities were obtained for NaCl at 0.3 g ml^{-1}, KCl at 0.25 g ml^{-1} and Na_2SO_4 at 0.2 g ml^{-1}. Relative responses to pH 7 with no salt addition are given in Table 2. As can be seen, the highest increase in the responses was obtained when NaCl was used mainly for lower chlorinated phenols.

3.4. Effect of extraction temperature and time

The effect of sample temperature on SPME was examined from 25 to 60 °C in 5 °C increments and the temperature extraction profiles of some CPs are shown in Fig. 2a. The highest relative responses for mono- and dichlorophenols were obtained between 30 and 40 °C, whereas the affinity of the analytes for the fibre coating increased with temperature for the most chlorinated phenols, being maximum in the range 50–60 °C. As a compromise, 40 °C was chosen as the optimum extraction temperature.

The extraction time profiles of the CPs were then studied up to 65 min (Fig. 2b). Monohalogenated CPs attained equilibrium in 20 min, whereas the other compounds needed more than 65 min to reach equilibrium. An extraction period of 50 min was chosen for subsequent experiments as a compromise between extraction efficiency and analysis time.

3.5. Quality parameters

To evaluate the performance of the SPME procedure, the figures of merit were studied. Several chlorinated and brominated phenols were evaluated as internal standards. Only 3-BP and 4-BP were suitable for SPME analysis because they achieved equilibrium in less than 50 min, were desorbed from the fibre in only 2 min and eluted at appropriate retention times. 3-BP was chosen as internal standard for further studies, although 4-BP can also be used. The linearity of the optimised SPME–LC–ED method was examined over the range 0.02–300 μg l^{-1}, expressed as the initial concentration of CPs in Milli-Q water, using 3-BP as internal standard at 25

Table 3
Quality parameters of the SPME–LC–ED method

Compound	Linear range[a] (μg l^{-1})	Precision[b] (RSD %)	
		Run-to-run[c]	Day-to-day[d]
2-CP	0.06–65	6	9
3-CP	0.08–65	5	5
4-CP	0.08–65	5	5
2,3-DCP	0.05–50	4	6
2,4-DCP	0.05–60	4	6
2,5-DCP	0.05–50	7	9
2,6-DCP	0.07–60	4	6
3,4-DCP	0.05–40	5	7
3,5-DCP	0.05–40	9	10
2,3,4-TCP	0.04–90	10	11
2,3,5-TCP	0.04–85	6	9
2,3,6-TCP	0.05–100	6	7
2,4,5-TCP	0.05–85	10	11
2,4,6-TCP	0.05–100	7	7
3,4,5-TCP	0.04–85	10	11
2,3,4,5-TeCP	0.08–150	4	8
2,3,4,6-TeCP	0.05–125	6	8
2,3,5,6-TeCP	0.05–100	7	10
PCP	0.05-125	7	10

[a] Correlation coefficients (r^2), 0.996–0.999.
[b] Concentration: 4 μg l^{-1}.
[c] $n=5$.
[d] $n=5$ replicates×3 days.

μg l^{-1}, and the results are given in Table 3. All CPs showed good linearity with correlation coefficients (r^2) greater than 0.996.

Run-to-run and day-to-day precision were determined by analysing, consecutively, five replicates of Milli-Q water spiked with CPs on one day and on three days, respectively (Table 3). RSDs for run-to-run precision ranged between 4 and 10% and for day-to-day precision between 5 and 11%. Detection limits (LODs), expressed as ng l^{-1} and based on a signal-to-noise ratio of 3:1, were determined experimentally in Milli-Q water spiked at <10 ng l^{-1} of CPs and analysed using the optimised procedure, and ranged from 3 to 8 ng l^{-1}, which are similar to the values reported using on-line SPE–LC with ED (amperometric) detection [34].

