Automatic Preconcentration of Chlorophenols and Gas Chromatographic Determination with Electron Capture Detection

M. A. Crespín / E. Ballesteros / M. Gallego / M. Valcárcel*

Department of Analytical Chemistry, Faculty of Sciences, University of Córdoba, 14004 Córdoba, Spain

Key Words

Gas chromatography
Electron capture detection
Solid phase extraction
Chlorophenols
Water analysis

Summary

A solid-phase extraction system coupled to a gas chromatograph fitted with an electron capture detector was developed for the determination of chlorophenols in waters. The continuous system consists of an XAD-2 adsorbent column where chlorinated phenols are preconcentrated and subsequently eluted with ethyl acetate. The sensitivity of the method is proportional to the number of chlorine substituents in the phenol; thus, the detection limit for monochlorophenols is ca. 10 μg L^{-1} and that for pentachlorophenol about 2 ng L^{-1}. The method was used to determine chlorophenols in treated waters, with good precision; however, no mono or dichlorophenols were detected at the levels afforded by the proposed method.

Introduction

Phenol compounds occur widely in nature; they are building units for plants and are formed as products in metabolic processes. Phenols are intermediates in many industrial processes including those of the petroleum industry, the pulp and paper industry, as well as in the production of plastics, dyes, pharmaceuticals and pesticides [1]. Phenols, particularly chlorophenols, are toxic to fish and other aquatic life forms, in addition to many other mammals including humans [2]; at low concentrations, they also have an adverse effect on the taste and odour of drinking water [3]. For these reasons, most of them have been included in environmental legislation and are present in both the European Community (EC) and the US EPA lists of priority pollutants [4, 5]. The current EC Maximum Admissible Concentration for phenols in drinking water is 0.5 μg L^{-1} [6].

Phenols are usually determined by chromatographic techniques; however, environmental waters cannot be analysed without some sample pretreatment because they are too dilute or too complex. Traditionally, liquid-liquid extraction has been used as the sample pretreatment [7], even through it is labour-intensive and time-consuming, and requires large volumes of toxic organic solvents. On account of recent regulatory pressures intended to reduce the use of organic solvents in analytical laboratories, solid-phase extraction (SPE) has undergone substantial development as a reliable, convenient alternative to liquid-liquid extraction [8]. The solid phases employed in this technique are generally similar to those used in column liquid chromatography; thus, C_{18} and C_8-bonded silica [9, 10], styrene-divinylbenzene copolymers [11–13] and graphitic carbon black [14] have been used as adsorbents for preconcentrating phenols.

Coupling SPE on-line to liquid chromatography (HPLC) is very easy, and has proved highly efficient for the preconcentration of organic compounds in environmental samples [15]. Most SPE-HPLC systems are equipped with a UV-diode array spectrophotometer [16], or an electrochemical detector [17], or, occasionally, with a more specific detector such as an enzyme-based biosensor [18] for the determination of phenol compounds in waters. The gas chromatographic (GC) technique has the advantage of a high resolving power and offers a wide range of very sensitive and selective detection modes [15]. However, on-line coupled SPE-GC has not yet become a routine application to the same extent as on-line SPE-HPLC. This is simply the result of the presence of water posing no problem in SPE-HPLC and of SPE-GC requiring an interface for direct coupling of an aqueous, reversed-type LC part to a strictly non-aqueous GC part. A wholly automated, on-line, SPE-GC-MS system including three, six-port switching valves, a solvent delivery unit for the auto-

0009-5893/96/12 633-07 $ 03.00/0 © 1996 Friedr. Vieweg & Sohn Verlagsgesellschaft mbH

mated SPE sequence, drying with nitrogen, desorption with ethyl acetate and coupled MS (including on-column injection and three chromatographic columns) was developed by Brinkman et al. [19]. The system allows large volumes to be introduced into the capillary column (50–100 μL) and the determination of organic pollutant traces (ng L^{-1} levels) in waters with recoveries of at least ca. 70 %. Although several studies have demostrated the versatility and robustness of SPE-GC, Barceló and Hennion [15] claim that the problem of residual water on the adsorbent column remains a hindrance to its widespread acceptance.

