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High-density solvent-based de-emulsification microextraction technique combined with fiber optic-linear array detection spectrometry for fast determination of ppb-level phenol index

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ABSTRACT

In this work, a simple, rapid, and efficient solvent-based de-emulsification microextraction technique using high-density solvent has been developed for determining phenol index in water samples for the first time. The extraction of phenolic compounds in the aqueous sample solution was performed by using chloroform (as extraction solvent) and acetone (as dispersive solvent) in the presence of 4-aminoantipyrine (4-AAP) as chromogenic reagent. A de-emulsification solvent (ACN) was then injected into the sample solution to break up the emulsion, and then obtained emulsion cleared into two phases quickly, with no centrifugation step. The lower layer organic phase transferred into a microcell of a fiber optic-linear array detection spectrophotometry. The effect of various parameters on the extraction recovery was investigated. Under the optimized conditions and preconcentration of 10 mL of sample, the enhancement factor of 140 and the detection limit of 0.6 $\mu g\,L^{-1}$ were obtained. Validation of the method was performed by spiking recovery method and comparison of results with those obtained by American Society for Testing and Materials standard method.

Keywords: Fiber optic-linear array detection spectrophotometry; Phenol index; High-density solvent based de-emulsification microextraction technique; Water samples

1. Introduction

Phenols are one of the most important organic pollutants of natural water that arrive at water areas from both anthropogenic and natural sources [1]. Phenolic compounds are present in the aquatic and environment due to their widespread use in industrial applications. These compounds are generated in the production of plastics, dyes, drugs, pesticides, antioxidants, and paper, and by the petrochemical industry [2]. Many investigations had confirmed the presence of phenols in many ecosystems: surface and ground waters, bottom sediments, atmospheric air, and soils.

Possible routes of human exposure to phenols are inhalation, ingestion, and eye and dermal contact [3]. The monitoring of the total concentration of phenol and its derivatives in water, the phenol index (PhI), is preferred in the routine analytical monitoring of water quality. Most common method for the determination of PhI is based on the reaction of phenol compounds with 4-AAP and forming colored compounds under

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particular conditions [1]. The official American Society for Testing and Materials (ASTM) D1783 standard method is based on the oxidative coupling of phenols with 4-AAP in alkaline medium, extracting the colored derivative compound in chloroform and photometric determination. The main disadvantage of this standard method from the point of view of green analytical chemistry is the use of large amounts of chloroform as an extraction solvent which is a hazardous organic solvent. Several methods have been developed for eliminating this solvent [4–8]. In comparison with the standard method, these procedures are more environmentally friendly and more sensitive. Among these methods, dispersive liquid–liquid microextraction (DLLME) is a safer and simpler method which has been recently applied to the determination of individual phenols [9,10]. The method is based on the ternary component solvent system. In this method, a cloudy solution is formed when an appropriate mixture of extraction and dispersive solvents is injected into an aqueous sample containing the analytes of interest. The hydrophobic solutes are enriched in the extraction solvent, which is dispersed into the bulk aqueous solution. Due to the considerably large surface area between the extraction solvent and the aqueous sample, the extraction of the analytes is achieved quickly. After centrifugation, determination of the analytes in the settled phase can be performed by conventional analytical techniques. The advantages of DLLME are simplicity of operation, low cost, low consumption of organic solvent, high recovery, and high enrichment factor. The basic common characteristic of the above-mentioned DLLME approaches is that phase separation is accomplished by a centrifugation step. The centrifugation step leads to low precision and makes microextraction technique difficult to be automated. Moreover, it is difficult to handle large-volume centrifugation [11]. Centrifugation step can be avoided by the recently introduced alternative of "solvent-based de- emulsification" [12–14]. In this method, the extraction is ended by the addition of a second portion of a water miscible solvent, e.g. the disperser solvent which acts as a de-emulsifier and promotes physical phase separation without centrifugation. In this technique, by adding more disperser solvent into the emulsion, the ratio of solvents (extraction solvent, water, and disperser solvent) is changed and de-emulsification is occurred. In previous works with solvent-based de-emulsification DLLME (SD-DLLME), low-density extraction solvents (toluene, m-xylene, n-hexane, or 1-octanol) were used. After de-emulsification, the upper layer was collected and analyzed but there was a problem with collecting the upper layer after microextraction; therefore, special homemade extraction devices were needed. In order to overcome this problem, a novel modality of SD-DLLME, termed high-density extraction solvent-based solvent de-emulsification dispersive liquid–liquid microextraction (HSD-DLLME), was proposed in 2013 [11]. In this method, instead of low-density extraction solvents, a solvent of higher density than water (chloroform) is employed as an extraction solvent. To best of our knowledge, there is no report on the use of HSD-DLLME for the microextraction and determination of phenol index.

