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Determination of phenols in water samples by single-drop microextraction followed by in-syringe derivatization and gas chromatography–mass spectrometric detection

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Abstract

Trace analysis of phenolic compounds in water was performed by coupling single-drop microextraction (SDME) with in-syringe derivatization of the analytes and GC–MS analysis. The analytes were extracted from a 3 ml sample solution using 2.5 μl of hexyl acetate. After extraction, derivatization was carried out in syringe barrel using 0.5 μl of *N,O*-bis(trimethylsilyl)acetamide. The influence of derivatizing reagent volume, derivatization time and temperature on the yield of the in-syringe silylation was investigated. Derivatization reaction is completed in 5 min at 50 °C. Experimental SDME parameters, such as selection of organic solvent, sample pH, addition of salt, extraction time and temperature of extraction were studied. Analytical parameters, such as enrichment factor, precision, linearity and detection limits were also determined. The limits of detection were in the range of 4–61 ng/l (S/N = 3). The relative standard deviations obtained were between 4.8 and 12% ($n = 5$).

Keywords: Single-drop microextraction; Derivatization; Environmental analysis; Phenols

1. Introduction

Phenols and substituted phenols are important pollutants in water because of their wide use in many industrial processes, such as the manufacture of plastics, dyes, drugs, antioxidants and pesticides. They are of great environmental concern owing to their high toxicity [1]. For this reason, a number of phenolic compounds are listed in the US Environmental Protection Agency (EPA) list of priority pollutants.

Many analytical techniques have been used for the trace determination of phenols in aquatic environments. High-performance liquid chromatography (HPLC), capillary electrophoresis (CE) and gas chromatography (GC) have been commonly used for the determination of phenolic compounds [2–6]. Although HPLC methods are frequently applied for the analysis of phenols, GC is often preferred, due to its inherent advantage of high resolution, rapid separation, low cost and easy linkage with sensitive and selective detectors.

In GC analysis, because of high polarity of phenols, they tend to give broad, tailed peaks, and these effects led to high detection limits. To avoid this drawback, the phenols have to be derivatized with a suitable derivatization reagent before injection into the GC. There are many derivatization methods including acylation, silylation, alkylation and others to convert phenols to less polar compounds, with better chromatographic characteristics [7–9]. Phenols acetylation with acetic anhydride seems to be the most studied derivatization method [3,10–12]. Using acetic anhydride, chloro- and alkylphenols can be acetylated [12]. Unfortunately, acetylation is not satisfactory for some nitro- and dinitrophenols [12,13]. Silylation is another common derivatization method for the derivatization of phenols [14–16]. In this method, hydroxy functional groups present in the target analytes can be readily derivatized, and the reaction mixture can be directly injected into the gas chromatograph without further sample pretreatment. A broad range of phenolic compounds including nitrophenols can be silylated quantitatively using silylating reagents [15–17]. It also has the added advantage in that trialkylsilyl groups increase the total ion current and, therefore, the sensitivity using positive ion MS. *N,O*-Bis(trimethylsilyl)acetamide (BSA) is one of the most powerful

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silyl donor reagents to produce TMS ethers of phenolic compounds [15,16].

Conventional extraction methods, such as liquid–liquid extraction [18] and solid-phase extraction [19] are the most commonly used techniques for preconcentration and cleanup of phenols prior to GC. In addition to the standard methods for sample preparation, the technique of solid-phase microextraction (SPME) has been applied for extraction of phenolic compounds from water samples [10,12,20–22]. SPME is a solvent-free, simple and fast extraction method. For SPME–GC of polar compounds, such as phenols, derivatization can be performed in the aqueous sample [10,12,22] or in the SPME fiber after the concentration step [23–25]. The latter method is preferred when water-sensitive derivatization reagents, such as silyl donor compounds are employed. In recent years, the attractive technique of single-drop microextraction (SDME) has been developed as an alternative to SPME [26–28]. This method provides analyte extraction in a few microliters of organic solvents. SDME avoids some problems of the SPME method, such as sample carry-over and fiber degradation; it is also fast and inexpensive and uses very simple equipment.

Recently, Bagheri et al. [29] investigated determination of phenol and some chlorophenols in water samples by SDME–GC–MS analysis. They derivatized the compounds prior to extraction using acetic anhydride in basic media. A drop of butyl acetate was used for extraction of acetylated phenols from water.