Continuous liquid-liquid extraction-derivatization in combination with GC and flame ionization detection have been used for determining various phenol compounds [20, 21] with increased sensitivity, selectivity, precision, throughput and economy relative to manual alternatives; however, the detection limits are higher (ca. 0.2 mg L^{-1}) than the maximum permissible concentration for phenols in drinking water (0.5 μg L^{-1}), thus excluding application to natural waters. The determination of phenols at concentrations from 0.1 to 4 μg L^{-1} in waters remains a problem, even for specialist laboratories, so sensitive analytical methods are required for the determination of these compounds in waters; the best way of ensuring high preconcentration factors is SPE, which can be used in combination with sensitive, selective detection. In this work, an on-line SPE method was developed for the determination of seven chlorophenols in waters by use of gas chromatography and electron capture detection. The proposed extraction system was tested with several adsorbents; the advantages and constraints of the ensuing method are discussed.

Experimental

Reagents

Chlorophenols [2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 3,4-dichlorophenol (3,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP)] were from Aldrich-Chemie (Madrid, Spain). 2,3,4,6-Tetrachlorophenol (2,3,4,6-TCP) was from Dr. Ehrenstorfer (Augsburg, Germany). Ethyl acetate, ethanol, methanol, acetone, acetonitrile and n-hexane, in HPLC grade, were supplied by Romil Chemical (Loughborough, England). The adsorbents, viz. RP-C_{18} (polygosyl-bonded silica reversed-phase with octadecyl functional groups, 40–63 μm), activated carbon (Darco 20–40), XAD-2 (styrene-divinylbenzene) and silica gel 100 were from Sigma Chemical Co. (Madrid, Spain), Aldrich-Chemie, Serva Feinbiochemica (Heildelberg, Germany) and Merck (Darmstadt, Germany), respectively.

Standard solutions of each chlorophenol were prepared at a concentration of 1 g L^{-1} in acetone and stored in glass-stopped bottles at 4 °C. Optimal GC conditions were established using a mixture of chlorophenols in ethyl acetate.

Equipment

Experiments were carried out by using a Hewlett-Packard 5890 A gas chromatograph equipped with an electron capture detector (^{63}Ni). Chromatographic assays were performed on a cross-linked 100 % poly(dimethylsiloxane) fused-silica column (15 m × 0.53 mm i.d., 0.3 μm) by Hewlett-Packard (HP-1). Peak areas were measured with a Hewlett-Packard 3392 A integrator. The injector and detector temperatures were kept at 220 °C and 325 °C throughout. The column temperature was raised from 60 °C (2 min) to 100 °C at 6 °C min^{-1} (2 min), and then to 215 °C at 12 °C min^{-1} (2 min). The flow-rate of the carrier gas (nitrogen) was 20 mL min^{-1}.

The solid-phase extraction flow system consisted of a Gilson Minipuls-2 peristaltic pump, two Reodyne 5041 injection valves and PTFE tubing, 0.5 mm i.d., for coils. Poly(vinyl chloride) and Solvaflex pumping tubes for aqueous and ethanol solutions, respectively, and a displacement bottle for pumping ethyl acetate, were also used. Laboratory-made adsorption columns packed with XAD-2, activated carbon, RP-C_{18} and silica gel 100 were employed. A six-port injection valve (Knauer 633200) mounted over the injection port of the gas chromatograph (injected volume, 5 μL) was also used [21].

The adsorbent column body was a 3 mm i.d. PTFE tube, and the column end-caps were formed by fitting a 30 × 0.5 mm i.d. PTFE tube into a 10 × 1 mm i.d. PTFE tube, which facilitated insertion into the continuous system. The column was packed with different amounts of adsorbent and sealed on both ends with small plugs of cotton wool to prevent material losses. It was conditioned by passing ethanol and Milli-Q water at a flow-rate of 1 mL min^{-1} for 1 min.

