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Evaluation of two solid-phase extraction procedures for the preconcentration of chlorophenols in drinking water

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Abstract

Two off-line concentration procedures for the determination of sixteen chlorophenols in drinking water were developed. One involves acetylation of the samples and their subsequent preconcentration over graphitized carbon black cartridges. In the other, chlorophenols are derivatized following preconcentration over cross-linked styrene–divinylbenzene. The two proposed procedures are compared in terms of chlorophenol recoveries, throughput and breakthrough volume of the cartridges. The acetylated derivatives of chlorophenols are determined highly selectively at the concentration levels established by international legislation using gas chromatography in combination with microwave induced plasma atomic emission spectroscopy. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Sample handling; Chlorophenols; Phenols

1. Introduction

Chlorophenols are present as pollutants in the aquatic environment as a result of the degradation of pesticides in general and insecticides in particular [1]; also, they can be formed from non-chlorinated phenols during chlorinating of water.

The US Environmental Protection Agency (EPA) [2] has compiled a list of eleven phenol compounds considered to be priority pollutants in the aquatic medium; among them, chlorophenols are especially toxic and potentially carcinogenic. In 1982, the EEC issued another pollutant list [3] that included many polychlorophenols and established their maximum allowable concentration in drinking waters (0.5 ng/ml).

Although several techniques are currently used for the analytical determination of phenols, including liquid chromatography (LC) [4–8], solid-phase micro-extraction (SPME) [9], and capillary electrophoresis (CE) [10,11], in the case of drinking water samples, this determination is most often carried out by using gas chromatography (GC) on account of its high sensitivity and resolving power; however, the high polarity of phenols hinders their correct chromatographic resolution [12]. This shortcoming has

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been circumvented by using various derivatization procedures that convert phenols into less polar, more easily resolved compounds [13,14]. Prominent among them is acetylation with acetic anhydride [15,16], which provides high yields for chlorophenols and can be implemented prior to or after extraction of the starting compounds [13,17].

In any case, the need to determine phenols at concentrations below 0.5 ng/ml entails preconcentrating samples prior to injection into the gas chromatograph. Solid-phase extraction (SPE) on cartridges and membranes is gradually superseding traditional liquid–liquid extraction procedures for this purpose. Historically, C_{18} was one of the earliest sorbents used for concentrating phenols [13,18–20]; it provided acceptable recoveries for most phenols, albeit at highly variable breakthrough volumes (100–1000 ml) depending on the polarity of the compounds concerned [21]. Converting phenols into their acetylated derivatives prior to preconcentration decreases polarity differences among them and levels off their breakthrough volumes [22,23].

Graphitized carbon black (GCB) has also been used in the preconcentration of phenols and other polar pollutants [4–8] with quantitative recovery for volumes larger than 1 l. Styrene–divinylbenzene copolymers are one other group of sorbents of recent use for preconcentrating phenols [12,24–27] and other polar compounds; their breakthrough volumes are dependent on the extent of cross-linking of the polymers.

These sorbents have been compared in terms of recovery; however, the concentration levels considered were well above the typical levels in natural and drinking waters allowed by international legislation. As a result, the sample volumes tested cannot be compared with those to be processed in the analysis of drinking water. In this work, we developed and compared two different procedures for the off-line preconcentration of chlorophenols in drinking waters based on solid-phase extraction with GCB and polymer sorbents. One involves direct acetylation of the chlorophenols in the water by using acetic anhydride and K_2CO_3, followed by concentration over GCB cartridges. The other concentrates water samples on cross-linked styrene–divinylbenzene cartridges. Following elution, chlorophenols are acetylated prior to injection into the chromatographic system. In both cases, the acetylated derivatives are selectively determined by using the gas chromatography–microwave induced plasma atomic emission spectroscopy (GC–MIP-AED) technique.

2. Experimental

2.1. Reagents

Methanol, hexane, potassium carbonate and acetic anhydride of maximum purity were supplied by Merck (Darmstadt, Germany). Tetramethylammonium hydroxide (TMAOH), 25% in methanol, was supplied by Aldrich (Milwaukee, WI, USA).

