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Immersed solvent microextraction of phenol and chlorophenols from water samples followed by gas chromatography–mass spectrometry

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Abstract

A homemade immersed solvent microextraction (SME) device was successfully developed for the trace enrichment of phenols from aqueous samples. A microdrop of butyl acetate was suspended from the tip of a microsyringe needle, immersed in an aqueous spiked solution for a preset time. The microdrop was then retracted into the microsyringe and injected directly into a gas chromatography–mass spectrometry (GC–MS) injection port. Effects of different parameters such as the type of solvent, extraction time, stirring rate, and temperature were investigated and optimized. To reduce the polarity of phenols and prevent tailing effects, all the phenols were derivatized prior to extraction using acetic anhydride in basic media. The enrichment factor and linearity was studied by preconcentration of 1 ml of HPLC-grade and river water, spiked with a standard solution of phenols at a concentration range of 0.05–50 $\mu g\,l^{-1}$ (R.S.D. < 10%). The correlation coefficient was satisfactory ($r^2 > 0.98$) for all the studied analytes. Detection limits were obtained using HPLC-grade and river water, i.e. 5–22 $ng\,l^{-1}$. The proposed method was successfully applied to the extraction and determination of some environmentally important phenols in different water samples.
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Keywords: Water analysis; Immersed solvent microextraction; Phenol; Chlorophenols

1. Introduction

Phenolic compounds are considered major environmental risks, either directly, as industrial effluents, or indirectly, as conversion products from natural and synthetic chemicals, including pesticides [1]. Owing to their toxicity both the US Environmental Protect Agency and the European Community (EC) have included some phenols, mainly nitrophenols and chlorophenols, in their lists of priority pollutants. The EC legislation requires that the maximum admissible concentration of phenols in drinking water should be 0.5 $\mu g\,l^{-1}$ for the total content and 0.1 $\mu g\,l^{-1}$ for an individual one [2]. So, detection limits below 0.1 $\mu g\,l^{-1}$ are required.

Analytical techniques used in determination of phenols are mainly high-performance liquid chromatography (HPLC), particularly reversed-phase liquid chromatography (RPLC), and also capillary electrophoresis in combination with ultraviolet detection (UV), fluorescence detection, electrochemical detection, or mass spectrometry (MS) [3–5]. Moreover, gas chromatography (GC) with flame ionization detector, electron capture detector or MS is a common tool for the analysis of phenols, usually after derivatization [6–9]. To achieve the necessary levels of sensitivity, an enrichment step is needed before the chromatographic analysis.

Liquid–liquid extraction (LLE) [10] and solid-phase extraction (SPE) are the most commonly used techniques for isolation and/or enrichment of phenols prior to chromatographic analysis [11–16]. But these methods have many disadvantages, as they are tedious, labor-intensive and time-consuming. LLE in particular requires the use of large amounts of highly-purity solvents, which are often hazardous and result in the production of toxic laboratory waste. Prior to the chromatographic analysis, when LLE and SPE are

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employed, there is a need for solvent evaporation in order to preconcentrate the samples. Although SPE is less time-consuming than LLE, it still requires an appreciable amount of toxic solvent for analyte desorption. Solid-phase microextraction (SPME), initially introduced for analysis of volatile compounds, has been developed for extraction of phenols [17,18]. This technique has important advantages over conventional extraction techniques due to its ease of use, being rather rapid, portable and solvent-free. Nevertheless, SPME also has some drawbacks including its limited lifetime, fragility of fibers and possibility of sample carry-over [19].

Since 1995, a solvent-minimized sample pretreatment procedure, known as SME, has been developed. It is fast, inexpensive, and due to the need for small volume of solvent, there is minimal exposure to toxic organic solvents. In this technique, which has gained increasing attention [20–25], the analytes are distributed between the bulk aqueous phase and a microdrop of organic solvent, suspended directly at the tip of a microsyringe needle that is immersed in a stirred aqueous sample solution. After a certain time, when sufficient amounts of analytes are transferred into the organic extractor, the microdrop is retracted into the microsyringe, and subsequently part or all of the organic solvent is injected into the chromatographic system. An important additional feature of SME is the integration of extraction and injection in a microsyringe, making it possible to employ this miniaturized medium for extraction as well as an injection device for the GC [23,24,26,27]. Apart from being inexpensive, SME requires only common laboratory equipment and does not suffer from carry-over between extractions that may be experienced using SPME. Solvent microextraction, in combination with GC, has been successfully applied for the quantitation of chlorobenzenes [27] and pesticides in water samples [28] as well as for the screening of cocaine and cocaine metabolites in urine [29].