Manifold and Procedure

Figure 1 depicts the continuous system used for the SPE and determination of chlorophenols. In the preconcentration step, 25 mL aqueous sample or standard solution containing chlorophenols at different concentrations (4 ng L^{-1}–480 μg L^{-1}) at pH 2 was passed through the column (located in the loop of injection valve IV_1) at 4 mL min^{-1}; retention of chlorophenols was instantaneous and the sample matrix was sent to waste (W_1). In the drying step, IV_1 was switched and a nitrogen stream was passed via IV_2 by the column at 1 mL min^{-1} for 3 min; simultaneously, the loop of IV_2 was filled with eluent. In the elution step, IV_2 was switched and the loop (containing 60 μL eluent) was injected into the same nitrogen stream used in the drying step, and passed through the column to elute the chlorophenols. Finally, the eluate was homogenized in a 75 cm mixing coil (MC) and transferred to IV_3 in the in-

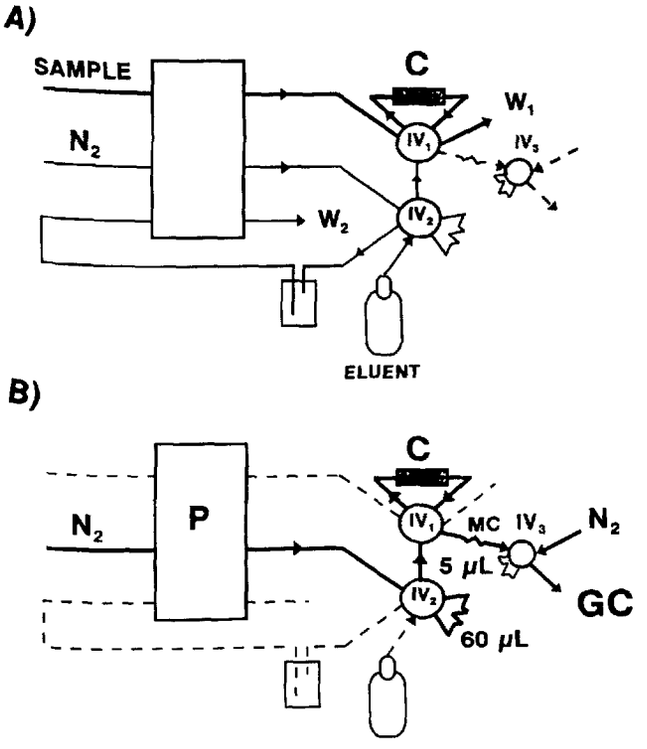

Figure 1
Manifold for chlorophenol determination: A) Preconcentration and drying step; B) Elution and determination step. P: pump; C: XAD-2 adsorbent column; IV: injection valve; W: waste; MC: mixing coil; GC: gas chromatograph.

terface unit, and the contents of the 5 µL loop were injected (30 s after IV_2 was switched, elution step) into the nitrogen carrier gas and transferred to the injection port. After each analysis, the adsorbent column was washed with 1 mL ethanol and 1 mL water.

Results and Discussion

Preconcentration

Reagents were selected and experimental variables optimized using an automated system similar to that depicted in Figure 1. The eluate from the adsorbent column was collected in 4 mL glass vials containing anhydrous sodium sulphate, and 2 µL fractions were injected manually into the chromatograph by syringe. Seven representative chlorophenols were selected, namely: 2-CP, 4-CP, 2,4-DCP, 3,4-DCP, 2,4,6-TCP, 2,3,4,6-TCP and PCP.

Preliminary experiments were to find the best adsorbent for the SPE system. Various solid-phase adsorbents have been used for the uptake of phenol compounds in different matrices, of which we studied XAD-2, activated carbon, RP-C_{18} and silica gel 100. An aqueous sample containing seven chlorophenols at concentrations 50 µg L^{-1}–100 mg L^{-1} at pH 2 was passed at 2 mL min^{-1} through columns packed with 50 mg of each adsorbent. Fractions of 1 mL sample were collected above and below the column in glass vials and the chlorophenols extracted with 1 mL ethyl acetate, a 2 µL aliquot of extract being analysed by GC. After each sample was processed, the column was rinsed with ethyl acetate and water for 1 min to remove adsorbed analytes. The results showed that chlorophenols were adsorbed quantitatively on XAD-2 (ca. 100 %), but only by 40, 20 and 15 % on activated carbon, silica gel 100 and RP-C_{18}, respectively. XAD-2 was thus selected as it exhibited the best adsorption and desorption properties.