The standards used: 2-chlorophenol (2CP), 3-chlorophenol (3CP), 4-chlorophenol (4CP), 2,6-dichlorophenol (26DCP), 2,4-dichlorophenol (24DCP), 3,5-dichlorophenol (35DCP), 2,3-dichlorophenol (23DCP), 3,4-dichlorophenol (34DCP), 2,4,6-trichlorophenol (246TCP), 2,3,6-trichlorophenol (236TCP), 2,3,5-trichlorophenol (235TCP), 2,4,5-trichlorophenol (245TCP), 2,3,4-trichlorophenol (234TCP), 2,3,5,6-tetrachlorophenol (2356TCP), 2,3,4,6-tetrachlorophenol (2346TCP) and pentachlorophenol (PCP) were supplied by Aldrich and Merck.

Stock solutions of 3.0 mg/ml were prepared for each of the standards in methanol. These solutions were stored at 4°C, and light protected. Working solutions were prepared by mixture and appropriate dilution from the individual stocks.

Tap water or Milli-Q water samples with or without addition of chlorophenols were preconcentrated by means of GCB cartridges, Supelclean, ENVI-Carb SPE (Supelco, Bellefonte, PA, USA) of 0.25 g. (3 ml, non porous, 120–400 mesh); or by means of cross-linked styrene–divinylbenzene copolymer cartridges, (International Sorbent Technology, UK) of 0.20 g (6 ml, 40–140 μm, 850 Å pore size).

2.2. Apparatus

A HP 5890 Series II chromatograph from Hewlett-Packard (Avondale, PA, USA) furnished with a HP 7673 split/splitless autoinjector and coupled to a HP 5921A microwave-induced plasma atomic emission

detector was used. The whole system was controlled by a HP 3590A Chemstation. A 30 m×0.25 mm I.D. DB-5 methylphenylsilicone capillary column of 0.25 μm film thickness supplied by J&W Scientific (Folsom, CA, USA) and 99.999% helium as carrier gas were also employed. Optimum settings for the determination of chlorophenols are summarised in Table 1.

2.3. Acetylation of standards

The procedure followed for the acetylation of phenols standards used for calibration is based on that proposed by Renberg and Lindstrom [18], and recently optimized [28,29]. In it, 2 ml of a 5% K_2CO_3 solution and 2 ml of hexane containing 200 μl of acetic anhydride are added to 1 ml of a methanolic solution with different concentrations of the studied chlorophenols. Then the mixture is shaken manually for 1 min and the organic phase separated. The aqueous phase (methanol–water) is extracted again with 1 ml of hexane (now without derivatizing agent). Both hexane phases are mixed, dried over anhydrous sodium sulphate and injected in the GC–AED system. By derivatizing various concentrations of phenols, calibration graphs were constructed as plots of the concentration of each phenol against the peak height of its acetylated derivative.

Table 1
GC–AED conditions used for the separation of chlorophenols (as acetates)

GC parameters	
Injection mode	Split-splitless
Purge time on	120 s
Injection port temperature	250°C
Injected volume	1 μl
Column head pressure	85 kPa
Split flow	8 ml/min
Oven temperature program:	
Initial temperature	60°C
Initial time	1 min
Rate	15°C/min
Temperature	115°C
Time	5 min
Rate	3°C/min
Temperature	175°C
Rate	30°C/min
Final temperature	250°C
Final time	10 min
AED parameters	
Transfer line temperature	260°C
Cavity block temperature	260°C
Wavelength	480.192 nm
Helium make-up flow	44 ml/min
Ferrule purge	28 ml/min
Spectrometer purge flow	2 l/min (N_2)
Solvent vent time	8.5 min
Reagent gas	Oxygen

2.4. Sample preparation

Two different off-line extraction process were carried out using two different cartridges: carbon cartridges (250 mg) and cross-linked styrene–divinylbenzene cartridges (200 mg). A known volume of Milli-Q purified water or prefiltered tap water was spiked with a standard of chlorophenols in methanol (spiked samples), and concentrated using one of both cartridges. When tap water was used, sodium thiosulphate (200 mg/l water) was added to avoid oxidation of the analytes.