In this paper, the application of single-drop microextraction of phenols from aqueous samples followed by in-syringe derivatization and GC–MS detection was studied. To our knowledge, this is the first time that the combination of SDME and in-syringe derivatization is investigated. The method was applied in the determination of phenolic compounds, including chloro-, methyl- and nitrophenols. BSA was selected to produce trimethylsilyl (TMS) derivatives of the studied compounds. As BSA is sensitive to moisture, derivatization was performed in the syringe barrel after extraction. Effect of the extraction solvent, together with microextraction and derivatization conditions in the performance of the analytical procedure was investigated.

2. Experimental

2.1. Chemicals and standard solutions

The phenolic compounds phenol (Ph), 2-chlorophenol (2CP), 4-chlorophenol (4CP), 2-nitrophenol (2NP), 4-nitrophenol (4NP), 2,4-dichlorophenol (24DCP), 2,4,-dimethylphenol (24DMP), 2,4,6-trichlorophenol (246TCP), 4-chloro-2-methsylphenol (4C2MP), 2,4-dinitrophenol (24DNP), 2-methyl-4,6-dinitrophenol (2M46DNP) and pentachlorophenol (PCP) were obtained from Merck (Darmstadt, Germany). A standard stock solution of phenolic compounds was prepared by dissolving 13.9 mg of Ph, 18.5 mg of 2CP, 14.7 mg of 4CP, 24 mg of 2NP, 16 mg of 4NP, 13.6 mg of 24DCP, 15.8 mg of 24DMP, 14.5 mg of 246TCP, 15.5 mg of 4C2MP, 22 mg of 24DNP, 23 mg of 2M46DNP and 24 mg of PCP in 50 ml of acetonitrile and stored in the refrigerator. The concentrations in the mixture were about 480 mg/l. An intermediary standard solution at the concentration of 8 mg/l was prepared by diluting stock standard solution in acetonitrile:water (40:60). More diluted working solutions were prepared daily by diluting intermediary standard solution with double distilled water or river water. Water samples were prepared by spiking double distilled water with analytes at known concentrations (about 80 μg/l) to study extraction performance under different conditions. The stock solution of internal standard was prepared by dissolving 30 mg of pentachlorobenzene (PCB) in 10 ml *n*-hexane.

HPLC-grade acetonitrile and hexane were used for the preparation of standard solutions (Caledon Labs., Georgetown, Canada). The pH of water samples was adjusted with sulphuric acid (Merck). Other reagents were purchased from Merck.

2.2. Single-dropt microextraction and derivatization procedure

A 10-μl GC microsyringe model 701N (gauge 26s and point style 2) from Hamilton (Bonaduz, Switzerland) was used to perform SDME experiments. A water sample (3 ml) spiked with an appropriate amount of phenolic compounds and adjusted at different pH from 2 to 6, was introduced in a 4-ml glass vial (Supelco, Bellefonte, PA, USA) equipped with a screw cap and a silicon septum. The vial was placed in a water-bath on a magnetic stirrer (CB162, Bibby, UK). A circulating water-bath (Fanazma, Iran) was used to maintain the sample at desirable temperature. A 2.5-μl volume of organic solvent containing internal standard was drawn into the syringe. The syringe needle was inserted through the silicone septum and immersed into the solution. The microsyringe was then positioned in the extraction vial in such a way that the tip of the extraction needle protruded to a depth of about 1 cm below the surface of the aqueous solution. Then, the plunger was pressed to cause the solvent to form a 2.5 μl drop suspended from the needle tip. The sample solution was stirred at 250 rpm during the extraction. After 15-min extraction, the organic solvent was retracted into the syringe. After finishing the extraction step, 0.5 μl BSA was drawn into the syringe and mixed well with the solvent by the successive movement of plunger through the syringe barrel. Then, the microsyringe was sealed by placing a GC septum over the syringe needle tip and heated at 50 °C for 5 min in a heating oven. Finally, the sample was injected into the GC.