In continuation of our research interests on the trace determination of phenolic compounds in aquatic matrices [13–16], an immersed SME-based technique for the ultra trace determination of phenol and chlorophenols in water was developed. A microdrop of an organic solvent was employed as the extraction medium, while the extraction temperature could be controlled using a water-jacketed vessel. Effects of various influential parameters were also examined and the developed method was applied to real samples.

2. Experimental

2.1. Reagents

Phenolic compounds studied include phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and flourene, used as internal standard (IS) in the drop, were obtained from Merck (Darmstadt, Germany). Standard solutions (1000 mg l^{-1}) from each individual compound were prepared in methanol and stored in the refrigerator. A mixture of these phenolic compounds was prepared weekly by diluting the standard solutions with methanol, and more diluted working solutions were prepared daily by diluting these solutions with double distilled water or river water. Methanol (HPLC-grade), toluene, cyclohexane, *n*-hexane, and *n*-octane, all of analytical grade, acetic anhydride (98% minimum), potassium carbonate and sodium chloride (99.5% minimum) were purchased from Merck. Butyl acetate (99% minimum) was purchased from Riedel de Haën (Seelz, Germany).

2.2. Apparatus

A Hewlett-Packard (HP, Palo Alta, USA) HP 6890 series GC equipped with a split/splitless injector and a HP 5973 mass-selective detector system were used. The MS was operated in the EI mode (70 eV). Helium (99.999%) was employed as carrier gas and its flow rate was adjusted to 1 ml/min. The separation of phenols was performed on a 30 m × 0.25 mm i.d. fused-silica capillary column coated with a 0.25 μm bonded film of HP-5 MS. The GC column temperature was programmed at 40 °C for 1 min and then raised to 220 °C at 20 °C/min. The injector temperature was set at 260 °C, and all injections were carried out on the splitless mode. The GC–MS interface was maintained at 280 °C. The MS was operated in the total ion current (TIC) mode, scanning from *m/z* 40 to 350. For quantitative determination, the MS was operated in time scheduled selective ion monitoring (SIM) mode. Quantitation was performed by calculating peak areas relative to the IS.

2.3. Acetylation of phenols in standard solutions

The acetylation of phenols was carried out according to the procedure reported previously [14,30,31]. A volume of 1 ml of a methanol solution containing the phenols was mixed with 2 ml of 5% K_2CO_3 and 2 ml of *n*-hexane containing 200 μl of acetic anhydride. The mixture was shaken for 1 min and the organic phase was separated. The aqueous phase was then extracted with a further 1 ml of *n*-hexane, without adding any derivatizing reagent. The two *n*-hexane portions were mixed and then injected into the chromatographic system. After performing the derivatization process on samples containing various concentrations of phenols, calibration curves were constructed as plots of the concentration of each phenol against the peak area of its acetylated derivative.

2.4. Sample preparation

A known volume of double distilled water or pre-filtered river water was spiked with phenol standards in methanol and the pH was adjusted to 11–11.5 with K_2CO_3 (spiked samples). After adding appropriate amount of acetic anhydride (5 ml/l of water sample) the mixture was shaken for 15 min.