When carbon was used in the preconcentration process, water samples, spiked or not with chlorophenols, were acetylated according a previously optimized procedure [29]: firstly water pH was adjusted to 11–11.5 with K_2CO_3, then acetic anhydride (5 ml/l water sample) was added and the mixture stirred mechanically for 5 min. A volume of methanol equivalent to ca. 2% of the water sample volume was then added and the mixture was forced through a preconditioned carbon cartridge with help of a vacuum pump. The cartridge was preconditioned by washing with 5 ml of methanol and 5 ml of Milli-Q water at pH 2–3 [30]. When the sample had passed through, the cartridge was dried with a stream of nitrogen for 20 min and turned upside down for elution with 3 ml of hexane containing 1% TMAOH. This backflush elution can be easily carried out by means of the device described by Di Corcia et al. [7]. The final extract was concentrated to 0.5 ml under a stream of nitrogen at 55 kPa at room temperature using a Turbo Vap II workstation from Zymark (Hopkinton, MA, USA).

When styrene–divinylbenzene cartridges were used, water samples were adjusted to pH 2.5–2.8 with 1 *M* HCl and then forced through a cartridge, preconditioning in the same way than carbon car-

tridges. When the sample had passed through, the cartridge was clean with 10 ml of Milli-Q water, dried with a stream of nitrogen and turned upside down for elution (using the same device mentioned above) in this case using 4 ml of methanol. The methanolic extract was derivatized in the same way that calibration standards, the two hexane phases mixed and reduced to 0.5 ml before their injection into the GC–AED system.

3. Results and discussion

3.1. Elution of cartridges

The type and volume of solvent to be used to elute chlorophenols from the two types of cartridges tested were optimized by passing samples of 250 ml of Milli-Q water spiked with 5 ng/ml concentrations of the analytes. The cartridges were preconditioned as described in Section 2.4.

3.1.1. Preconcentration with styrene–divinylbenzene cartridges

An eluent volume of 3 ml was sufficient to achieve quantitative recoveries of mono- di- and trichlorophenols with elution in the same direction as the cartridge was loaded with the water samples; the recoveries thus obtained for tetrachlorophenols were only about 30% and that for pentachlorophenol virtually zero. Subsequent fractions of methanol completely eluted tetrachlorophenols and even pentachlorophenol (the latter required 12 ml of methanol, however).

If methanol was passed through the cartridge in the opposite direction to the water samples, a volume of 4 ml sufficed to completely elute all chlorophenols. This suggests that the styrene–divinylbenzene polymer exhibits a high affinity for tetrachlorophenols and, especially, pentachlorophenol, all of which are retained at the top of the cartridge before it is inverted.

3.1.2. Preconcentration with GCB cartridges

Acetylated chlorophenols retained on GCB cartridges were quantitatively eluted by 4 ml of *n*-hexane; exceptionally, pentachlorophenol could not be recovered not even with such a large eluent volume as 10 ml. Adding 1% TMAOH to *n*-hexane allowed the acetates of the sixteen chlorophenols studied to be quantitatively recovered with 8 ml of eluent. Finally, if the selected eluent (*n*-hexane containing 1% TMAOH) was passed in the opposite direction to the sample, a volume of 3 ml sufficed to elute all the compounds studied. No pH adjustment is needed for the eluent because eluates show an apparent pH of 7–8 thus indicating that TMAOH is completely retained in the cartridge. This is important because traces of TMAOH in the final eluates should degrade rapidly chromatographic columns performance.

The use of TMAOH-modified eluents for carbon cartridges was introduced by Di Corcia and coworkers [4,31]. They pointed out the need to use quaternary ammonium salts to overcome the strong interaction between the anions of the more acidic phenols (PCP and dinitrophenols) and positively charged benzpyrylium groups present in GCB. However, because the chlorophenols were acetylated prior to concentration on the carbon, the potential interaction of the resulting esters with benzpyrylium groups and the action of TMAOH were not as obvious.