3.6. Analysis of environmental samples

To examine the feasibility of the SPME method, a spiked drinking water sample was analysed in triplicate and using the optimised conditions. Quantitative analysis was carried out using external calibration with 3-BP as internal standard at 25 μg l^{-1}. SPME–LC–ED was found to be highly selective for the analysis of CPs in drinking water. Fig. 3 shows chromatograms of nonspiked and spiked (0.3–0.5 μg l^{-1}) water samples. The detection limits (from 5 to 9 ng l^{-1}) were similar to those obtained with Milli-Q water, showing no important matrix effects. Although these LODs are 10-fold higher than those obtained for natural waters by on-line SPE–LC with coulimetric detection [5], they are better than those

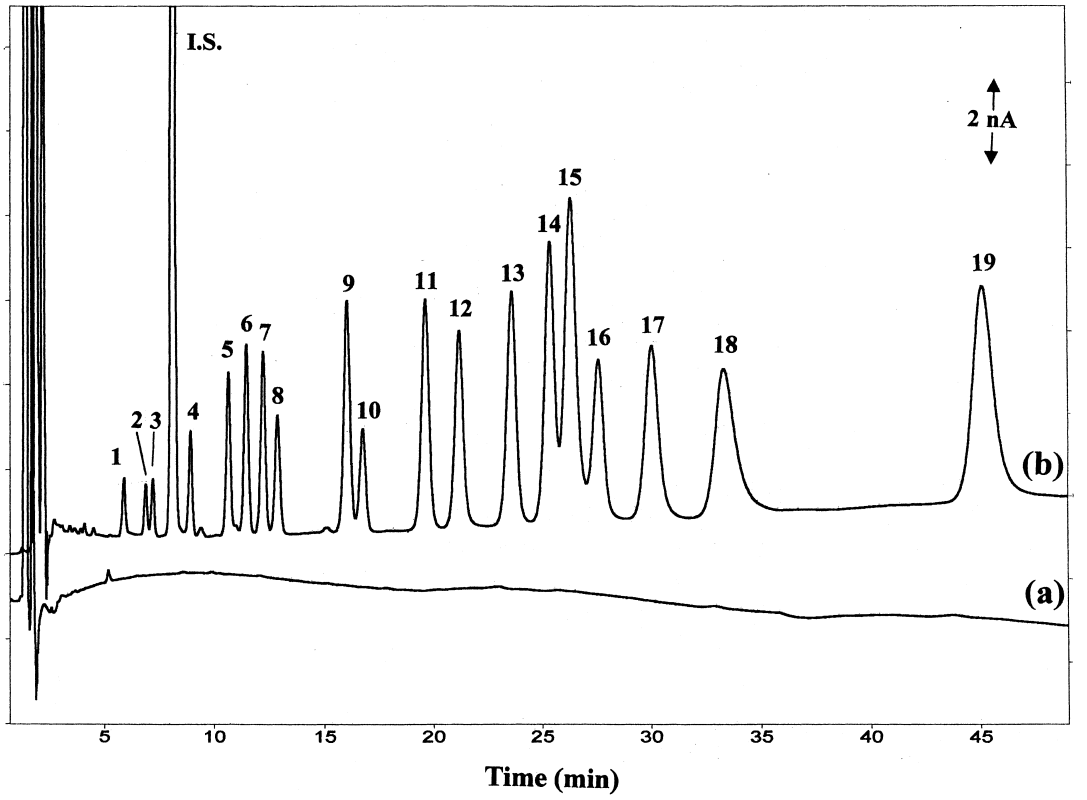

Fig. 3. SPME–LC–ED chromatogram of (a) nonspiked and (b) spiked (0.3–0.5 μg l^{-1}) drinking water. Peaks: 1=2-CP; 2=4-CP; 3=3-CP; 4=2,6-DCP; 5=2,3-DCP; 6=2,5-DCP; 7=2,4-DCP; 8=3,4-DCP; 9=2,3,6-TCP; 10=3,5-DCP; 11=2,4,6-TCP; 12=2,3,4-TCP; 13=2,4,5-TCP; 14=2,3,5-TCP; 15=2,3,5,6-TeCP; 16=3,4,5-TCP; 17=2,3,4,6-TeCP; 18=PCP; 19=2,3,4,5-TeCP; and I.S.=3-BP.

