



Solid phase extractive preconcentration coupled to gas chromatography–atomic emission detection for the determination of chlorophenols in water samples

Latif Elci*, Nina Kolbe, Sukru G. Elci¹, Jan T. Anderson

Institute of Inorganic and Analytical Chemistry, University of Muenster, Corrensstrasse 30, 48149 Muenster, Germany

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ABSTRACT

Solid-phase extraction (SPE) followed by derivatization and gas chromatography–atomic emission detection (GC–AED) was evaluated for the determination of five chlorophenols (CPs) in water samples. The derivatization was based on the esterification of phenolic compounds with ferrocenecarboxylic acid. The determination of the derivatized phenols was performed by GC–AED in the iron selective detection mode at 302 nm. The described method was tested on spiked water samples. The overall method gave detection limits of 1.6–3.7 ng L⁻¹ and recoveries of 90.9–104.5% for the examined mono- to trichlorophenols in 10 mL water samples. The CPs extracted from a 10 mL water sample with SPE were concentrated into 100 µL of organic solvent, a preconcentration factor of 100. The method was applied to lake and tap water samples, and CP contents between 6 and 51 ng L⁻¹ in lake water and between below the detection limit and 8 ng L⁻¹ in tap water were found for different CPs. The method is quick, simple and gives excellent recoveries, limits of detection and standard deviations.

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1. Introduction

Chlorinated phenols are widely used in the production of pesticides, herbicides, wood preservatives, antiseptic and disinfectants, as well as in the plastic, dye and pharmaceutical industries [1]. These compounds are thought to be highly toxic and lower chlorinated members have shown carcinogenic traits [2]. Owing to the toxicity of these compounds, both the US Environmental Protection Agency (EPA) [3] and the European Community (EC) [4] have included some phenols, mainly chlorophenols (CP) and nitrophenols, in their lists of priority pollutants. Four chlorophenols (2-CP, 2,4-DCP, 2,4,6-TCP, and PCP) as the most representative chlorophenols in water samples have been classified as priority pollutants by the U.S. Environmental Protection Agency [5]. The EC has mandated that the maximum admissible concentration of phenols in drinking water is 0.5 µg L⁻¹ for the total content and 0.1 µg L⁻¹ for individual ones [6].

Chlorophenols can be produced as a result of hydrolysis, oxidation and microbial degradation of chlorinated pesticides in the environment. They can enter water systems through various trans-

port mechanisms and can also chemisorb onto soil surfaces and aquatic sediments. Moreover, chlorine treatment of drinking water can generate CPs to create a major health threat [7]. Therefore, CPs are regarded as important environmental pollutants and can frequently be found in surface water, tap water, industrial and domestic wastewaters [8,9].

The need for monitoring and controlling the presence of these compounds in the aqueous environment is now well recognized, being essential for achieving good water-quality objectives. Many analytical methods, including capillary electrophoresis [10,11], high-performance liquid chromatography (HPLC) [12] and gas chromatography [1] are available for the determination of CPs in water samples. Gas chromatography (GC), usually after derivatization, with flame-ionization detection (FID) [13,14], electron-capture detection (ECD) [15], mass spectrometric detection (MS) or microwave-induced plasma atomic emission spectrometry (MIP-AES) [16–19] is a common tool for the determination of phenols because of its high separation power and low limits of quantification.

Atomic emission detection (AED) is a selective and sensitive alternative to the use of other detectors for derivatized chlorinated phenols. It probably does not show any advantages for CPs if these are monitored using the chlorine emission since this emission is not very strong and the selectivity vs. carbon is only ca. 27,000 [20]. The AED may be more interesting if an element with better detection characteristics than chlorine can be introduced into the chlorophenol through a derivatization reagent. An excellent choice is iron, which offers very low limits of detection (ca. 0.1 pg/s) and

* Corresponding author. Permanent address: Pamukkale University, Art and Science Faculty Chemistry Department, Kinikli, TR-20017 Denizli, Turkey, Tel.: +90 258 2963596, fax: +90 258 2963535.

E-mail address: elci@pau.edu.tr (L. Elci).

¹ Izmir Institute of Technology, Science Faculty, Chemistry Department, Urla, TR-35430 Izmir, Turkey.