3.2. Breakthrough volume

The breakthrough volumes of the GCB cartridges for acetylated chlorophenols and those of the styrene–divinylbenzene cartridges for underivatized chlorophenols were determined by using volumes of Milli-Q water from 200 to 2000 ml that were spiked with five chlorophenols, viz. 2CP, 24DCP, 246TCP, 2356TCP and PCP (one per group of position isomers present among the sixteen chlorophenols studied), at a 5 ng/ml concentration. The spiked water samples were passed through the cartridges at a flow-rate of 25 ml/min.

The recoveries thus obtained with the carbon cartridges (Table 2) provided a breakthrough volume about 1000 ml for 2CP; on the other hand, the average recoveries of 24DCP, 246TCP and 2356 TCP varied little with the water volume between 1000 and 2000 ml the standard deviation, however, increased with increasing volume. Also, the recovery of PCP decreased with increasing water volume from

Table 2
Mean recoveries (R) ($n=3$) obtained by SPE using carbon cartridges (0.25 g) and variable volumes of a solution containing 5 ng/ml chlorophenols in Milli-Q water

Compound	Sample volume (ml)									
	200		500		1000		1500		2000	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
2CP	105.5	9.3	103.2	4.5	102.7	3.9	67.6	14.3	57.5	15.2
24DCP	82.8	7.1	88.7	2.6	86.0	4.5	87.3	12.9	91.0	13.8
246TCP	83.5	8.1	92.7	4.1	85.2	5.6	84.9	10.1	85.1	10.9
2356TCP	84.4	10.3	82.9	3.5	81.0	7.5	79.1	11.1	74.6	8.9
PCP	73.3	9.3	75.3	6.2	76.0	4.9	67.6	6.9	59.4	9.0

1000 to 2000 ml owing to incomplete elution of the cartridge (with 3 ml of n-hexane containing 1% TMAOH) rather than to its breakthrough caused by the strong interaction between carbon and this chlorophenol.

Sample volumes in the range 200–2000 ml resulted in no breakthrough of styrene–divinylbenzene cartridges by any of the compounds studied (Table 3).

Table 4 lists the limits of quantitation (LOQs) at a signal-to-noise ratio of 10 obtained for the derivatized chlorophenols by applying the GC–MIP-AED technique to standards and water samples concentrated over GCB or styrene–divinylbenzene cartridges.

3.3. Sample flow-rate

One interesting practical feature of both types of cartridge tested is the economy resulting from their reusability. Properly rinsed by passing 10–15 ml of methanol and conditioned, the cartridges can be used to analyse a large number of samples (4–5). The rate at which samples were passed through the cartridges was dictated by the type of stationary phase involved. Carbon cartridges (0.25 g) initially afforded high flow-rates but rapidly underwent compacting of the carbon bed, which increased its resistance to passage of samples. This prevented the use of flow-rates above 25 ml/min even with samples filtered through membranes of 0.45 μm pore size; as a result, concentrating a water volume of 1000 ml in order to determine chlorophenol concentrations below 0.5 ng/ml took about 40 min.

Styrene–divinylbenzene cartridges (0.20 g) were not subject to the compacting problem, so they afforded flow-rates up to 100 ml/min. While such high rates resulted in too short sample–stationary

Table 3
Mean recoveries (R) ($n=3$) obtained by SPE using cross-linked styrene–divinylbenzene copolymer cartridges (0.20 g) at variable volumes of a solution containing 5 ng/ml chlorophenols in Milli-Q water

Compound	Sample volume (ml)									
	200		500		1000		1500		2000	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
2CP	89.8	6.3	98.7	9.9	104.4	8.0	104.3	3.2	80.0	5.6
24DCP	85.2	2.6	86.7	6.1	91.2	4.6	81.6	4.1	81.1	8.1
246TCP	87.9	4.4	84.1	5.9	86.2	5.2	86.3	3.1	85.1	7.7
2356TCP	89.2	6.2	97.3	5.8	95.3	9.1	85.9	3.4	87.8	3.5
PCP	89.3	7.1	106.1	10.6	101.0	9.9	94.4	8.5	102.7	12.7