2.3. GC–MS analysis

Gas chromatographic analysis was carried out using a Fisons Instrument (Rodano, Italy) model 8060 fitted with a split/splitless injector and Trio 1000 mass spectrometer (Fisons Instruments, Manchester, UK) detector. Helium was used as the carrier gas at linear velocity of 54 cm/s. The components were separated on a 25 m × 0.32 mm I.D., 0.1-μm film thick OV-1 column (Mega, Legnano, Italy). The injector temperature was set at 240 °C and all injections were made in splitless mode. The column was initially maintained at 60 °C for 2 min; subsequently, the temperature was increased to 180 °C at a rate of 15 °C/min (1 min hold) and then was increased to 230 °C (30 °C/min, 5 min

Table 1
Retention times, selected ions, time window and dwell time of TMS derivatives of phenolic compounds

Compound	Retention time (min)	Selected ions (*m*/*z*)	Time window (min)	Dwell time (s)
2CP	6.72	200, 194, 185, 179	6.3–7.0	0.08
24DMP	6.82	200, 194, 185, 179	6.3–7.0	0.08
4CP	6.87	200, 194, 185, 179	6.3–7.0	0.08
4C2MP	7.26	234, 219, 214, 196	7.0–8.0	0.08
24DCP	7.49	234, 219, 214, 196	7.0–8.0	0.08
2NP	7.59	234, 219, 214, 196	7.0–8.0	0.08
246TCP	8.22	255, 250, 211, 196	8.0–9.0	255 (0.07), 250 (0.05), 211 (0.12), 196 (0.15)
4NP	8.26	255, 250, 211, 196	8.0–9.0	255 (0.07), 250 (0.05), 211 (0.12), 196 (0.15)
PCB (IS)	8.37	255, 250, 211, 196	8.0–9.0	255 (0.07), 250 (0.05), 211 (0.12), 196 (0.15)
PCP	10.42	323, 338	10.3–11.8	0.08

hold). The GC–MS interface and the ion source temperature were set at 230 and 200 °C, respectively. The mass spectra were acquired as full scans from *m*/*z* 35 to *m*/*z* 400 (3.5 scans/s) under a 70-eV ionization potential. In order to increase sensitivity, quantitative analysis was performed in time scheduled selected ion monitoring (SIM) mode. Table 1 lists the analytical SIM conditions for the determination of TMS derivatives of studied compounds.

2.4. River water samples

Water samples were taken from Kashkan (Khorramabad, Iran) and Zayandeh-rood (Isfahan, Iran) rivers. Many chemical plants and large industrial area are located along the Zayandeh-rood river. The river receives several treated and untreated industrial sewage effluents. The Zayandeh-rood river water sample (total organic carbon, 3 mg/l; conductivity, 1080 μS/cm) was collected on its way through the city of Isfahan. The Kashkan river water sample (total organic carbon, 1.6 mg/l; conductivity, 650 μS/cm) was collected from an agricultural area. The river water samples were filtered through a 0.45-μm nylon membrane filter (Millipore, Bedford, MA, USA).

3. Results and discussion

3.1. Derivatization

Preliminary SDME experiments were performed in order to study the influence of different parameters on the in-syringe derivatization process. Three parameters, amount of BSA, reaction time and reaction temperature, were investigated to achieve the highest derivatization reaction yield. Water sample at spiked concentration level of 45–80 μg/l and pH 3 was used for single-drop microextraction. Three milliliters of water sample were poured into a 4-ml glass vial. The extraction was carried out using a 2.5-μl drop of hexyl acetate for 15 min at room temperature. After extraction, in-syringe derivatization conditions were evaluated.

The influence of derivatizing reagent volume (0.2, 0.5, 0.8 and 1.0 μl), derivatization time (from 5 to 20 min) and temperature (room temperature and 50 °C) on the yield of the in-syringe silylation was investigated using GC–MS detection. Peak area ratio of analytes to IS was used as the analytical signal. Table 2 shows relative peak area of each analyte after extraction and in-syringe derivatization of phenols at different derivatization conditions. One of the important factors affecting the yields of derivatization is the amount of the reagent used. The maximum derivatization reaction yield was observed using BSA volume between 0.2 and 0.5 μl. Higher amount of BSA did not produce higher yields, but resulted in the increase of background peaks due to impurities of the reagent. Moreover, using BSA volumes higher than 0.5 μl led to peak broadening in the chromatograms, because a small extent of water may be extracted with the solvent and may hydrolyze BSA. Therefore, it is necessary to use excess reagent in derivatization reaction. Therefore, 0.5-μl volume of BSA was chosen as optimum reagent volume.

At a temperature of 25 °C, the peak heights of the analytes increased by increasing the reaction time from 5 to 10 min.