The amount of adsorbent material was optimized by varying the length of the column (packed with 10–60 mg of XAD-2). A series of calibration graphs were run for each phenol and column by passing 25 mL aqueous standard solutions at pH 2 and eluting with 75 µL ethyl acetate. The adsorption efficiency for each adsorbent amount was related to the sensitivity (slope of calibration graph). As seen in Figure 2, the sensitivity of the method increased with increasing amount of adsorbent for all phenols; above 45 mg of adsorbent, the sensitivity remained virtually constant. On the other hand, the slope of the calibration graph also increased with increasing number of chlorine substituents in the phenol through increased sensitivity of the ECD. A working column packed with 50 mg XAD-2 was adopted for further experiments.

The phenols could be uncharged at low pH and therefore retained on the adsorbent; other organic compounds (i.e. aromatic amines) would be ionized at acid pH and hence not retained. The pH was thus critical to the selectivity of the method. The influence of the sample pH on retention of chlorophenols was studied over the range pH 1–11, adjusted with dilute HNO_3 or NaOH. Peak areas for mono and dichlorophenols remained constant over wider ranges (up to about pH 8) than they did for tri and tetrachlorophenols (up to about pH 6) or pentachlorophenol (up to about pH 4), above which retention of the phenolics decreased. In subsequent experiments, samples were prepared in 10^{-2} mol L^{-1} HNO_3 (pH 2.0). The ionic strength of the samples, adjusted with potassium nitrate, did not affect the signal up to 1.75 M.

The effect of the sample flow rate (25 mL solution) through the column during the preconcentration step on adsorption efficiency was studied between 1–4 mL min^{-1}. Results confirmed that the uptake of chlorophenols by the adsorbent was rapid and efficient; a flow rate of 4 mL min^{-1} was therefore chosen to ensure maximum possible sample throughput.

Elution

Problems arising from the presence of water in the chromatographic column can be overcome by drying the adsorbent column with nitrogen at ambient temperatures before the elution step. Passing a stream of N_2 at 1 mL min^{-1} for 3 min was sufficient to dry the column; under these condition, the GC column can be used daily with no risk of damage or loss of resolution for about six months.