Table 4
Limits of quantitation (at $S/N=10$) obtained with the proposed GC–MIP-AED system

Compound	LOQ in standards (μg/ml)	LOQ in water samples (ng/ml)	
		0.25 g GCB cartridges (1000 ml of water)	0.20 g styrene-divinylbenzene cartridges (2000 ml of water)
2CP	0.51	0.26	0.13
3CP	0.46	0.23	0.12
4CP	0.63	0.32	0.16
26DCP	0.40	0.20	0.10
24DCP	0.37	0.19	0.10
35DCP	0.40	0.20	0.10
23DCP	0.38	0.19	0.10
34DCP	0.42	0.21	0.11
246TCP	0.18	0.09	0.05
236TCP	0.19	0.10	0.05
235TCP	0.20	0.10	0.05
245TCP	0.22	0.11	0.06
234TCP	0.23	0.12	0.06
2356TCP	0.21	0.11	0.06
2346TCP	0.19	0.10	0.05
PCP	0.30	0.15	0.08

phase contact times, they had no effect on chlorophenol recoveries (Table 5).

3.4. Recovery of chlorophenols from tap water

Chlorophenol recoveries with both SPE procedures were also assessed by using tap water instead of Milli-Q water. The samples were filtered across membranes of 0.45 μm pore size and supplied with thiosulphate to remove any free chlorine introduced at the purifying plant in order to avoid oxidation of the chlorophenols. Preliminary tests on samples to which no chlorophenols were added revealed the absence of all the compounds studied (Fig. 1A).

Table 5
Influence of the flow-rate on the recoveries (R) obtained by using cross-linked styrene–divinylbenzene copolymer cartridges (0.20 g)

Compound	Flow-rate (ml/min)					
	50		75		100	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
2CP	98.7	9.9	105.2	8.4	106.3	7.4
3CP	101.9	10.2	88.3	12.3	87.0	5.2
4CP	100.3	10.2	103.0	5.2	103.2	8.0
26DCP	84.1	5.9	78.2	5.5	85.7	4.3
24DCP	86.7	6.1	85.6	5.1	92.9	3.7
35DCP	84.1	5.9	85.8	4.3	92.7	4.1
23DCP	95.7	7.7	90.3	8.1	97.5	3.9
34DCP	93.6	9.4	93.5	8.4	101.3	8.1
246TCP	81.0	4.9	82.5	2.5	84.7	4.5
236TCP	84.1	5.9	84.2	3.4	92.3	4.6
235TCP	82.7	5.8	85.4	3.4	92.8	5.7
245TCP	83.0	5.7	88.2	3.8	96.7	6.8
234TCP	92.2	7.4	102.2	9.2	104.5	5.2
2356TCP	97.3	5.4	85.7	4.4	98.6	7.9
2346TCP	84.3	5.9	92.4	5.5	92.1	7.4
PCP	106.5	10.6	103.1	12.4	102.2	8.2

Results obtained for samples of 500 ml Milli-Q water ($n=3$) containing 2 ng/ml of each chlorophenol.

