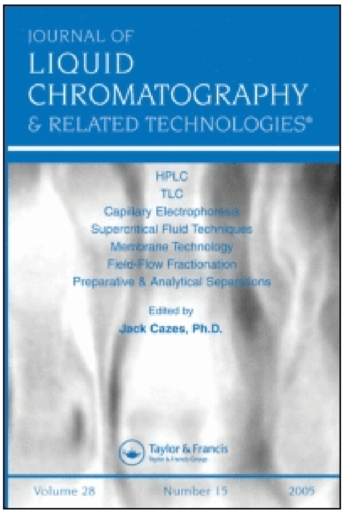

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Simultaneous Determination of 19 Chlorophenols in Water by Liquid Chromatography-Mass Spectrometry with Solid-Phase Extraction

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Abstract: A method to simultaneously determinate 19 chlorophenols (CPs) in water by liquid chromatography, coupled with atmospheric pressure chemical ionization mass spectrometry (LC-APCI-MS), and a solid-phase extraction utilizing Oasis® HLB cartridges to preconcentrate the target analytes was developed. The method was linear in the range 0.5 ~ 25.0 μg/L with a good correlation coefficient ($r > 0.996$) for all CPs. The limits of detection (LODs) were 0.4 ~ 30.0 ng/L, extraction recoveries were 87.5 ~ 100.4%, intra-day RSDs were 5 ~ 12%, and inter-day RSDs were 7 ~ 15%. This method has been successfully applied to the analysis of water samples. In addition, a comparison was obtained between APCI-MS and ESI-MS for the determination of the 19 CPs.

Keywords: Drinking water, Chlorophenol, Liquid chromatography-mass spectrometry, Solid-phase extraction

INTRODUCTION

Chlorophenols (CPs) have been some of the most important contaminants present in the environment; they have been used in several industrial processes and in

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agriculture.[1–3] Also, they could be formed from non-chlorinated phenols during chlorination of water.[4] As a result, they have often been found in waters,[5,6] soils,[7] and sediments.[7,8] It is well known that CPs are toxic, even at low levels, and are persistent in the environment. For this reason, some of them have been included in the lists of priority pollutants of several countries and they have been subject to legislation.[5] In fact, four of the chlorophenols (2-CP, 2,4-DCP, 2,4,6-TCP, and PCP) had been classified as priority pollutants by the U.S. Environmental Protection Agency (EPA).[9] Also, the European Union had set the maximum total and individual permitted phenols concentrations in water used for human consumption at 0.5 μg/L, and 0.1 μg/L, respectively.[10] To reach the concentration levels required by legislation, conventional methods of determining phenolic compounds involve preconcentration.

Solid-phase extraction (SPE) has been the most frequently used preconcentration technique for CPs.[8,11–13] Villoslada et al.[12] reported a method for the preconcentration of 2-CP, 4-chloro-3-methylphenol, 2,4-DCP, 2,4,6-TCP and PCP in water using an XAD-4 adsorbent resin. Rodríguez et al.[13] proposed a method for the off-line concentration procedure for the determination of 16 CPs in drinking water by graphitized carbon black cartridges. Wissiack et al.[8] reported a comparison of six different SPE materials (C HD, Polymer Labs PLRP-s, Hamilton PRP-1, Hysphere GP, Hysphere SH, and Waters Oasis® HLB) for on-line SPE of 2-CP, 2,4-DCP, 2,4,6-TCP, and PCP in water. However, many papers have reported that some of the CPs were preconcentrated by C_8, C_{18}, XAD-4 adsorbent resin, and graphitized carbon black cartridges. As we know, a few papers reported the simultaneous preconcentration of 19 CPs in water utilizing SPE cartridges. Moreover, since environmental waters are very complex matrices, there is a need for reliable identification of sample constituents, which can only be achieved by mass spectrometric (MS) methods which have been applied to the determination of several CPs,[8,14,15] including using APCI-MS and ESI-MS. As we know, a comparison for the determination of the 19 CPs between them was not found.

In this paper, a new method for the simultaneous preconcentration and determination of 19 chlorophenols, including 3 monochlorophenols (MCPs), 6 dichlorophenols (DCPs), 6 trichlorophenols (TCPs), 3 tetrachlorophenols (TeCPs) and PCP in water samples, using LC-APCI-MS in the negative mode, has been described. This method can be used for the routine analysis of these chlorophenolic compounds in water samples.