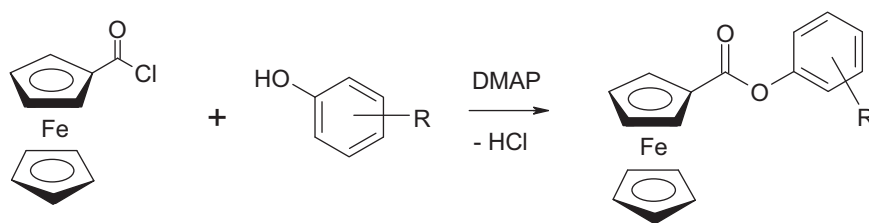


Fig. 1. The reaction of phenols with ferrocenecarboxylic acid chloride, introducing iron as the element to be detected by GC–AED.

extremely high selectivity vs. carbon (ca. 4.6 million) [20]. This element is easily introduced into phenols through their coupling with the acid chloride of ferrocenecarboxylic acid to yield the ferrocenecarboxylic acid esters (Fig. 1) [17–19].

In the reaction between ferrocenecarboxylic acid chloride (FCC) and a phenolic compound, each phenol is labelled with one iron atom. The method has been successfully applied to the determination of some phenolic compounds in non-aqueous materials like petroleum as well as for the determination of *o*-phenylphenol as a pesticide on citrus fruits [17,18]. To the best of our knowledge there has been no application of the method to the analysis of water samples. Due to the hydrolytic sensitivity of the acid chloride, phenols in water samples have to be transferred into a non-aqueous solvent before the derivatization step, thus necessitating an extraction procedure. Such procedures are commonly applied prior to GC analysis of CPs to extract and simultaneously to concentrate them to achieve the concentration levels required by legislation. Thus extensive liquid–liquid [21,22] or solid-phase extraction (SPE) [5,23–25] methodologies followed by derivatization have been applied prior to GC analysis. Solid-phase extraction is the most frequently used technique for preconcentration of CPs and consequently we make use of an SPE column here as an ideal way of transferring the phenolic compounds from water samples into an organic solvent.

Recently, several studies have shown that phenols, including CPs, can be extracted using SPE based on polystyrene-divinylbenzene (PS-DVB) with good recoveries and detection limits at the sub-mg/L level [26,27]. PS-DVB resins have greater analyte retention, mainly for polar compounds, than bonded silicas because their hydrophobic surface contains a large number of active aromatic sites, which allow π – π interactions with unsaturated analytes [28]. It is well known that the retention of phenols on PS-DVB resins is the result of a reversed-phase mechanism. As a result, here Amberchrom 161C, a PS-DVB resin, is explored as the solid phase material for SPE because of its large surface area and small particles.

This paper reports a method for the determination of 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) in water samples, therefore including the EU and EPA priority pollutants 2-CP, 2,4-DCP and 2,4,6-TCP. The method involves a solid phase extraction procedure using an Amberchrom 161C resin column, then a derivatization of the CPs with ferrocenecarboxylic acid chloride followed by their determination with GC–AED. The proposed method was successfully applied to the determination of CPs in lake and tap water samples.

2. Experimental

2.1. Material and chemicals

2-Chlorophenol, 3-chlorophenol, 4-chlorophenol (98% w/w purity), 2,4-dichlorophenol and 2,4,6-trichlorophenol standards of 99% purity were obtained from commercial suppliers (Aldrich, Fluka, Merck and Riedel-de Haën). A stock solution, which is a

mixture of the chlorophenols at 100 mM was prepared in toluene, diluted to the required concentration to produce working solutions, and then stored in the dark at 4 °C in a refrigerator. The used water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA).

4-fluoro-2-methylphenol ferrocenecarboxylic acid ester (4F2MPE) and 4-fluoro-2-methylphenol (4F2MP), both purchased from Sigma–Aldrich, Germany, were used as quantification internal standards for esterification, and the combination of the SPE and derivatization, respectively. Toluene, cyclohexane, and dichloromethane (all pesticide grade, Fluka) were purified by percolation through aluminum oxide before use. Further chemicals used were anhydrous sodium sulfate (99%, Fluka) and 4-(dimethylamino)pyridine (DMAP, 99%, Acros). Aluminum oxide (chromatography grade, neutral, Fluka) was activated at 450 °C, and stored at 160 °C for at least 24 h for a water content of 1.2%. The derivatization reagent ferrocenecarboxylic acid chloride (FCC) was synthesized from ferrocene carboxylic acid with oxalyl chloride, following the published procedure [17,19]. While the deeply red product is stable for almost one year if stored at –18 °C in the dark under argon gas, solutions in dichloromethane should be prepared freshly just prior to use.