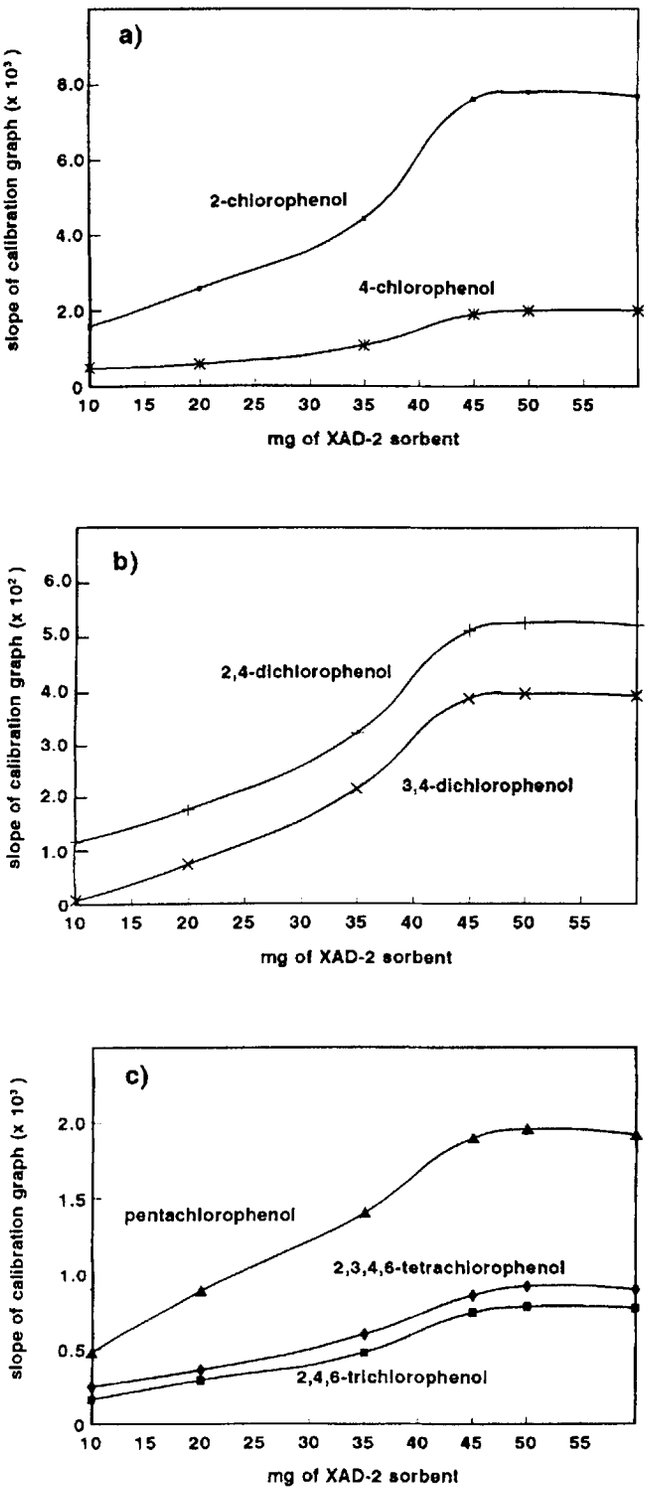

Figure 2

Influence of amount of adsorbent on the adsorption of chlorophenols on the XAD-2 material. a) monochlorophenols (25–500 μg L^{-1}); b) dichlorophenols (250–8000 ng L^{-1}); c) tri-, tetra and pentachlorophenol (10–1500 ng L^{-1}).

Several organic solvents of variable polarity were assayed as eluents for the chlorophenols adsorbed on XAD-2 material, namely: acetone, acetonitrile, methanol, ethyl acetate and ethanol. For this, 25 mL of an aqueous solution containing chlorophenols (100 μg L^{-1} 2- and 4-CP, 1 μg L^{-1} 2,4- and 3,4-DCP, 150 ng L^{-1} 2,4,6-TCP and 2,3,4,6-TCP, and 50 ng L^{-1} PCP) at pH 2 was passed through the adsorbent at 4 mL min^{-1}. The loop of IV_2 (75 μL) was filled with different eluents using a displacement bottle, eluent being transported through the column by a nitrogen stream at 1 mL min^{-1}. Ethyl acetate proved to be the most effective eluent for the chlorophenols because the resulting analytical signals were twice those achieved with acetone and acetonitrile and 3 times as high as those for ethanol and methanol. We therefore chose ethyl acetate as eluent.

The effect of eluent volume was studied between 25–125 μL by changing the loop of IV_2 (see Figure 1). Elution efficiency increased with increasing volume injected up to 60 μL (complete elution), above which the signal decreased because the eluted analytes were more dilute in the larger eluent volumes. An injection of 60 μL was selected as optimal, which was confirmed with a second elution without sampling, where no carryover was observed. A coil of 75 cm (0.5 mm i.d.) was inserted into the flow system to homogenize the eluted fraction before injection into the gas chromatograph (30 s after IV_2 was switched).

On-Line Injection into Gas Chromatograph

The optimized SPE system was fitted to the gas chromatograph via an injection valve (IV_3) similar to that used elsewhere to couple an extraction unit to a gas chromatograph [21]. The loop of the injection valve (5 μL) was of PTFE, and the valve was connected to the instrument via a 4 cm × 0.3 mm i.d. PTFE tube with a needle at the end for direct insertion into the septum of the injection port. The carrier gas (nitrogen) stream was split into two lines, one directly connected to a port of valve IV_3 and the other to the chromatographic injection port. The flow rate of the carrier gas was varied between 15–25 mL min^{-1} to minimize adsorption in the connecting tube and improve chromatographic resolution of peaks. An overall gas flow rate of 20 mL min^{-1} (flow rates through the valve and injection port, 14.4 and 5.6 mL min^{-1}, respectively) was selected as optimal.

Analytical Figures of Merit

The dependence on the concentration of the chromatographic signal for the seven chlorophenols studied was only determined at one integrator sensitivity under optimum conditions by using the flow system in Figure 1. The figures of merit for the method for a sample volume of 25 mL (pH 2) are summarized in Table I. As expected, the sensitivity increased significantly with increasing