EXPERIMENTAL

LC-MS System

An Agilent 1100 series LC/MSD Trap SL System (Agilent Technologies Inc., Germany), consisting of quaternary pump (G1311A), a column thermostat (G1316A), a degasser unit (G1379A), an autosampler (G1313A), a diode array detector (1315B), and an ion trap mass spectrometer with an APCI and an ESI interfaces. The LC-APCI-MS and LC-ESI-MS systems were controlled, and data were analyzed, with a computer equipped with LC/MSD Trap Software 4.2 (Bruker). All tubings used for connections were PEEK (0.25 mm i.d., Agilent Technologies Inc., Germany).

Chemicals and Solvents

The acetonitrile (MeCN) and methanol (MeOH) (Merck, Darmstadt, Germany) used were HPLC grade. The water employed was supplied by a Milli-Q water purification system from Millipore (Molsheim, France). The CPs studied were obtained from the following sources: 2-CP (>98%), 3-CP (>97%), 4-CP (>99%), 2,4-DCP (>99%), 2,3,4-TCP (>95%), 2,3,5-TCP (>97%), 2,3,6-TCP (>95%) and 2,4,5-DCP (>98%) from Merck (Darmstadt, Germany); 2,3-DCP (>98%), 2,5-DCP (>98%), 2,6-DCP (>99%), 3,4-DCP (>97%), 3,5-DCP (>97%), 2,4,6-DCP (>98%), 3,4,5-DCP (>98%), 2,3,4,5-TeCP (>97%), 2,3,4,6-TeCP (>99%), 2,3,5,6-TeCP (>98%) and PCP (>99%) from Sigma-Aldrich (Milwaukee, WI, U.S.A). Anhydrous sodium sulfate, dichloromethane, and hydrochloric acid were obtained from Shanghai Reagent Company (Shanghai, China).

Individual stock standard solutions of each of the CPs (2.0 mg/mL) were prepared, by weight, in MeCN. Working standard solutions of 50.0 mg/L were prepared weekly in MeCN. Stock and working standards were stored at 4°C in the refrigerator. The aqueous solutions were prepared daily by diluting the working solution with Milli-Q water.

Preparation

Real samples (from river and tap water plant, 50 mL) were acidified to pH 2.5 by 0.10 mol/L hydrochloric acid, and then filtered through a 0.45 μm nylon membrane filter (Agilent Technologies Inc., Germany) before analysis. Then, the samples were extracted using Oasis® HLB (3 mL/60 mg, Waters) cartridges that first were conditioned with 4.0 mL dichloromethane, 4.0 mL methanol, and 5.0 mL water. The flow rate of the samples was 5.0 mL/min. The elution was done with 5.0 mL MeOH and 5.0 mL dichloromethane, which were then evaporated to dryness by a gentle stream of nitrogen. The final volume was made up to 0.50 mL with the HPLC mobile phase. All experiments were performed in duplicate.

HPLC-APCI-MS Analysis

A carbamate analysis C_8 column (250 mm × 4.0 mm, 5 μm particle size, (Pickering Laboratories, California, U.S.A.) was used. Injection volume was

20 μL. Mobile phase was acetic acid-ammonium acetate (5 mmol/L, pH = 4.5)/acetonitrile/methanol (65:28:7) in isocratic elution mode. Detector was an APCI-MS or ESI-MS in selected ion monitoring (SIM) mode. The SIM peak areas were integrated for quantification. The eluate of the diode array detector for the ESI-MS was split (1:4) using a stream splitter, so that about 0.2 mL/min was delivered to ESI-MS and the rest to waste, and for the APCI-MS, there was no split.

The Agilent 1100 series LC/MSD Trap SL mass spectrometer was used in the negative mode with full-scan mass spectra over the m/z range 80 ~ 300 amu using a cycle time of 1 s, a peak width of 0.1 s, a corona current of 4.0 μA, a capillary voltage of 2.0 kV, a capillary exit voltage of −85 V, a dry temperature of 325°C, a vaporizer temperature of 450°C, a high purity nitrogen (99.999%) dry gas of 5.0 L/min, a nitrogen nebulizer pressure of 60.0 psi, and a dwell time of 200 ms. The APCI interface and mass spectrometric parameters were optimized to obtain maximum sensitivity. Analytes were detected with atmospheric pressure chemical ionization (APCI) in the negative mode in selected ion monitoring (SIM). The ions used for quantitation were the molecular ions for each of the CPs, respectively (see Table 1). The SIM peak areas were integrated for quantitation.