The Amberchrom 161C resin was supplied by Supelco. It consists of a polystyrene–divinylbenzene copolymer (PS–DVB), contains a hydrophobic structure and is a spherical resin with an average particle size of 50–100 μm , an average pore size of 150 Å and a surface area of 720 m^2/g [25]. Empty SPE glass columns with PTFE frits were purchased from Merck (Darmstadt, Germany).

2.2. Apparatus

The Agilent GC–AED system consists of a 6890N GC and a G2350A AED, equipped with a 30 $\text{m} \times 0.25 \text{ mm i.d.} \times 0.25 \mu\text{m}$ film thickness DB-5ms column (J&W Scientific, Folsom, CA, USA), a Gerstel MPS2 autosampler, and a Gerstel CIS-injector (Gerstel, Mülheim a.d.R., Germany). The instrumental parameters were taken from Ref. [18]. The oven temperature was programmed as follows: 60 °C starting temperature, kept for 0.5 min, temperature ramp at 45 °C/min to 295 °C, then at 2 °C/min to 300 °C, kept for 3 min. Other GC–AED conditions were: injector initial temperature, 60 °C, heated at 12 °C/s to 300 °C; helium carrier gas with 40 cm/s constant velocity; transfer line and cavity temperature 300 °C. Helium make-up flow for the AED is 240 mL/min ; hydrogen and oxygen plasma pressures are 15 and 20 psi, respectively.

2.3. Sampling

The water from the Lake Aasee in Münster was collected daily in glass sampling bottles which were chemically cleaned using acetone and dichloromethane successively before the collection. It was taken from a depth of 10 cm and was filtered through a glass-fiber filter (0.45 μm pore size) to eliminate particulate matter before the preconcentration step. The samples were analyzed on the same day to avoid any microbial degradation of analytes. Tap water samples were taken directly from the tap in a laboratory at the University of

Münster. The pH of the tap water and the lake water samples was measured as 6.0 and 6.5, respectively.

2.4. Solid phase extraction cartridges

Amberchrom 161C resin packed cartridges were prepared from empty SPE glass cartridges (3 mL). 0.5 g of Amberchrom 161C resin was packed into the cartridge after a PTFE frit had been placed at the cartridge bottom. Another PTFE frit was introduced at the top of the cartridge to fix the height of the resin. The dry resin bed height in the column was approximately 2.5 cm. It was washed successively with DCM and twice distilled water. The column could be reused at least ten times for the preconcentration of CPs from water samples.

To prepare the mini aluminum oxide column, ca. 1.7 g of aluminum oxide was packed into a 3 mL SPE glass cartridge under DCM. The column was used to separate ferrocenecarboxylic acid esters from the excess of FCC and DMAP in the derivatization solution [19]. These columns were used only once.

2.5. Esterification of chlorophenols with ferrocenecarboxylic acid chloride

The esterification with FCC has been used previously for the determination of alkylated phenols [17–19]. Since CPs have not been investigated in this procedure previously, their derivatization was first evaluated by determination of spiked toluene solutions. To 5 mL of toluene was added 50 μ L of a 100 μ M mixed solution of 2-CP, 3-CP, 4-CP, 2,4-DCP and 2,4,6-TCP, and 50 μ L of a 100 μ M ferrocenecarboxylic acid ester of 4-fluoro-2-methylphenol

(4F2MPE) in toluene as a quantification internal standard. The derivatives are stable for several months at 5 °C. The known esterification procedure [18] was used as detailed below.

2.6. Preconcentration and derivatization for water analysis

A 10 mL portion of the water samples collected either from the Lake Aasee in Münster or from a tap at the University of Münster was passed through the SPE column packed with Amberchrom 161C resin at a flow rate of 2 mL/min. The residue of water in the resin was removed by attaching the column to a pump and lowering the pressure, and then the resin was dried by introducing a gentle flow of argon gas at the column head for 25–30 min. Finally, the retained chlorophenols were recovered by eluting the column with 5.0 mL of dichloromethane at a flow rate of 1 mL/min into a 10 mL vial containing ca. 1.0 g of anhydrous sodium sulfate to remove any residual water from the solution. 4-Fluoro-2-methylphenol as internal standard was added to the vial. To recondition the column for the next sample, it was washed once with 5.0 mL of DCM and then twice with 5.0 mL of twice distilled water.