Table 4
Determination of CPs in drinking water using SPME–LC–ED

Compound	Target value ($\mu g\ l^{-1}$)	Mean[a] ($\mu g\ l^{-1}$)	RSD (%)
2-CP	0.36	0.37	7.7
3-CP	0.37	0.36	4.9
4-CP	0.39	0.39	2.5
2,3-DCP	0.45	0.44	2.4
2,4-DCP	0.49	0.48	1.8
2,5-DCP	0.45	0.44	1.6
2,6-DCP	0.53	0.51	2.8
3,4-DCP	0.45	0.44	2.4
3,5-DCP	0.39	0.39	2.4
2,3,4-TCP	0.47	0.47	3.9
2,3,5-TCP	0.50	0.52	4.2
2,3,6-TCP	0.42	0.41	2.9
2,4,5-TCP	0.47	0.50	8.7
2,4,6-TCP	0.40	0.41	3.0
3,4,5-TCP	0.47	0.47	9.5
2,3,4,5-TeCP	0.50	0.46	10.0
2,3,4,6-TeCP	0.46	0.45	2.1
2,3,5,6-TeCP	0.49	0.53	9.0
PCP	0.42	0.42	8.5

[a] $n=3$.

reported for CPs in tap water by on-line SPE–LC with amperometric detection [3,34,35].

The values obtained for the quantitative analysis of the spiked sample are given in Table 4, where it can be observed that the precision is lower than 10% for all CPs. The SPME procedure was also used to determine PCP in two wood samples, candidates for reference materials. The samples were analysed as for the water sample but NaCl was not added because better extraction efficiency for PCP was obtained under these conditions (Table 2). Standard addition instead of external calibration was used to avoid matrix effects from the wood samples. The LOD of PCP in wood based on a signal-to-noise ratio of 3:1 was 45 ng g^{-1}. This value was calculated by spiking at low concentrations (65 ng g^{-1}) 1 g wood sample without detectable quantities of PCP. A LC–ED chromatogram obtained by SPME with a 50 μm CW-TPR fibre is given in Fig. 4 for one of the wood samples (sample 2). As can be seen, SPME–LC–ED is also a highly selective procedure for the analysis of PCP in wood, because no interference from other compounds potentially present in the sample matrix was observed. The results obtained for both samples are given in Table 5, where the mean and standard deviation (SD) values obtained by our laboratory using Soxhlet extraction and the mean of all the European laboratories which participated in two inter-laboratory exercises are also given. The results obtained with SPME agreed with the mean values obtained by our laboratory using Soxhlet extraction and also with the mean values reported by the European laboratories. SPME–LC–ED showed some advantages over the Soxhlet extraction method, such as the avoidance of organic solvents, labour-intensive sample manipulation steps and a shorter analysis time.

4. Conclusions

The feasibility of SPME–LC–ED for the analysis of CPs in water has been demonstrated. The CW-TPR fibre was found to be the most effective coating for the analysis of CPs, especially for dihalogenated

Table 5
Determination of PCP in wood samples using the SPME–LC–ED method

Sample	SPME–LC–ED[a,b]		Soxhlet extraction[c,d]		Inter-laboratory exercise	
	Mean ($\mu g\ g^{-1}$)	SD ($\mu g\ g^{-1}$)	Mean ($\mu g\ g^{-1}$)	SD ($\mu g\ g^{-1}$)	Mean ($\mu g\ g^{-1}$)	SD ($\mu g\ g^{-1}$)
1	6.04	0.39	5.87	0.52	6.24[e]	1.11
2	3.54	0.21	3.77	0.28	3.64[d]	0.19

[a] Sample intake: sample 1, 0.1 g; sample 2, 0.2 g; pH adjusted to 3.5.
[b] $n=3$.
[c] Sample intake: sample 1, 4 g; sample 2, 2 g.
[d] $n=6$.
[e] $n=9$.