The conditions employed by ESI-MS were the same as those for the APCI-MS, except for a dry temperature of 350°C, a flow rate of dry gas of 9.0 L/min, and a nebulizer pressure of 35.0 psi. The ESI interface and mass spectrometric parameters were optimized to obtain maximum sensitivity.

RESULTS AND DISCUSSION

Optimization of the Chromatographic Separation

Complete separation between the 19 CPs studied was obtained using the isocratic mobile phase 65:28:7 acetate buffer pH 4.5/acetonitrile/methanol on a carbamate analysis C_8 column, as can be seen in the chromatogram of a standard solution (Fig. 1). Other mobile phases were tested in such way that the pH of the buffer solution was as different as possible from the pK_a of TeCPs and PCP. A mobile phase of the acetate buffer solution pH 5.5-acetonitrile-methanol (65:28:7) was carried out with the19 CPs studied. The main inconvenience of this eluent was that a wide-tailed peak was obtained for TeCPs and PCP, which pK_a's were less than 6, because the pH of the mobile phase was very close to their pK_a values. According to many experimental results, the pH of the mobile phase significantly affects the peak shape and the retention time for TeCPs and PCP, and the lower the pK_a, the more significantly the CPs were affected, especially for PCP, for which the pK_a was 4.74. The peak shape and the retention time for the MCPs and DCPs of $pK_a > 7$ were hardly affected by the mobile phase pH variation. The pK_a of the CPs are given in Table 2.

Table 1. Selected ion monitor (SIM) acquisition

Chlorophenols	Rentention time (min)	Identification ions (m/z, %) (relative abundance)	Quantification ions (m/z)
2-Chlorophenol	4.19	127(100), 129(33.3)	127
3-Chlorophenol	5.51	127(100), 129(33.3)	127
4-Chlorophenol	4.88	127(100), 129(33.3)	127
2,3-Dichlorophenol	8.01	161(100), 163(66.7), 165(11.1)	161
2,4-Dichlorophenol	9.83	161(100), 163(66.7), 165(11.1)	161
2,5-Dichlorophenol	8.88	161(100), 163(66.7), 165(11.1)	161
2,6-Dichlorophenol	6.72	161(100), 163(66.7), 165(11.1)	161
3,4-Dichlorophenol	10.51	161(100), 163(66.7), 165(11.1)	161
3,5-Dichlorophenol	14.12	161(100), 163(66.7), 165(11.1)	161
2,3,4-Trichlorophenol	17.34	195(100), 197(100), 199(33.3)	195
2,3,5-Trichlorophenol	20.55	195(100), 197(100), 199(33.3)	195
2,3,6-Trichlorophenol	13.15	195(100), 197(100), 199(33.3)	195
2,4,5-Trichlorophenol	18.83	195(100), 197(100), 199(33.3)	195
2,4,6-Trichlorophenol	16.01	195(100), 197(100), 199(33.3)	195
3,4,5-Trichlorophenol	23.35	195(100), 197(100), 199(33.3)	195
2,3,4,5-Tetrachlorophenol	37.42	229(75.0), 231(100), 233(50.0)	231
2,3,4,6-Tetrachlorophenol	25.94	229(75.0), 231(100), 233(50.0)	231
2,3,5,6-Tetrachlorophenol	22.51	229(75.0), 231(100), 233(50.0)	231
Pentachlorophenol	31.12	263(60.0), 265(100), 267(66.7)	265

Optimization of the SPE Conditions

Effect of pH

Waters Oasis® HLB cartridges were selected for the SPE because good results were obtained with them previously for some of the phenolic

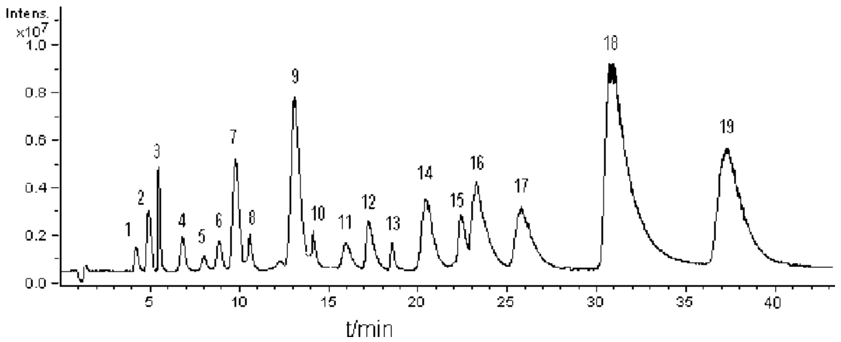

Figure 1. HPLC-APCI-MS SIM of spiked $0.1 \sim 1.0\,\mu g/L$ tap water. Column: A carbamate analysis C_8 (250 mm × 4.0 mm, 5 μm particle size). Injection volume: 20 μL. Mobile phase: Acetic acid-ammonium acetate (5 mmol/L, pH = 4.5)/acetonitrile/methanol (65:28:7) in isocratic elution mode. Peaks identification: 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.