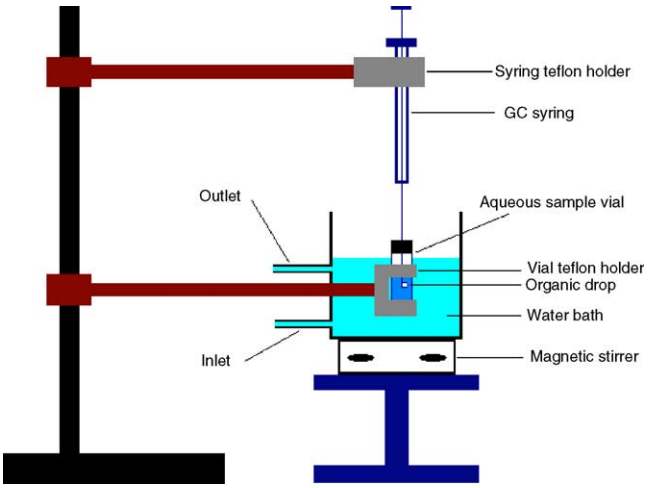

Fig. 1. Schematic diagram of the SME set-up.

2.5. Extraction apparatus and SME procedure

In this work, a homemade SME device was developed for the preconcentration of phenols from aqueous sample. A sample vial was placed in a special constructed glass water-jacketed vessel and maintained at a constant temperature by a water bath. During the extraction, a 10 μl microsyringe was clamped above the sample vial so that the syringe needle tip was below the surface of the aqueous sample. The solution was stirred at a constant rate. The type of microsyringe employed here contains a needle with a 22° bevel (Fig. 1). Two Teflon-based units were constructed to hold the syringe and the vial firmly, making the alignment between the syringe and the vial more convenient.

The SME procedure has been already described previously [27,28]. An aliquot of 2–3 μl of butyl acetate containing 100 μg l^{-1} of I.S. was withdrawn into syringe. The syringe plunger was depressed by 0.5 μl to produce a small drop at the tip of the syringe needle and then was immersed into the 1 ml stirred sample solution to a depth of 0.5 cm below the surface. The syringe was held in place by a clamp. The syringe plunger was depressed to expose a 2.5 μl drop of solvent to the sample. Extraction of analytes of interest on this droplet continued for a preset time. The drop was retracted into the syringe, and the needle was subsequently removed from the sample vial. The plunger was then depressed to the 1 μl position, and the needle tip was cleaned carefully with a tissue and all possible water contamination was removed. The extract was finally injected into the GC–MS system.

3. Results and discussion

SME is based on the partition of analytes between two immiscible liquid phases; often a non-polar organic solvent is used to extract the analytes of interest from an aqueous solution. Extracting polar organic compounds, i.e. phenolic compounds, then, becomes rather more difficult as they tend to stay in aqueous media. Furthermore, headspace SME seems to be an inefficient method due to the low volatility of analytes with polar characteristics. The feasibility of an immersed SME method was, therefore, considered in order to bring the extracting phase in direct contact with the analytes, enhancing the overall mass-transfer coefficient with respect to the organic phase, β_o, an influential factor affecting observed rate constant (S^{-1}) given by:

$$k = A_i \beta_o \left(\frac{K}{V_{aq}} + \frac{1}{V_o} \right) \quad (1)$$

where A_i is the interfacial area, K the distribution constant, and V_{aq} and V_o are the volumes of the organic and aqueous phases, respectively [6,31]. Clearly, the higher β_o value is an indication of higher efficiency for the extraction process. According to this equation and the film theory convective-diffusive mass transfer [23], an immersed SME method for preconcentration of phenols from aqueous samples looked quite promising.

However, to prevent the peak broadening and also reduce the polarity of analytes, all phenolic compounds in the standard solutions and spiked water samples were derivatized prior to extraction and GC–MS determination. From practical point of view, two Teflon-based units were constructed to hold the syringe and the vial firmly, making the alignment between these two units more convenient and practical.

3.1. Optimization

A univariate approach was employed to optimize influential factors in this method. Various parameters affecting the SME efficiency including the type of solvent, stirring rate, extraction time, temperature of sample solution, and ionic strength were optimized. The ratio of peak area of each individual phenol and that of internal standard was used to assess the extraction efficiency under various conditions. Enrichment factor (E_e), defined as the ratio of the GC–MS response after extraction and the one prior to extraction, was used for all quantitative analysis.