Table I. Features of calibration graphs and determination of chlorophenols

Chlorophenol	Regression equation[a]	Corr. coef.	Linear range	Detection limit	R.S.D. (%)	Preconc. factor[b]
2-Chlorophenol	$A = 9.4 \times 10^3 X + 27.9 \times 10^3$	0.999	10–480 $\mu g\ L^{-1}$	5 $\mu g\ L^{-1}$	2.9	400
4-Chlorophenol	$A = 2.8 \times 10^3 X + 39.5 \times 10^3$	0.999	15–480 $\mu g\ L^{-1}$	8 $\mu g\ L^{-1}$	3.2	405
2,4-Dichlorophenol	$A = 6.4 \times 10^2 X - 16.3 \times 10^3$	0.998	150–8000 ng L^{-1}	80 ng L^{-1}	3.7	390
3,4-Dichlorophenol	$A = 4.9 \times 10^2 X - 10.2 \times 10^3$	0.993	175–8000 ng L^{-1}	90 ng L^{-1}	3.6	395
2,4,6-Trichlorophenol	$A = 9.8 \times 10^2 X + 34.2 \times 10^3$	0.997	30–1400 ng L^{-1}	20 ng L^{-1}	2.6	405
2,3,4,6-Tetrachlorophenol	$A = 1.1 \times 10^3 X + 18.7 \times 10^3$	0.999	30–1400 ng L^{-1}	15 ng L^{-1}	3.7	410
Pentachlorophenol	$A = 2.7 \times 10^3 X + 51.5 \times 10^3$	0.999	4–1000 ng L^{-1}	2 ng L^{-1}	4.1	415

[a] A, peak area; X, concentration, expressed in ng L^{-1} except for 2- and 4-chlorophenol ($\mu g\ L^{-1}$)
[b] Preconcentration factor (sampling volume, 25 mL)

Table II. Determination of chlorophenols in water samples (ng L^{-1})

Compound	Waste water1	Waste water2	Purified waste water2	Pond water[a]	Pond water[b]	Pond water[c]
2-Chlorophenol	ND	ND	ND	ND	ND	ND
4-Chlorophenol	ND	ND	ND	ND	ND	ND
2,4-Dichlorophenol	ND	ND	ND	ND	ND	ND
3,4-Dichlorophenol	ND	ND	ND	ND	ND	ND
2,4,6-Trichlorophenol	170 ± 5	95 ± 3	220 ± 7	3410 ± 100	2710 ± 75	1115 ± 30
2,3,4,6,-Tetrachlorophenol	220 ± 8	805 ± 30	2560 ± 95	2015 ± 70	1620 ± 60	1405 ± 50
Pentachlorophenol	430 ± 20	460 ± 20	1550 ± 60	310 ± 10	305 ± 10	200 ± 8

ND: not detected; Pond water treated with 15 mg L^{-1} of sodium hyplochlorite,[a] plus 3 mg L^{-1} [b] or 6 mg L^{-1} [c] potassium permanganate.

number of chlorine substituents in the phenol, which modified its linear range. The detection limits obtained for a given sample volume (calculated as minimum concentrations providing a chromatographic signal three times background noise) varied between a few ng L^{-1}–$\mu g\ L^{-1}$ levels. Repeatability was then assessed from the results for aqueous solutions containing the seven chlorophenols (100 $\mu g\ L^{-1}$ for monochlorophenols, 500 ng L^{-1} for dichlorophenols, 100 ng L^{-1} for tri- and tetrachlorophenols, and 50 ng L^{-1} for pentachlorophenol) at pH 2. The relative standard deviation varied between 2.6 and 4.1 % (n = 11).

The sensitivity can be increased by increasing the sample volume. Preconcentration factors were calculated as the ratios of the slopes of the calibration graphs obtained by using the flow system in Figure 1 and those provided by manual injection of standards containing the seven chlorophenols (at concentrations of a few mg L^{-1} for mono and dichlorophenols and $\mu g\ L^{-1}$ for tri, tetra and pentachlorophenols) in ethyl acetate. The preconcentration factors were proportional to the sample volume; thus, the mean values were 80, 150 and 400 for 5, 10 and 25 mL, respectively. Higher preconcentration factors could be achieved by using higher sample volumes, but at the expense of decreased sample throughput.