Derivatization of the preconcentrated CPs and 4F2MP [17–19]: 20 mg FCC as derivatization agent and 20 mg DMAP as catalyst were added to the vial. Because of the probable residual water in the effluent we added more than 15 mg of FCC and DMAP. After a reaction time of 10 min at room temperature, the solution was added to the top of the aluminum oxide column and the ferrocenecarboxylic acid esters of the CPs were eluted with 5.0 mL of dichloromethane (the DMAP and the excess FCC remained on the column). The derivatized sample in the vial was further concentrated almost to dryness using a gentle flow of nitrogen at 40 °C. The remaining material was dissolved in 100 μ L of cyclohexane for analysis by GC–AED.

3. Results and discussion

The ferrocenecarboxylic acid derivatization provides a very sensitive and selective method to analyze CPs as ferrocenecarboxylic

acid esters (FE) based on GC–AED in the iron selective mode [20]. The conventional derivatization procedures (acetylation, silylation) are less sensitive and selective method than the derivatization with ferrocenecarboxylic acid, for AED. Because, an element (e.g. chlorine) which is less sensitive than iron, is used as analyzed element in the combination of conventional derivatizations with GC–AED. The advantage of using this new derivatization procedure is high selectivity and sensitivity. This derivatization reaction has previously been used for alkyl- and phenyl substituted but not for chlorinated phenols. Since the electronic situation in these different kinds of phenols is completely different, it was necessary to investigate the optimum conditions for the coupling of the CPs with ferrocenecarboxylic acid chloride.

3.1. Optimization of the derivatization with ferrocenecarboxylic acid chloride

Variables such as the amount of FCC (derivatizing reagent) and of DMAP (catalyst), derivatization time and effect of microwave energy were studied for the derivatization of the CPs. For this, each variable is changed in turn, while the others are held constant, until a maximum derivatization yield (%) has been found. 4F2MPE was used as an internal standard.

The effect of FCC and DMAP amounts at 10 min reaction time was investigated first at a constant amount of DMAP (10 mg) and a constant amount of FCC (15 mg), respectively. The best yields were obtained with 15 mg of FCC and 15 mg of DMAP, which were the largest amounts tested in these experiments. The derivatization yields for 2-CP, 3-CP, 4-CP, 2,4-DCP and 2,4,6-TCP were found to be 92.5, 91.6, 91.2, 81.6 and 83.6%, respectively. Obviously the esterification yield of CPs depends on the amount of both FCC and DMAP.

We also tested the effect of reaction time on the yield. The yields hardly varied for reaction times between 5 and 15 min at constant amounts of FCC (15 mg) and DMAP (10 mg). Thus it seemed advisable to work with at least 15 mg of DMAP, 15 mg FCC and a reaction time of 10 min. Finally the effect of microwaves on the reaction yield was tested. The derivatization solution was exposed to microwaves for 2 min. The derivatization yields for 2-CP, 3-CP, 4-CP, 2,4-DCP and 2,4,6-TCP were found to be 90.3, 93.4, 87.5, 90.6 and 88.9%, respectively, for an average yield of 90.1% vs. 88.1% without microwaves above. Microwaves therefore do not seem to improve the yield and this technique was not used any further.

3.2. Optimization of the solid phase extraction

The optimization of the complete method – the combination of SPE and derivatization – was first evaluated by determination of the standard CPs in 50 μ L of a 100 μ M solution spiked into 10 mL of distilled water. The water was also spiked with 50 μ L of a 100 μ M solution of 4-fluoro-2-methylphenol (4F2MP) as the quantification internal standard. During the optimization of the SPE step, the amounts of FCC and DMAP were ca. 20 mg, more than their optimum amounts given above because of probable residual water or moisture in the effluent from the SPE that might decompose the acid chloride.

The pH of the sample solution is generally accepted as the key parameter for a quantitative extraction of phenols. We chose pH 2 and 6 as test pHs based on pK_a values of the examined CPs. The recoveries of the CPs were obtained with the model solution containing a mixture of five CPs in distilled water. The complete procedure was applied. As indicated in Table 1, the recovery values of the CPs for pH 2 and 6 ranged from 83.5 to 104.2% and from 84.3 to 99.4%, respectively. There was no significant dependence of the recoveries on the pH in the range 2.0–6.0 with the exception of 2,4,6-TCP. An increase in pH produced a decrease in recovery of

Table 1
Effect of sample pH on the SPE recovery (%) of the CPs.