Table 2
Peak area ratio of analytes to internal standard (mean of three determinations) at different in-syringe derivatization conditions

Compund	5-min derivatization at 25 °C; BSA volume (μl)				10-min derivatization at 25 °C; BSA volume (μl)				5-min derivatization at 50 °C; BSA volume (μl)			
	0.2	0.5	0.8	1.0	0.2	0.5	0.8	1.0	0.2	0.5	0.8	1.0
2CP	3.8	4.1	4.3	3.7	4.2	3.9	4.2	3.8	4.5	4.3	4.2	4.4
24DMP	3.9	4.0	3.5	4.1	4.6	4.6	4.0	3.8	4.7	4.7	4.1	4.3
4CP	3.3	3.7	3.1	3.0	3.6	3.7	3.5	2.6	4.0	3.9	3.2	3.6
4C2MP	3.8	3.8	3.3	3.2	4.1	3.9	3.4	2.9	4.2	4.1	3.3	3.2
24DCP	3.8	3.7	3.6	3.7	3.9	4.1	3.8	3.7	3.9	4.1	3.7	3.7
2NP	3.7	3.6	3.6	3.7	3.6	3.7	3.6	3.0	3.6	3.8	3.7	3.4
246TCP	2.5	2.9	2.6	2.3	2.5	3.0	2.7	2.7	3.1	3.1	2.8	2.6
4NP	1.3	1.4	1.4	1.2	1.4	1.4	1.5	1.4	1.5	1.4	1.3	1.2
PCP	0.23	0.22	0.21	0.24	0.20	0.22	0.20	0.21	0.24	0.26	0.18	0.23

On the other hand, derivatization at 50 °C leading to higher derivatization yields in shorter reaction time (5 min). Higher temperatures were not examined due to the risk of damaging the microsyringe. Using 0.5 μl of BSA, the optimum in-syringe silylation time and temperature were fixed at 5 min and 50 °C, respectively. Under different derivatization conditions, 24DNP and 2M46DNP in both free and derivatized forms did not appear in the chromatograms. It may be because of low extraction efficiency and/or low derivatization reaction yield. Severer derivatization conditions, i.e. longer reaction time and higher temperature, may improve reaction yield for these two compounds. On the other hand, for other phenols, under the mentioned conditions, derivatization reaction was complete, and non-derivatized compounds were not detected. Therefore, 24DNP and 2M46DNP were not considered in further studies.

3.2. SDME optimization

There are several parameters common to SDME that control the optimum performance of extraction including nature of solvent, extraction time, stirring and ionic strength of solution, etc. These parameters were separately evaluated to develop optimized extraction condition.

Seven water-immiscible solvents (Fig. 1) were chosen to select the best one for extraction. Although, water-immiscible alcohols, such as *n*-octanol, have been extensively used for SDME [30–32], they could not be used in this work because of performing derivatization reaction between alcohol and BSA. Bagheri et al. [29] reported that butyl acetate has good extraction efficiency for SDME of some acetylated phenols from water samples. The data presented in Fig. 1 indicate, although butyl acetate provides higher extraction capability than solvents, such as toluene, xylene, chloroform and methyl isobutyl ketone, the best extraction efficiency was achieved using hexyl acetate. In addition, among the solvent studied, only hexyl acetate has capability to extract 4-nitrophenol from water. Moreover, hexyl acetate drops were found easy to manipulate with the lowest of drop loss (0.2 μl under the optimized conditions). The only disadvantage using hexyl acetate is the fact that solvent peak interferes with phenol compound in the chromatogram. When

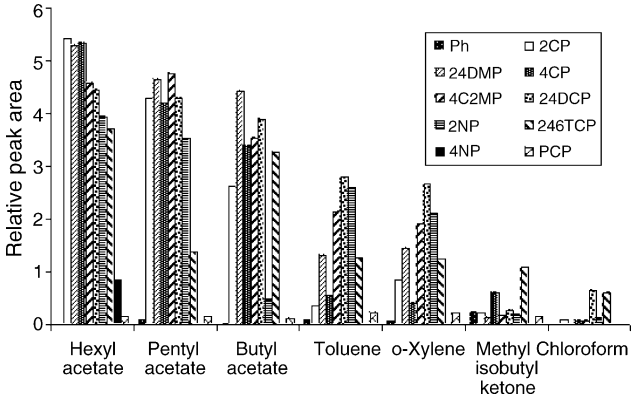

Fig. 1. Effect of different organic solvents on the extraction efficiency. Concentration of analytes: 45–80 μg/l, solvent volume: 2.5 μl, solution temperature: 45 °C, sample pH 3, extraction time: 15 min, salt addition: no NaCl added.