3.1.1. Solvent selection

Four water-immiscible solvents with different polarity and water solubility were examined in order to find the most suitable solvent for extraction. Solvent selectivity was evaluated for the extraction of 1 ml of sample containing 20 μg l^{-1} of each phenol, already derivatized into its corresponding phenyl acetate, in deionized water. The stirred solution (250 rpm) was sampled at 27 °C for 15 min using 2 μl of appropriate organic solvent. These solvents have various water solubilities, and longer sampling times, higher sample temperature and faster stirring rates were, therefore, avoided. The results are given in Fig. 2. The extraction efficiency was based on the average peak area of each analyte for three replicate analyses. Apparently, butyl acetate, as

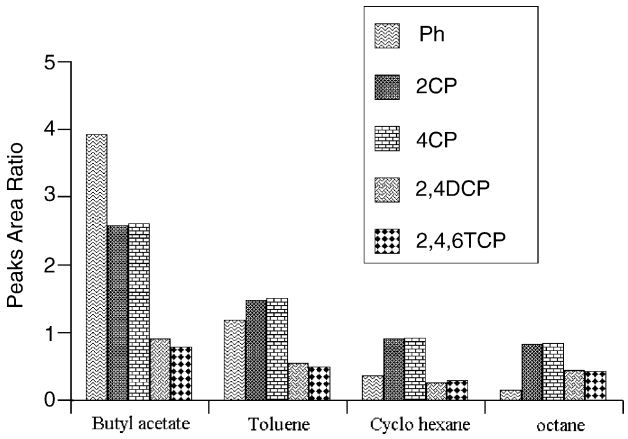

Fig. 2. Extraction efficiencies obtained for different organic solvents.

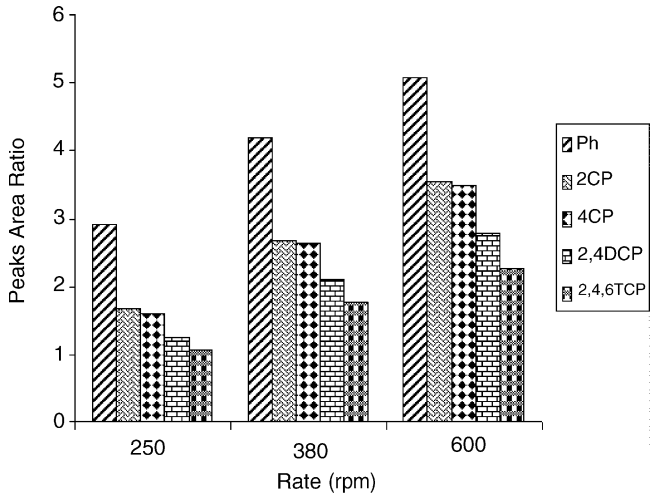

Fig. 3. Effect of stirring rate on the extraction efficiency of phenols from aquatic medium.

the extraction solvent, shows higher extraction efficiency in comparison with other solvents. The primary reason could be attributed to the higher polarity of butyl acetate ($\log K_{ow}$ = 1.505, the octanol–water partition coefficient), which favors interaction with polar compounds. Clearly, the higher value of octanol–water partition coefficient indicates the less hydrophilic character for the substance of interest. In addition, when butyl acetate is used, the dipole–dipole interactions become more pronounced and extraction efficiency for the more polar analyte, acetylated phenol, is enhanced (Fig. 2). In the mean time, the butyl acetate microdrop could be more easily manipulated preventing the drop loss even when faster stirring rates were used. Other solvents including cyclohexane ($\log K_{ow}$ = 2.588), octane ($\log K_{ow}$ = 3.767) and toluene ($\log K_{ow}$ = 2.454) were, therefore, excluded from further investigation.