compounds.[13–15] The effect of acidity of the sample on the extraction efficiency was studied by changing the pH from 2.5 to 7.0. The recoveries obtained at different pH's are given in Table 2. The effect of pH on the recoveries of CPs was as expected, based on their pK_a values. For example, compounds with high pK_a values, such as mono- and most of the dichlorophenols, showed no significant change in the recoveries when the pH was varied from 7 to 2.5. However, for compounds with pK_a values between 4.7 and 7.0, the decrease in pH produced an increase in the recoveries from 65.2% to more than 90%, especially, for TeCP and PCP, with $pK_a < 6$. This was because the acidity affected the ionization of the CPs in solution and the rate of adsorption and desorption on the SPE cartridges. To obtain good recoveries, a pH of 2.5 was chosen.

Effect of Sample Volume

Different volumes of HPLC-grade water spiked with the 19 CPs at low levels (10.0 μg/L), in pH 2.5 solution, was percolated through the SPE cartridges (Oasis® HLB, 3 mL/60 mg) and the recoveries were measured (Table 2). These volumes were chosen so that breakthrough did not occur, which was verified by comparing the recoveries with different amount analytes. Table 2 showed that all the tested sample volumes from 10 mL to 200 mL yielded good recoveries, which were between 87.5% and 100.4%.

Table 2. Effect of sample pH and volume on SPE (Oasis® HLB,3 mL/60 mg) extraction efficiencies of CPs[a] (%, n = 3)

		50 mL			pH 2.5			
Compounds	pK_a[b]	pH 2.5	pH 4.0	pH 7.0	10 mL	20 mL	100 mL	200 mL
2-CP	8.52	90.4	89.1	90.4	95.9	93.5	89.4	88.7
3-CP	9.37	91.3	92.1	91.0	93.8	93.5	87.7	85.3
4-CP	8.97	93.2	95.2	91.7	100.5	94.3	92.1	83.2
2,3-DCP	7.90	94.8	91.1	87.9	92.1	90.3	90.2	89.4
2,4-DCP	6.80	94.6	91.2	91.2	92.0	94.5	89.3	81.2
2,5-DCP	7.51	95.6	93.2	88.9	94.2	94.1	92.5	94.2
2,6-DCP	7.71	100.4	95.4	95.9	94.3	97.8	95.6	94.3
3,4-DCP	8.60	87.5	90.1	94.3	94.9	95.3	89.4	82.1
3,5-DCP	8.25	88.3	86.3	88.4	87.4	89.3	84.2	77.2
2,3,4-TCP	5.80	94.3	90.3	73.1	88.4	89.2	90.5	88.4
2,3,5-TCP	6.00	99.6	94.1	65.2	100.3	93.5	90.9	88.5
2,3,6-TCP	7.00	93.8	89.4	87.4	89.4	87.2	88.3	73.8
2,4,5-TCP	6.72	95.9	94.2	66.7	84.7	87.1	88.4	85.2
2,4,6-TCP	6.43	95.4	93.2	84.0	94.1	94.2	90.8	91.4
3,4,5-TCP	7.55	93.6	90.2	73.7	99.3	99.5	95.6	91.3
2,3,4,5-TeCP	5.02	93.2	80.5	73.5	101.3	93.1	89.9	76.2
2,3,4,6-TeCP	5.22	91.5	85.3	67.8	98.2	93.5	84.6	81.3
2,3,5,6-TeCP	5.64	94.8	84.7	65.4	92.4	89.4	83.8	81.3
PCP	4.74	90.1	84.1	76.7	91.3	94.2	90.4	86.5

[a] Concentration: 10.0 μL.

[b] Reference[4].

Method Validation

Calibration curves were obtained for the 19 CPs studied using a series of standard solutions over the concentration range from 0.1 to 50.0 μg/L. Three replicate injections of standard at each concentration were performed. All calibration curves were linear over the concentration ranges from 0.5 to 25.0 μg/L, with correlation coefficients $r > 0.996$ (Table 3).