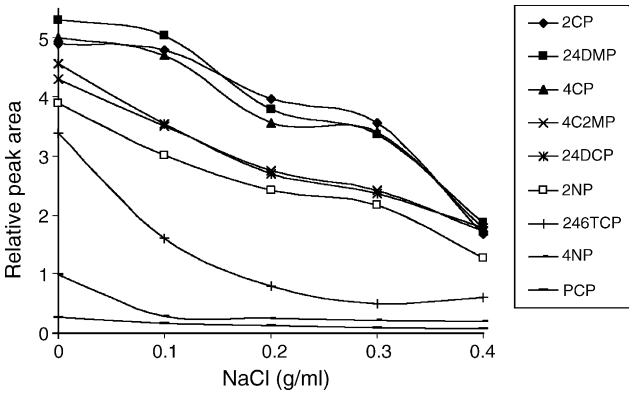

Fig. 2. Effect of ionic strength on the extraction efficiency. Concentration of analytes: 45–80 μg/l, solvent volume: 2.5 μl of hexyl acetate, solution temperature: 45 °C, sample pH 3, extraction time: 15 min.

it is not necessary to determine phenol, the best solvent for the extraction of studied compound was hexyl acetate.

The effect of increasing the ionic strength of the water sample was evaluated. The results were shown in Fig. 2. As can be seen in the figure, the relative peak area of analytes decrease with increase in NaCl concentration. Similar behavior was also observed by other researchers [29,32–35]. To increase extraction efficiency, no salt addition was performed in further studies.

Sample pH is an important factor, which may affect on the extraction recovery of phenols from water. To increase the extraction recovery of phenols in conventional extraction methods, such as liquid–liquid, solid-phase and solid-phase microextraction it is necessary to acidify the sample [12,19,36]. When the pH is low, the acid–base equilibrium for the acidic phenols shift significantly toward the neutral forms, which have greater affinities toward the non-polar solvent and the extraction efficiencies are, therefore, increased. The effect of the acidity of the sample on the extraction efficiency was studied by changing the sample pH from 1.5 to 5.7 (Fig. 3). The amount of extracted phenols increase with decrease in sample pH from pH 5.7 to 3. In more acidic solutions, a decrease in signal is observed. This observation may be explained by this fact that by increasing the content of sulphuric acid at low pH, ionic strength of the solution will also increase. On the other hand, as it was seen in Fig. 2,

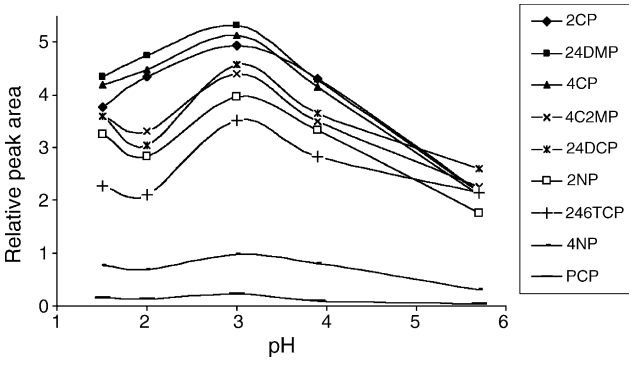

Fig. 3. Effect of sample pH on the extraction efficiency. Concentration of analytes: 45–80 μg/l, solvent volume: 2.5 μl of hexyl acetate, solution temperature: 45 °C, extraction time: 15 min, salt addition: no NaCl added.

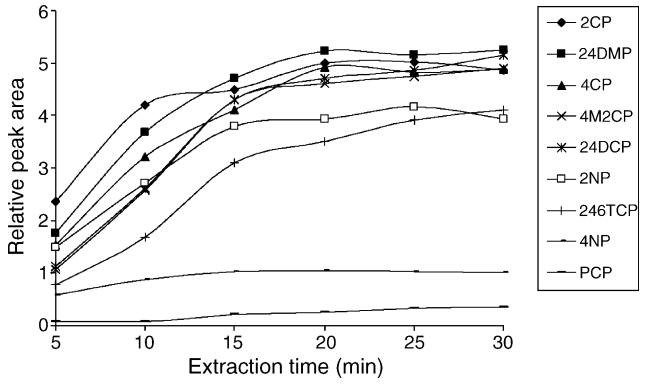

Fig. 4. Effect of extraction time on the extraction efficiency. Concentration of analytes: 45–80 μg/l, solvent volume: 2.5 μl of hexyl acetate, solution temperature: 45 °C, sample pH 3, salt addition: no NaCl added.

enhancing ionic strength of the solution reduces the extraction efficiency of phenols.