3.1.2. Stirring rate

Sample agitation enhances extraction efficiency and reduces extraction time, especially for higher molecular mass analytes [19]. For the purpose of the present study three replicate analyses were taken at three different stirring rates: 250, 380 and 600 rpm. Faster stirring rates were avoided as they resulted in dislodgement of the organic drop from the needle tip. In all cases, the 2 μl butyl acetate drop was exposed at 27 °C for 15 min to a 1 ml water sample spiked with 20 μg l^{-1} of each analyte. Fig. 3 shows that the agitation improves the extraction efficiencies of acetylated phenols significantly. This is in agreement with the expected behavior of solvent microextraction based on the film theory convective–diffusive mass transfer [23]. This theory assumes no movement of the solution at the layer immediately adjacent to the interface and a gradually increasing vigorousness of convection of the solution at location farther away from the interface. Considering the film theory under this condition, which is rather difficult to treat mathematically, it is approximated that uniform, instantaneous and complete convective mixing exists at some distance δ_{aq}, the Nernst diffusion film, away from the liquid–liquid interface. At steady state the aqueous phase mass transfer coefficient for the solute is defined by:

$$\beta_{aq} = \frac{D_{aq}}{\delta_{aq}} \quad (2)$$

where D_{aq} is the diffusion coefficient in the aqueous phase, and β_{aq} the mass transfer coefficient. At faster stirring rates δ_{aq} decreases causing the increase of β_{aq} and, hence, the extraction rate increases as well.

Although high stirring rates increase the enrichment factors considerably, the stability of a micro drop at the tip of the needle could be dramatically affected when a high stirring rate is used. This is especially true when prolonged sampling times are applied. Thus, for all further experiments a stirring rate of 600 rpm was used. Using a small magnet with consistent stirring rate and avoiding any temperature convection was quite essential for achieving an acceptable precision.

3.1.3. Extraction time

Extraction time is a major parameter affecting the extraction efficiency. This effect was studied in the range of 5–30 min at room temperature keeping the stirring rate constant at 600 rpm. A series of spiked-water samples (20 μg l^{-1}) were prepared and the variation of the analytical signal for each analyte was studied as a function of exposure time. Fig. 4 shows that the analytical signal increases quickly with sampling time in the range of 5–20 min, and after 20 min the rate of increase slows down. It can be seen, however, that equilibrium has not been reached even after 30 min. An extraction time of 10 min was selected as a reasonable compromise between enrichment factor and analysis time. Using a longer time could reduce the size of microdrop due to its dispersion at conditions above ambient temperature.

3.1.4. Temperature effect

Temperature is a major parameter affecting extraction efficiency. Increasing the reaction temperature by 10 K approximately doubles the rate of reaction [32]. This part of work

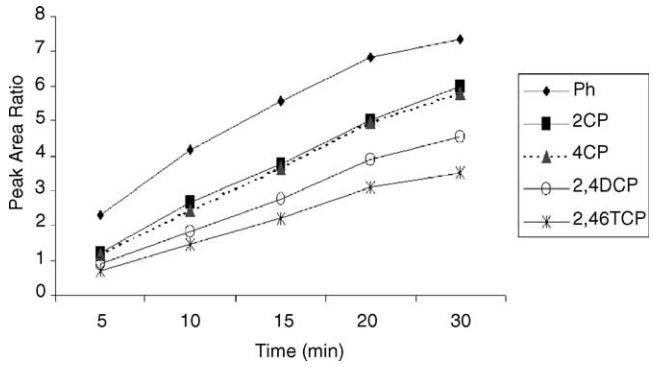

Fig. 4. SME time profiles obtained for the studied phenols.

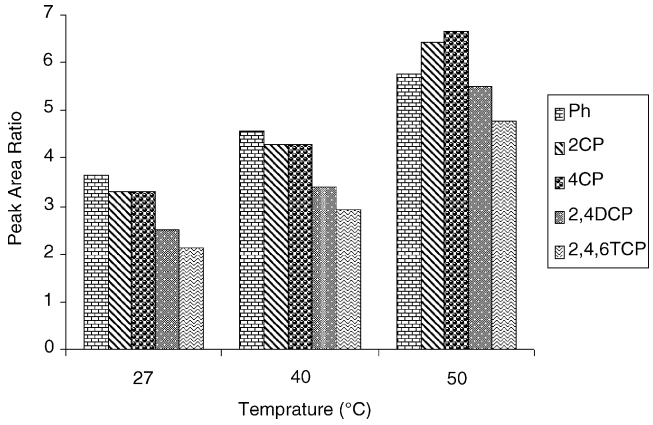

Fig. 5. Extraction efficiencies obtained at various extraction temperatures.