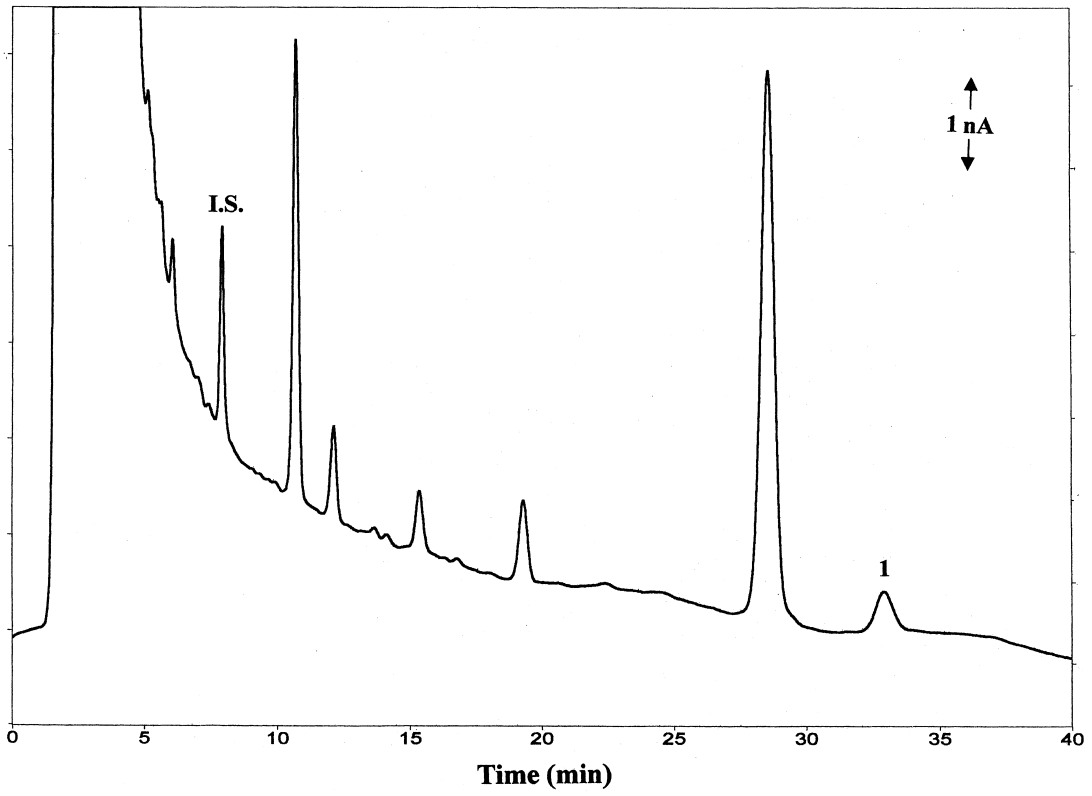

Fig. 4. SPME–LC–ED chromatogram of a wood sample (sample 2). Peak: 1=PCP; I.S.=3-BP.

ones. SPME in conjunction with LC–ED gave good precision (run-to-run precision lower than 10% and day-to-day precision lower than 11%), it was linear over three to four orders of magnitude and the detection limits were at the sub-ppb level.

Although the method can be used for the analysis of CPs in drinking water at levels even lower than 0.1 $\mu g\ l^{-1}$, which is the European Community legislation limit for individual phenols in drinking water [36], the lack of automatisation of the procedure makes SPME–LC inferior for routine analysis of CPs to on-line SPE–LC. In contrast, SPME can be proposed as a fast and accurate method for the analysis of PCP in wood and can be used instead of Soxhlet, which involves high volumes of solvents and time-consuming steps.

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