The effect of sample temperature was studied by extraction of spiked water samples at 25, 35 and 45 °C. Higher temperatures were not checked due to high incidence of solvent drop loss. It was observed that analyte extraction efficiency enhanced with temperature. To increase sensitivity, further experiments were performed at 45 °C.

To extract the maximum amount of analytes the effect of sampling time in the yield of the microextraction was optimized. Extractions were carried out at 5, 10, 15, 20, 25 and 30 min (Fig. 4). The extraction time profiles show that the equilibrium curves were attained in 20 min for all phenolic compounds. Although an extraction time of 20 min provided higher sensitivity, a 15-min extraction time was chosen for subsequent experiments as a compromise between extraction efficiency and analysis time.

3.3. Linearity, reproducibility, detection limit and enrichment factor

The calibration curves were constructed for all analytes in distilled water samples over the concentration range 0.05–50 μg/l. Each point of the calibration graph corresponded to the mean value obtained from three independent area measurements. The plots were linear for all compounds with r^2 values of over 0.992. In order to determine the precision of the analytical procedure, five consecutive analysis were performed by extracting water sample spiked with a mixture of all phenolic compounds at about 2.3–4 μg/l level. The precision for all analytes was satisfactory with a relative standard deviation value between 4.8 and 11.4%. The limits of detection were calculated with signal-to-noise ratio of the three based on peak-to-peak noise and were in the range of 4–61 ng/l. The limits of detection for all compounds are below the maximum allowable for drinking water. The enrichment factor was calculated as the ratio of final concentration of analytes in a droplet after extraction to initial concentration of analytes in the aqueous solution. The enrichment factors were obtained by three replicate extractions of water samples spiked with 2.3–4 μg/l of analytes. The results indicate that enrichment factors are between 92 and 146. Table 3 shows the results obtained for precision, limit of detection, enrichment factor and linearity range of the proposed method. The quality data of the method are comparable to those obtained by other microextraction techniques, such as SPME [12,22], SDME [29] and liquid-phase microextraction [36] for determination of phenols from water samples.

3.4. River water analysis

In order to investigate the applicability of the proposed SDME method in real sample analysis, determination of phenols in Kashkan and Zayandeh-rood river water samples were performed by standard addition technique. The analytes were added to the river water samples at concentration level about 0.05–4 μg/l. A good linear relationship between spiked amounts and relative peak areas of all analytes was observed for two river water samples ($r^2 > 0.99$). The enrichment factors and RSD for each analyte after the extraction of Zayandeh-rood and Kashkan river water samples spiked at 2.3–4 μg/l level are shown in Table 3. The detection limits and enrichment factors were almost similar to those obtained with purified water, showing no important matrix effects. Fig. 5 shows GC–MS–SIM chromatograms

Table 3
Linear calibration range, detection limits, precision and enrichment factor for the SDME/in- syringe derivatization/GC–MS of phenols

Compound	Purified water[a]		Zayandeh-rood river water[a]		Kashkan river water[a]		Linearity range (μg/l)	LOD[d] (ng/l)
	EF[b]	Precision[c]	EF	Precision	EF	Precision		
2CP	95	11.4	102	12.0	93	10.5	0.05–38	19
24DMP	105	6.2	107	9.3	99	7.8	0.05–33	25
4CP	92	7.3	89	8.9	95	8.3	0.05–31	4
4C2MP	126	7.1	115	6.3	125	6.0	0.05–33	14
24DCP	130	6.3	121	7.9	119	5.6	0.04–28	4
2NP	96	6.3	90	5.8	94	4.8	0.08–51	29
246TCP	146	8.5	135	7.1	139	8.0	0.05–31	22
4NP	93	4.8	86	6.8	98	6.5	0.05–33	38
PCP	144	10.7	138	9.3	140	10.2	0.08–51	61

[a] Spiked at concentration level of 2.3–4 μg/l.
[b] Enrichment factor.
[c] Precision expressed as RSD (%) at 2.3–4 μg/l concentration level, $n = 5$ replicates.
[d] Limit of detection for S/N = 3.