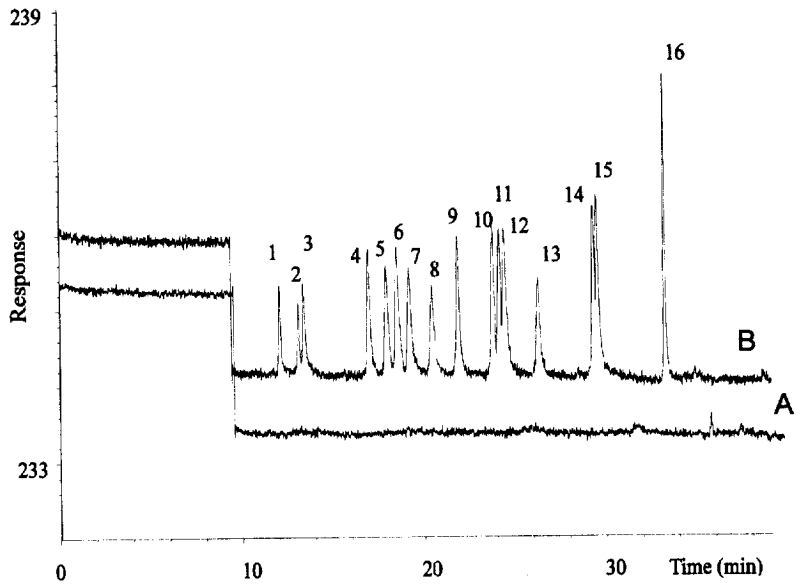

Fig. 1. GC–MIP-AED chromatogram for 1000 ml of tap water concentrated over cross-linked styrene–divinylbenzene cartridges. Trace A: without chlorophenol additions. Trace B: spiked with chlorophenols at the levels stated in Table 6. (1) 2CP, (2) 3CP, (3) 4CP, (4) 26DCP, (5) 24DCP, (6) 35DCP, (7) 23DCP, (8) 34DCP, (9) 246TCP, (10) 236TCP, (11) 235TCP, (12) 245TCP, (13) 234TCP, (14) 2356TCP, (15) 2346TCP, (16) PCP, all as acetates.

Table 6
Mean recoveries (R) obtained from samples of 1000 ml of tap water ($n=5$) spiked with chlorophenols

Compound	Concentration (ng/ml)	Carbon cartridge (0.25 g)[a]		Styrene–divinylbenzene cartridge (0.20 g)[b]	
		R (%)	R.S.D. (%)	R (%)	R.S.D.(%)
2CP	0.54	91.2	11.9	90.9	6.2
3CP	0.48	95.1	10.8	84.6	7.0
4CP	0.57	93.1	10.5	107.3	11.1
26DCP	0.54	80.5	10.3	91.1	8.3
24DCP	0.57	90.6	6.6	94.6	7.4
35DCP	0.62	86.7	10.0	92.9	6.6
23DCP	0.56	90.1	9.2	96.7	6.9
34DCP	0.55	90.3	13.0	97.1	9.3
246TCP	0.48	88.5	4.4	89.2	8.5
236TCP	0.54	87.1	8.5	92.2	8.1
235TCP	0.53	100.2	10.4	96.0	9.6
245TCP	0.55	99.0	9.8	95.4	11.1
234TCP	0.46	87.3	8.3	104.0	10.4
2356TCP	0.59	85.4	7.7	90.1	10.7
2346TCP	0.55	78.3	8.3	96.9	11.3
PCP	0.56	84.6	9.9	92.4	10.2

[a] Average flow-rate 25 ml/min.
[b] Average flow-rate 100 ml/min.

Recovery tests were carried out by using 1000 ml of water containing a 0.5 ng/ml concentration of each of the sixteen chlorophenols. They were pre-concentrated over GCB and styrene–divinylbenzene cartridges, at a flow-rate of 25 and 100 ml/min, respectively. The final extracts, containing the de-

rivatized phenols, were injected into the GC–MIP-AED system, which revealed the absence of interfering peaks (Fig. 1B). The recoveries obtained (Table 6) are consistent with those provided by the Milli-Q water samples (Tables 2 and 3,5).

4. Conclusions

GC–MIP-AED, in combination with the proposed SPE procedures based on carbon and styrene–divinylbenzene cartridges, allows the selective determination of chlorophenols at concentrations below 0.5 ng/ml with recoveries above 80% for all. However, extracting with cross-linked styrene–divinylbenzene cartridges has some advantages over GCB cartridges; in fact, the former can preconcentrate larger samples volumes in a shorter time and afford flow-rates four times as high as those enabled by the carbon cartridges. In addition, they use smaller amounts of acetylating reagents and involve less intensive sample manipulation.

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