was carried out using a temperature range of 27–60 °C employing a laboratory-made device. As Fig. 5, clearly, shows the extraction efficiency increases as the solution temperature is enhanced. This is expected behavior, since at higher temperature, the mass transfer coefficients along with the rate constants are enhanced. However, the microdrop tends to become depleted as temperature is raised. Using much higher temperatures was, therefore, avoided in order not to lose the drop size dramatically. Fig. 6 demonstrates the microdrop loss as temperature is increased. As other researchers have indicated earlier [28], at 55 °C irregular formations of

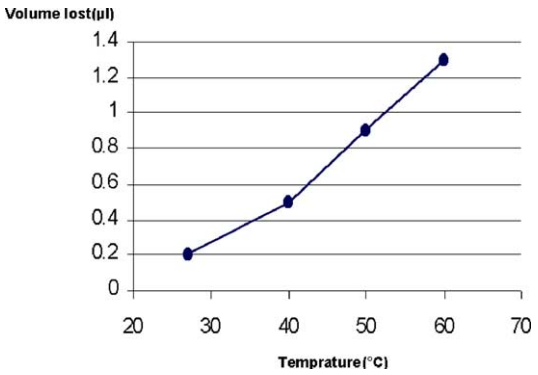

Fig. 6. Influence of temperature on microdrop loss after 15 min extraction time.

Table 1
Retention times, selected ions and scan start time of compounds studied by GC–MS

Compound[a]	Retention time (min)	Selected ions (*m*/*z*)	Scan start time (min)
Ph	5.51	66, 94, 136	4.8
2-CP	6.64	99, 128, 170	6.10
4-CP	6.88	99, 128, 170	6.10
2,4-DCP	7.72	133, 162, 204	7.2
2,4,6-TCP	8.37	167, 198, 238	8
FL	9.3	82, 139, 166	9

[a] All phenols were acetyled prior to extraction and subsequent determination.

bubbles could cause significant effects on the drop stability. To avoid such problems, the sample solution was sonicated prior to extraction and the extraction temperature was set at 50 °C.

3.1.5. Ionic strength

The influence of salt addition on the efficiency of SME was also investigated. Usually, the presence of salt increases the ionic strength of aqueous solution and would affect the solubility of organic solutes. This can be explained by the engagement of water molecules in the hydration spheres around the ionic salt. These hydration spheres reduce the concentration of water available to dissolve solute molecules. This should, then, drive additional solutes into a non-polar sorbent or extractant. This effect is rather important for SPME and addition of more than 1% of sodium chloride to enhance the extraction efficiency of the fibers have been reported [17–19]. Our results, however, show a decrease of efficiency for acetylated phenols (Fig. 6). The addition of salt might change the Nernst diffusion film physical properties and it reduces the diffusion rates of solutes into the micro drop, and consequently lowers the analytical signals.

3.2. GC–MS determination

After sample extraction, an aliquot of 1 μl of butyl acetate containing the extracted phenols was directly injected into the GC–MS system. To obtain the highest possible sensitivity, the

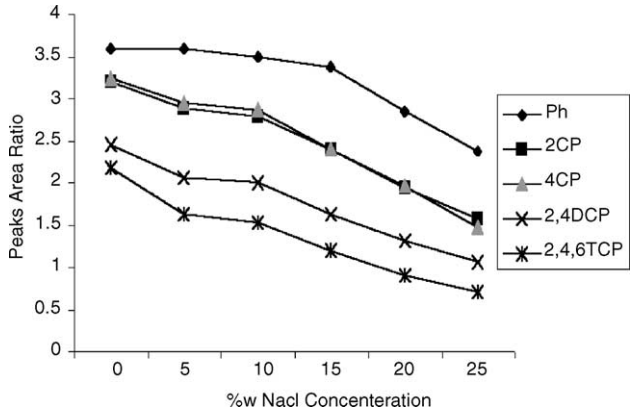

Fig. 7. Effect of ionic strength on the extraction efficiency of phenols from aquatic medium.