The limits of detection (LODs) were determined using a water sample free of CPs spiked at low concentrations of 0.5 to 5.0 μg/L standard solutions, preconcentration by SPE, detection in SIM mode, and evaluation by the criterion that the signal to noise ratio should be >10 for quantification purposes. Table 3 shows good LODs, ranging from 0.4 to 30.0 ng/L for the 19 CPs in water samples using APCI-MS. Table 3 also shows the LODs for the 19 CPs in water samples, using ESI-MS, ranged from 0.4 to 100.0 ng/L. As can be seen, both methods showed that LC-APCI(-)-MS for the determination of CPs, except PCP, was 1 to 20 times more sensitive than LC-ESI(-) -MS; only for PCP, the latter was about twice as sensitive as the former. This probably explains that the 19 CPs, except PCP, were easily ionized at the conditions of APCI; on the other hand, PCP was easily ionized at the conditions of ESI because of its lower pK_a and stronger polarity.

Intra-day precision was evaluated by continuously performing five repeated analysis of a spiked sample (added each CP, 10.0 μg/L, respectively) including SPE procedure. Intra-day precision (R.S.D.) on the basis of CP content for each of the CPs was between 5% and 12% (Table 3).

Inter-day precision was also evaluated by performing five repeated analysis of three spiked samples with SPE procedure each day on five different days within a 2 week period (added each CPs, 10.0 μg/L, respectively). Inter-day precision (R.S.D.) on the basis of CP content for each of the CPs was between 7% and 15% (Table 3).

Sample Determination

The three prepared water samples (spiked water, tap water, and river water) were analysed by HPLC-MS with APCI detection in the negative mode. The final concentrations of individual CPs are shown in Table 4. It shows that there were 5 kinds of CPs in the tap water sample, including 3 of the 5 priority CPs of the EPA. Fortunately, their values were less than the legislation of the EPA and consistent with that reported by Simpson et al.[16] which were obtained in tap water disinfected by chlorination of the water. Table 4 also shows that there were 0.035 μg/L of 2,6-DCP and 0.027 μg/L of 2,3,4,6-TeCP in the studied tap water, which were uncatalogued in the list of priority control of EPA. Moreover, Table 4 also shows that there were 0.58 μg/L of 4-CP and 1.53 μg/L of 2,4-DCP in the studied river water, which may be polluted by the local chemical industry.

Table 3. Quality parameters of the LC-APCI-MS method for the determination of CPs in water samples

Compounds	Regression equation	Linear range[a] (μg/L)	LOD[b] (S/N = 3) (ng/L)	RSD[c] (%) Intra-day[d]	RSD[c] (%) Inter-day[e]
2-CP	$C = 4.644 \times 10^{-7}A - 7.272 \times 10^{-3}$	2.0 ~ 50.0	30.0 (100)	6	9
3-CP	$C = 7.153 \times 10^{-8}A - 4.563 \times 10^{-3}$	0.1 ~ 50.0	2.5 (20)	7	7
4-CP	$C = 5.787 \times 10^{-9}A + 2.664 \times 10^{-3}$	0.1 ~ 50.0	0.4 (0.4)	6	7
2,3-DCP	$C = 1.372 \times 10^{-8}A - 9.271 \times 10^{-3}$	0.5 ~ 25.0	3.5 (100)	12	14
2,4-DCP	$C = 1.460 \times 10^{-8}A - 8.286 \times 10^{-3}$	0.5 ~ 50.0	5.0 (100)	6	8
2,5-DCP	$C = 1.565 \times 10^{-8}A + 2.273 \times 10^{-2}$	0.5 ~ 25.0	5.3 (100)	9	9
2,6-DCP	$C = 2.058 \times 10^{-8}A + 1.268 \times 10^{-2}$	0.5 ~ 25.0	6.2 (100)	10	11
3,4-DCP	$C = 4.841 \times 10^{-9}A + 4.062 \times 10^{-2}$	0.1 ~ 50.0	1.0 (2.5)	9	11
3,5-DCP	$C = 7.969 \times 10^{-9}A - 8.252 \times 10^{-3}$	0.1 ~ 25.0	2.3 (3.5)	6	9
2,3,4-TCP	$C = 3.546 \times 10^{-9}A + 5.266 \times 10^{-3}$	0.5 ~ 50.0	2.0 (32)	11	15
2,3,5-TCP	$C = 3.267 \times 10^{-9}A - 1.231 \times 10^{-2}$	0.5 ~ 50.0	2.0 (20)	9	12
2,3,6-TCP	$C = 3.649 \times 10^{-9}A + 6.766 \times 10^{-3}$	0.5 ~ 50.0	2.0 (32)	5	9
2,4,5-TCP	$C = 3.375 \times 10^{-9}A - 1.678 \times 10^{-2}$	0.5 ~ 50.0	2.0 (20)	7	10
2,4,6-TCP	$C = 3.312 \times 10^{-9}A - 1.311 \times 10^{-2}$	0.5 ~ 50.0	2.0 (32)	5	8
3,4,5-TCP	$C = 3.765 \times 10^{-9}A + 7.793 \times 10^{-3}$	0.5 ~ 50.0	2.0 (12)	8	12
2,3,4,5-TeCP	$C = 1.302 \times 10^{-9}A + 4.135 \times 10^{-2}$	0.5 ~ 50.0	0.7 (2.0)	8	10
2,3,4,6-TeCP	$C = 1.308 \times 10^{-9}A + 1.346 \times 10^{-2}$	0.5 ~ 50.0	1.5 (4.0)	5	8
2,3,5,6-TeCP	$C = 1.650 \times 10^{-9}A + 3.265 \times 10^{-2}$	0.5 ~ 50.0	1.7 (10)	12	15
PCP	$C = 1.117 \times 10^{-9}A + 2.234 \times 10^{-2}$	0.5 ~ 50.0	3.5 (2.0)	6	9