Compounds	pK _a ^a	Recovery, %	
		pH 2	pH 6
2-CP	8.52	104.2	99.4
3-CP	9.37	96.7	98.8
4-CP	8.97	101.7	93.6
2,4-DCP	6.80	83.5	84.3
2,4,6-TCP	5.80	102.7	91.6

^a from [25].**Table 2**
Analytical data for the determined chlorophenols.

CPs	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	Recovery (%) (n=6)	RSD (%) (n=6)
2-CP	1.6	4.3	104.5	4.1
3-CP	2.4	6.7	103.2	9.4
4-CP	3.7	9.9	90.9	12.0
2,4-DCP	3.4	8.5	93.6	14.8
2,4,6-TCP	3.1	7.5	101.1	11.8

^a Detection limits are calculated with a signal-to-noise ratio of 3.^b Quantification limits are calculated with a signal-to-noise ratio of 10.

this compound, probably because of its higher acidity compared to the other CPs.

There is no significant difference in recovery for sample volumes between 2 mL and 10 mL at a flow rate of 2 mL/min. The effect of sample volume was not examined for larger volumes than 10 mL. In such cases the preconcentration factor was 100.

3.3. Analytical performance

The following figures of merit were investigated for the full process under the optimal experimental conditions: limit of detection (LOD), precision and accuracy. The LODs for the chromatography step, based on peaks of a signal-to-noise ratio of 3, ranged from 1.6 ng L⁻¹ to 3.7 ng L⁻¹ (Table 2). The limits of quantification (LOQ) for the CPs were calculated using a signal-to-noise ratio of 10 (Table 2). Of note is the fact that the LOQs obtained were better than those obtained with both solvent extraction in EPA methods 604 (GC-FID) and 625 (GC-MS) [21,29]. The LOQs for 2-CP, 4-CP and 2,4-DCP were better than those obtained using HS-SPME-GC-MS but not for 2,4,6-TCP (2 ng L⁻¹) [30]. The LOQs obtained in this work are

Table 3
Recoveries of CPs from spiked tap and lake water samples (10 mL).

CPs	Added vol. ^a (μL)	Tap water (n=3 samples)			Lake water (n=3 samples)		
		Added (ng L ⁻¹)	Found ^b (ng L ⁻¹)	Recovery (%)	Added (ng L ⁻¹)	Found ^b (ng L ⁻¹)	Recovery (%)
2-CP	15	28.8	31.4	109.0	–	–	–
3-CP		28.8	34.8	93.1	–	–	–
4-CP		28.8	29.7	85.8	–	–	–
2,4-DCP		36.5	30.0	82.3	–	–	–
2,4,6-TCP		44.3	49.5	111.7	–	–	–
2-CP	25	48.0	50.0	104.2	48.0	49.2	102.4
3-CP		48.0	60.6	109.7	48.0	46.2	96.3
4-CP		48.0	48.3	90.2	48.0	53.8	112.2
2,4-DCP		60.8	62.7	103.2	60.8	51.6	84.9
2,4,6-TCP		73.8	72.2	97.9	73.8	58.9	79.9
2-CP	40	76.8	82.8	107.8	76.8	76.0	99.0
3-CP		76.8	95.3	113.7	76.8	74.4	96.9
4-CP		76.8	88.7	109.0	76.8	73.1	95.2
2,4-DCP		97.3	108.8	111.8	97.3	95.7	98.4
2,4,6-TCP		118.1	119.3	101.0	118.1	106.1	89.8

^a Added volume from the mixed solution of CPs as 100 μM.^b The concentrations in the spiked samples were calculated by subtracting the native concentration in the samples as determined independently (Table 4) from the measured total concentrations.

lower by a factor of 10–100 than those obtained with a purge-and-trap preconcentration coupled to a GC-AED (510 ng L⁻¹ for 2-CP, 300 ng L⁻¹ for 2,4-DCP and 77 ng L⁻¹ 2,4,6-TCP) [16]. This is probably due to the use of the more sensitive iron line here rather than the chlorine line at 479 nm. Purge-assisted headspace SPME combined with GC-MS gave lower LODs for some CPs (1.4 ng L⁻¹ for DCP and 1.1 ng L⁻¹ for 2,4,6-TCP) than the present GC-AED determination [1].

The precision of the procedure (relative standard deviation, RSD) was calculated. Six replicate determinations of CPs added as 20 μL of a 100 μM solution to 10 mL of tap water indicated that the RSDs range from 4.1 to 14.8% and the recoveries from 90.9 to 104.5%, both showing comparable values at this concentration level with the values given in the references mentioned above [1,16,30].