Table 2
Some quantitative data obtained after immersed SME of different waters spiked with the studied phenols

Compound[a]	HPLC-grade water spiked at 0.5 μg/L		HPLC-grade water spiked at 1.0 μg/L		River[b] water spiked at 0.5 μg/L		LOD (ng/L)
	E_e[c]	R.S.D. (%)[d]	E_e	R.S.D. (%)[d]	E_e	R.S.D. (%)[d]	
Ph	88	7.1	61	3.4	62	8.1	5
2-CP	71	7.8	54	1.8	50	6.7	12
4-CP	89	10.2	60	1.4	62	7.2	10
2,4-DCP	134	3.9	88	4.4	94	5.1	21
2,4,6-TCP	96	8.3	56	2	67	7.9	12

[a] All phenols were acetyled prior to extraction and subsequent determination.
[b] Zayandeh-rood river.
[c] Enrichment factor.
[d] $n = 3$.

MS detection was operated using time-scheduled SIM based on the selection of three mass peaks of the highest intensity for each compound. Table 1 lists the retention times, selected masses and the start scan times for each compound studied by GC–MS. The mass spectrum of each compound was already obtained by the direct injection of a standard solution of each analyte into the GC–MS.

3.3. Quantitative evaluation and real samples

The optimized method was examined for the extraction and determination of some environmentally important phenols in different water samples. Prior to any further investigation, the enrichment factor and linearity was studied by preconcentrating 1 ml of HPLC-grade water, spiked with