[a] Correlation coefficient (r^2), 0.996 ~ 0.999.

[b] The data in blacket were the detection limits by LC-ESI-MS.

[c] Concentration: 10.0 μg/L.

[d] $n = 5$.

[e] $n = 5$ replicates × 3 days.

Table 4. Determination of CPs in spiked water and environmental water using SPE-LC-APCI-MS(n = 3)

	Spiked sample			Tap water	River water
Compounds	Added (μg/L)	Found (μg/L)	Recovery (%)	(μg/L)	(μg/L)
2-CP	20.0	18.14 ± 0.86	90.7	n.d.[a]	n.d.
3-CP	10.0	9.02 ± 0.63	90.2	n.d.	n.d.
4-CP	10.0	8.93 ± 0.55	89.3	n.d.	1.03
2,3-DCP	20.0	18.84 ± 2.13	94.2	n.d.	n.d.
2,4-DCP	10.0	8.83 ± 0.44	88.3	0.43	0.58
2,5-DCP	10.0	9.18 ± 0.63	91.8	n.d.	n.d.
2,6-DCP	10.0	9.11 ± 0.73	91.1	0.035	n.d.
3,4-DCP	10.0	8.94 ± 0.81	89.4	n.d.	n.d.
3,5-DCP	20.0	18.02 ± 1.22	90.0	n.d.	n.d.
2,3,4-TCP	20.0	17.98 ± 2.01	90.0	n.d.	n.d.
2,3,5-TCP	20.0	20.15 ± 1.87	100.8	n.d.	n.d.
2,3,6-TCP	20.0	19.05 ± 1.13	95.0	n.d.	n.d.
2,4,5-TCP	20.0	19.10 ± 1.36	95.5	n.d.	n.d.
2,4,6-TCP	20.0	18.67 ± 1.02	93.4	0.24	n.d.
3,4,5-TCP	20.0	19.11 ± 1.57	95.6	n.d.	n.d.
2,3,4,5-TeCP	10.0	9.14 ± 0.71	91.4	n.d.	n.d.
2,3,4,6-TeCP	10.0	9.34 ± 0.50	93.4	0.027	n.d.
2,3,5,6-TeCP	20.0	17.86 ± 2.19	89.3	n.d.	n.d.
PCP	20.0	17.88 ± 1.02	89.9	0.055	n.d.

[a] n.d. Not detected.

CONCLUSIONS

The application of HPLC-APCI-MS to the rapid, simultaneous determination of 19 CPs in water samples has been studied. Good linearity and reproducibility (intra-day precision between 5% and 12% and inter-day precision between 7% and 15%) and good detection limits, ranging from 0.4 to 30.0 ng/L for water samples, were obtained. The described method demonstrates efficient separation and detection; it has been applied to the determination of the 19 CPs in tap water and river water samples.

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