To validate the accuracy of the complete method, the recoveries were evaluated for each compound in spiked water (10 mL) with varying amounts of the standard solution (15, 25 and 40 μL of a 100 μM solution of the CPs). As indicated in Table 3, the recovery values of the CPs spiked in tap water and lake water samples ranged from 82.3 to 113.7% and from 79.9 to 112.2%, respectively. These results demonstrate that the matrixes of the analyzed real-world water samples have no effect on this method.

3.4. Analysis of real water samples

After the analytical performance was found to be satisfactory, the next step was to determine how well the method works when applied to the analysis of CPs in lake and tap waters. The determined CP concentrations are presented in Table 4. As expected, the concentrations of the CPs in lake water were higher than those in the tap water. The chlorophenol contents in all water sample are lower than the maximum admissible concentration of phenols in drinking water by the EC legislations [6]. Four replicate determinations of the CPs present in 10 mL sample gave satisfactory RSD values, ranging from 5 to 16%.

In Fig. 2 is depicted the gas chromatogram with atomic emission detection of the lake water sample after derivatization with FCC. It can be seen that even at this low level of CPs (6–50 ng/L), an excellent signal-to-noise ratio is obtained. A few unidentified peaks are likely to be derived from other phenols from the water, such as phenol itself (eluting immediately after 2FP) and o-cresol (immediately following 4F2MP). The large peak immediately before that of 2FP is derived from a sideproduct of the derivatization and is thus

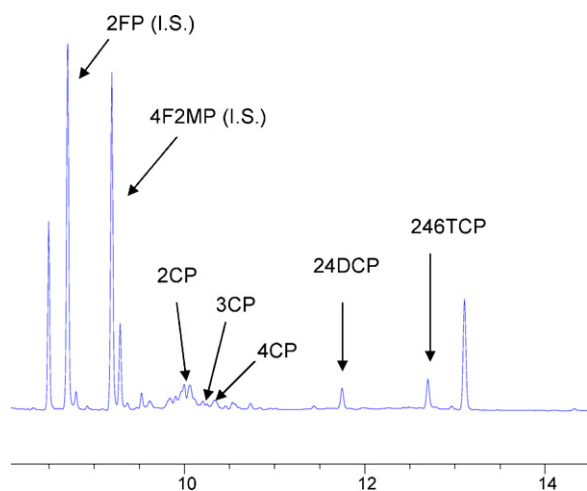


Fig. 2. A gas chromatogram with atomic emission detection of the lake water sample with the identified chlorophenols indicated. 2FP and 4F2MP are the internal standards (I.S.) 2-fluorophenol and 4-fluoro-2-methylphenol.

Table 4
Concentration of the CPs in lake and tap water samples.

Analytes	Tap water, mean \pm s (ng L ⁻¹), n = 4 samples	Lake water, mean \pm s (ng L ⁻¹), n = 4 samples
2-CP	ND ^a	18 \pm 3
3-CP	8 \pm 1	6 \pm 1
4-CP	5 \pm 1	15 \pm 1
2,4-DCP	ND	34 \pm 3
2,4,6-TCP	ND	51 \pm 5

^a ND indicates below the limit of detection.

not related to the sample. An unknown substance elutes very close to the peak for 2CP so that the integration of this peak area is not very reliable.

4. Conclusions

The results show that the SPE-derivatization method combined with GC-AED is successful for the determination of trace amounts of CPs in water samples. A 10 mL sample can be extracted with SPE and preconcentrated by a factor of 100 to give detection limits of 8.2–18.7 ng L⁻¹, about ten times lower than the maximum permissible levels in current legislation. A further reduction of the detection limits can be achieved by increasing the sample volume processed on SPE before the derivatization. The recoveries of CPs in the water samples exceed 90% with RSDs of less than 12% (except for 2-CP in lake water but this may be due to the coelution evident in Fig. 2 and the concomitant difficulty of identifying the peak inte-

gration limits). Based on the simplicity, low quantification limits, accuracy and repeatability, this method can be recommended to determine CPs in natural water samples such as river water, lake water, drinking water, waste water and ground water, etc.

The derivatization procedure is very rugged, rapid, and easy to perform. It may be concluded from almost quantitative derivatization yields that analyte losses are minimal during sample preparation and storage. Furthermore it is easily connected to a solid phase extraction of CPs.

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