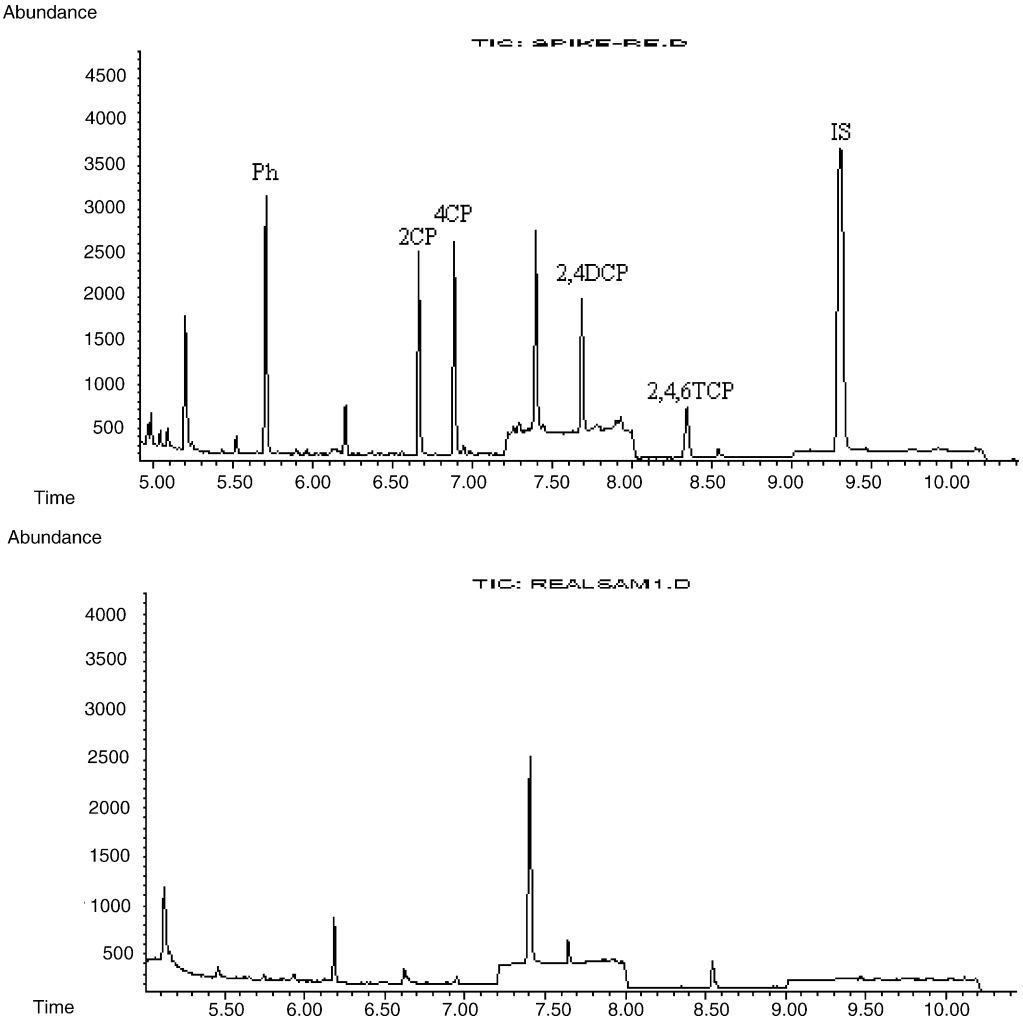

Fig. 8. Mass chromatograms obtained after immersed SME of 1 ml of blank Zayandeh-rood river water (bottom) and after immersed SME of 1 ml of Zayandeh-rood river water spiked with 0.5 μg l^{-1} from each phenol (above), using time-scheduled SIM mode.

a standard solution of phenols at a concentration range of 0.05–50 $\mu g\,l^{-1}$ (R.S.D. < 10%). The correlation coefficient was satisfactory ($r^2 > 0.98$) for all the analytes studied. Detection limits, based on a signal-to-noise ratio of S/N = 3, were obtained using HPLC-grade and river water, i.e. 5–22 $ng\,l^{-1}$. These levels, conveniently, meet the limits required by the US Environmental Protection Agency (EPA) and other international institutions.

Some quantitative data obtained after immersed SME of HPLC-grade water spiked at two different concentration levels are listed in Table 2. The results indicate that an enrichment factor of 70 or more were obtainable when a sample of water, spiked at 0.5 $\mu g\,l^{-1}$ level, was tested. Other researchers reported an increase of the enrichment factor by diluting the samples using SPME [33].

Fig. 7 shows two mass chromatograms obtained after immersed SME of 1 ml of Zayandeh-rood river (Isfahan-Iran) water spiked with the studied phenolic compounds at 0.5 $\mu g\,l^{-1}$ (above), and 1 ml of blank Zayandeh-rood river water (bottom) using time-scheduled SIM mode.

The enrichment factors along with the value of R.S.D. for each individual phenol after the immersed SME of Zayandeh-rood river water spiked at 0.5 $\mu g\,l^{-1}$ are shown in Table 2 and Fig. 8. SME is a non-exhaustive extraction procedure like SPME and for this reason the relative recovery, defined as the ratio of GC/MS peak areas of spiked river water extracts to spiked HPLC-grade water extracts, was used [28,33,34]. Surprisingly, the data show that for all phenols, the relative recoveries are 70.0%, although the peak area for each phenol is quite different. Comparing the results of river water with the data obtained from HPLC-grade water, both spiked with the selected phenols at 0.5 $\mu g\,l^{-1}$ level, along with the relative recoveries data reveals that matrix effect has some minor influence on the extraction recoveries.

4. Conclusion

In this work, an organic microdrop was used as the medium for extraction of some environmentally important phenols from aquatic samples and their determination was subsequently performed by GC–MS. The method was based upon direct contact of the extracting microdrop with the sample solution. Influential parameters such as the type of solvent, extraction time, stirring rate, temperature, and ionic strength were optimized. A volume of 1 ml of HPLC-grade water or river water, spiked with standard solutions at ppb and sub-ppb levels, was sufficient to establish the method and obtain good enrichment factors. In contrasts with our previous works using SPE [13–16], the extraction efficiency obtained for phenol is comparable with those of other phenols. The developed method is rather rapid, simple, linear, and reproducible. It is easy to use for the qualitative and quantitative analysis of phenols while small volumes of sample and micro-scale size of organic extracting solvent are required.

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