Application to Water Samples

The proposed on-line enrichment-separation system was applied to the analysis of six different water samples. As the purpose of this work was to determine chlorophenols, the concentrations of which in waste water is increased – at the expense of those of phenols – by the use or household bleaches, and in drinking waters treated with hypochlorite, the proposed method was applied to these types of water. Thus, two different waste water samples were analysed; one was collected from a purifying plant that uses sludge actives, before and after purification. These samples were found to contain filamentous bacteria that required treatment with hypochlorite (40 g m^{-3}), which increased the chlorophenol levels at the obvious expense of phenols. The other samples analysed were from a eutrophic pond used as a source of drinking water and contained high concentrations of humic and fulvic acids (phenols precursors); the water was treated at the laboratory with hypochlorite and permanganate, which favour the formation of chlorophenols. All the water samples were filtered through 0.45 µm filters (Micro Separations Inc, 4 mm diameter, Westboro, MA) to remove particulates, and adjusted to pH 2 with dilute HNO_3; 25 mL filtered water was analysed by the proposed continuous method. Table II lists the chlorophenol levels present in

the waters. As anticipated, purified waters had increased concentrations of chlorophenols, particularly tri, tetra and pentachlorophenols (no mono or dichlorophenols were detected). In some cases, concentrations fell outside the linear range of the method, so 10 mL rather than 25 mL water was preconcentrated. The pond sample treated simultaneously with hypochlorite and permanganate had decreased concentrations of tri and tetrachlorophenols, probably because they were oxidized. Figure 3 shows the chromatogram obtained following preconcentration of 25 mL waste water$_1$ and for the same sample spiked with mono and dichlorophenols. After 12 min, the background signal increased significantly; however, the chlorophenols were quantified without problem. As the waters analysed contained no mono or dichlorophenols at detectable levels, water samples containing no permanganate were spiked with the above compounds (at 50 μg L^{-1} for monochlorophenols and 500 ng L^{-1} for dichlorophenols). Recoveries thus obtained for three individual additions ranged from 95–103 % for all waters.

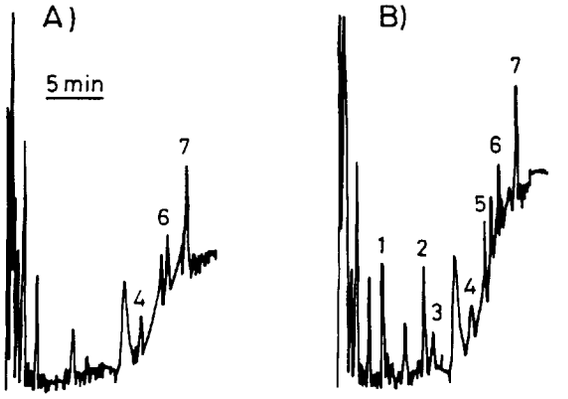

Figure 3
Chromatogram obtained after preconcentration of 25 mL waste water$_1$ at pH 2 (A) and same sample spiked with 100 μg L^{-1} and 1 μg L^{-1} monochlorophenols and dichlorophenols, respectively (B). **1** = 2-chlorophenol; **2** = 2,4-dichlorophenol; **3** = 4-chlorophenol; **4** = 2,4,6-trichlorophenol; **5** = 3,4-dichlorophenol; **6** = 2,3,4,6-tetrachlorophenol; **7** = pentachlorophenol.

Conclusions

The low concentrations of phenol compounds in industrial waste waters and, especially, in drinking and natural waters, hinder their detection in routine laboratories. The proposed method affords the determination of chlorophenols at sub-trace levels in water samples. The analytical figures of merit of other solid-phase extraction methods for the chromatographic determination of chlorophenols are summarized in Table III. Electrochemical detection coupled on-line to SPE-LC is a very sensitive technique; however, the detection limits it provides also depend on the adsorbent type and on whether the adsorbent is used in cartridges or disks [12, 17]. The detection limits for chlorophenols obtained with GC-ITDMS are the lowest. However, the method is rather complex: it involves preconcentrating 1 L of water at pH 11, filtration, derivatization, solid-phase extraction and evaporation of the extract down to 0.5 mL; this results in an overall sample preparation time of about 1 h. The proposed system is clearly superior to existing manual GC alternatives and similar to other on-line LC methods in terms of sample manipulation, detection limits, throughput, and so on.

Acknowledgment

This work was supported by a grant (PB-95-0977) from Spanish DIGICyT. The authors also wish to acknowledge Dr. R. Marin for his kind supply of the water samples used in this work.