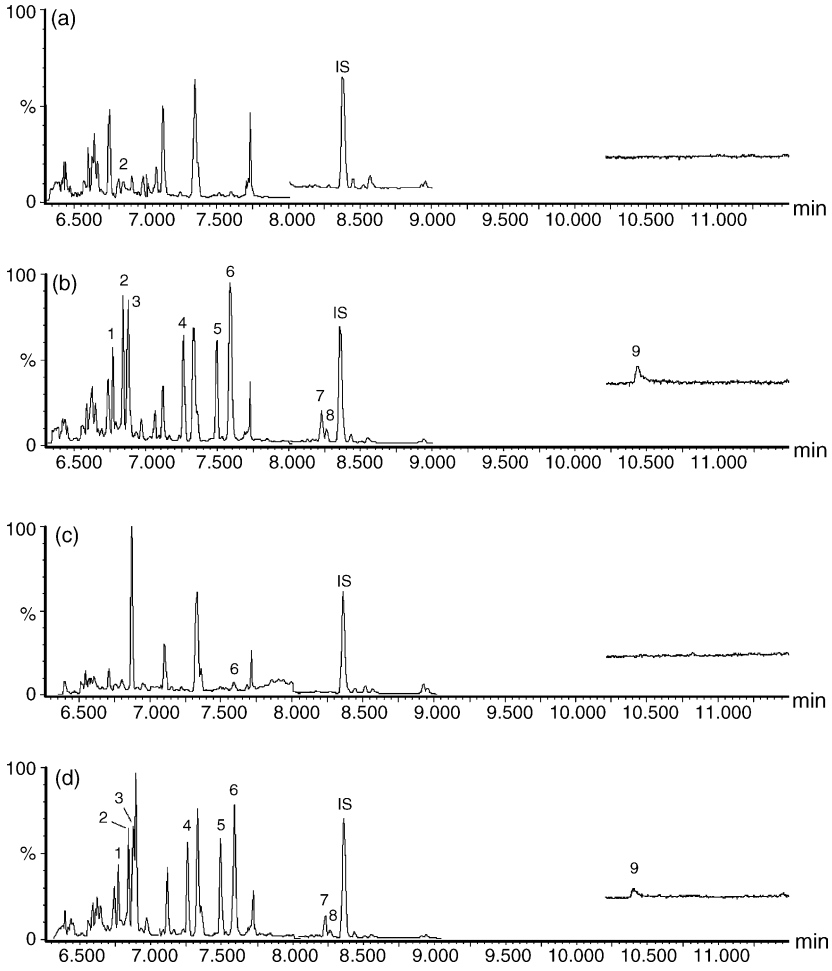

Fig. 5. GC–MS–SIM chromatograms obtained by SDME followed by in-syringe derivatization procedure of (a) Zayandeh-rood river water and (b) Zayandeh-rood river water spiked with 0.45–0.8 μg/l of phenols; (c) Kashkan river water and (d) Kashkan river water spiked with 0.45-0.8 μg/l of phenols. IS: internal standard, (1) 2CP, (2) 24DMP, (3) 4CP, (4) 4C2MP, (5) 24DCP, (6) 2NP, (7) 246TCP, (8) 4NP, (9) PCP.

obtained for spiked and unspiked Kashkan and Zayandeh-rood river water samples. The river water samples were spiked with 0.45–0.8 μg/l of standard solution of nine phenols. In the figure for the unspiked river water samples, two peaks that could be assigned to phenols can be observed. Analytes were identified in cases of identical retention times and relative abundance of selected ions (allowing a variation of 10%). One peak was assigned to 24DMP in the Zayandeh-rood river water blank chromatogram at a concentration of 68 ng/l. Also, a peak was assigned to 2NP in the Kashkan blank chromatogram at a concentration of 74 ng/l.

4. Conclusion

The analysis of phenolic compounds in the aqueous phase via SDME coupled with in-syringe derivatization has been successfully performed. In-syringe derivatization can be achieved in only 5 min with consumption of a very small amount (0.5 μl) of derivatization reagent. Excess amount of the BSA reagent and reaction by-products do not interfere with the determination and a clean-up step is not needed. The risks of contamination and analyte loss are minimized because the derivatization step was performed inside the needle barrel without an additional transfer step. Simplicity, short analysis time, low cost, ease of operation, low consumption of solvent and derivatization reagent are the main advantages of this technique. Linearity, reproducibility and detection limits obtained using this method are comparable to those achieved by other techniques.

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