References

[1] *E. Tesarová, V. Pacáková*, Chromatographia **17**, 269 (1983).
[2] *P. J. Vuorinen*, Chemosphere **14**, 1729 (1985).
[3] *L. H. Keith*, Advances in the Identification and Analysis of Organic Pollutants in Water, Vol. 1, Ann Arbor Science, Ann Arbor, MI, 1981.
[4] Drinking Water Directive 80/778/EEC Proposals for Modification Views of Eureau, Eureau. Brussels, 1991.
[5] EPA Method 604. Phenols in "Federal Register, Friday October 26, 1984, Environmental Protection Agency, Part VIII, 40 CFR Part 136", pp. 58.

Table III. Analytical figures of merit of on-line, solid-phase extraction methods for determination of chlorophenols by chromatographic techniques

Technique/Detection	Adsorbent	Sample volume (mL)	Detection limit	R.S.D. (%)	Recovery (%)	Ref.
LC/ED	PRLP-S	10	10–50 ng L^{-1}	4– 9	90–105	12
LC/UV	PRLP-S	100	10–500 ng L^{-1}	3– 6	80– 95	12
LC/DAD	PRLP-S	10	0.1–2 μg L^{-1}	8–10	–	16
LC/ED	RP-C_{18} (cartridge)	20	0.3–2 μg L^{-1}	2– 7	72– 99	17
GC/ITDMS	RP-C_{18} (disk)	1000	2–15 ng L^{-1}	4– 9	75–106	10*
GC/ECD	XAD-2	25	2–8000 ng L^{-1}	3– 4	95–103	This paper

LC = liquid chromatography; ED = electrochemical detection; UV = ultraviolet detection; DAD = diode array detection; GC = gas chromatography; ITDMS = ion-trap detector mass spectrometer; ECD = electron capture detection.
* with manual preconcentration and derivatization.

[6] *M. C. Hennion, V. Pichon, D. Barceló,* Trends Anal. Chem. **13**, 361 (1994).
[7] *M. M. Kopecni, M. V. Tarana, S. D. Cupic, J. J. Comor,* J. Chromatogr. **462**, 392 (1989).
[8] *L. A. Berrueta, B. Gallo, F. Vicente,* Chromatographia **40**, 474 (1995).
[9] *A. Gelencser, G. Kiss, Z. Krivacsy, Z. Varga-Puchony, J. Hlavay,* J. Chromatogr. **693**, 227 (1995).
[10] *M. L. Bao, F. Pantani, K. Barbieri, D. Burrini, O. Griffini,* Chromatographia **42**, 227 (1996).
[11] *E. Pocurrull, M. Calull, R. M. Marcé, F. Borrull,* Chromatographia **38**, 579 (1994).
[12] *D. Puig, D. Barceló,* Anal. Chim. Acta **311**, 63 (1995).
[13] *F. Navarro-Villoslada, L. V. Pérez-Arribas, M. E. León-González, L. M. Polo-Díez,* Anal. Chim. Acta **308**, 238 (1995).
[14] *W. Rudzinski, A. Gierak, R. Leboda, A. Dabrowski,* Fresenius J. Anal. Chem. **352**, 667 (1995).
[15] *D. Barceló, M. C. Hennion,* Anal. Chim. Acta **318**, 1 (1995).
[16] *E. Pocurrull, R. M. Marcé, F. Borrull,* Chromatographia **41**, 521 (1995).
[17] *M. T. Galceran, O. Jáuregui,* Anal. Chim. Acta **304**, 75 (1995).
[18] *E. Burestedt, J. Emnéus, L. Gorton, G. Marko-Varga, E. Dom-Rnguez, F. Ortega, A. Narváez, H. Irth, M. Lutz, D. Puig, D. Barceló,* Chromatographia **41**, 207 (1995).
[19] *A. J. H. Louter, J. J. Vreuls, R. T. Ghijsen, U. A. Th. Brinkman,* Int. J. Environ. Anal. Chem. **56**, 49 (1994).
[20] *E. Ballesteros, M. Gallego, M. Valcárcel,* J. Chromatogr. **518**, 59 (1990).
[21] *E. Ballesteros, M. Gallego, M. Valcárcel, Anal. Chem.* **62**, 1587 (1990).

Received: Jul 15, 1996
Revised manuscript
received: Sep 23, 1996
Accepted: Oct 15, 1996