The present study aims to develop a quick and sensitive method for the microextraction and determination of phenol index by HSD-DLLME and its determination by fiber optic-linear array detection spectrophotometry (FO-LADS). The fiber optic-linear array detection spectrometers based on CCD-detector (charge coupled device detector) have made a major impact on simultaneous and real-time data collection in analytical spectroscopy. Simultaneous determination of analytes using multiwavelength data acquisition using CCD linear array spectrophotometry is very powerful technique in this area. In addition, optical fibers have high light focalization that makes them suitable for preconcentration applications in which microliter volume of extraction solvent is used. So, the microliter sample volume can be measured easily, accurately, and precisely by means of FO-LADS using microcell [15–18]. This method was then utilized to analyze real environmental samples.

The ASTM standard method was used to confirm the results obtained by the proposed method.

2. Experimental

2.1. Reagents and chemicals

All chemical reagents (acetone, acetonitrile, chloroform, phenol, 4-AAP, and potassium hexacyanoferrate) were of analytical reagent grade. All chemicals were purchased from Merck (Darmstadt, Germany) or Aldrich (Chemical Co., Milwauke, WI, USA). All standard solutions were prepared in double-distilled deionized water (Milli-Q system, Millipore, USA). The stock standard solutions of phenol at a concentration of 1,000 mg L^{-1} were prepared by dissolving appropriate amount of phenol crystals (Merck, Darmstadt, Germany) in water. Standard working solutions were prepared freshly by proper dilutions of the standard stock solution. A buffer solution (pH 10.0) was composed of ammonia extra-pure solution and ammonium chloride salt. A solution of 0.02 mg L^{-1} 4-AAP was prepared daily by dissolving an appropriate amount of 4-AAP in the double-distilled deionized

water. A solution of 0.08 g mL^{-1} potassium hexacyanoferrate was prepared weekly by dissolving an appropriate amount of potassium hexacyanoferrate in water and stored in a dark place.

2.2. Apparatus

A UV–vis (Avantes, model 2048, Eerbeek, Netherlands) equipped with optical fiber and a CCD-linear array detector was used for FO-LADS. A 50 μL quartz cylindrical microcell (Hellma, Mullheim, Germany) was used as a determination cell. A Metrohm digital pH-meter (model 692, Switzerland) equipped with a glass-combination electrode was used. An adjustable sampler (50–200 μL) from Eppendorf (Hamburg, Germany) was applied for addition of ammonia buffers for pH adjusting. For collecting the organic phase, a 100 μL syringe (Reno, NV, USA) was used and the disperser and extraction solvents were injected into the sample solutions by a 1 mL syringe.

2.3. Instrumentation setup

Light beam was transmitted through the single-stand optical fiber (200 μm diameter) and the fiber connected to the spectrograph by SMA (Sub Miniature version A) connection. Spectrograph disperses light beam via a fixed grating across the 2048 element CCD-linear array detector, that responses in the range of 200–1,100 nm. The output data from CCD-linear array detector are transferred to personal computer by universal serial bus connection.

2.4. Procedure

0.1 mL buffer solution (pH = 10.0) was added to an aliquot of 10 mL water sample which was placed in a 15 mL glass centrifuge tube, and then 60 μL of 4-AAP (0.02 g mL^{-1}) and 60 μL of potassium hexacyanoferrate (0.08 g mL^{-1}) were, respectively added. This mixture was set aside for 2 min. A mixture containing 120 μL of chloroform (as extraction solvent) and 0.5 mL acetone (as dispersive solvent) was quickly injected into the solution by using a 1 mL syringe. A cloudy solution that consists of very fine droplets of the immiscible extraction solvent (chloroform) dispersed into solution was instantaneously formed. After 1 min, 1.5 mL of ACN, used as the de-emulsifier, was injected into the solution to break down the emulsion. Then, the emulsion cleared into two phases quickly. As a result, the fine droplets of extraction phase settled at the bottom of the tube (60 ± 5μL). Fifty microliters of the settled phase were removed by a 100 μL microsyringe and transferred into a 50 μL quartz cylindrical microcell and the absorbance was measured at 465 nm against a blank as a reference. Fig. 1 shows the spectrums of extract and blank.

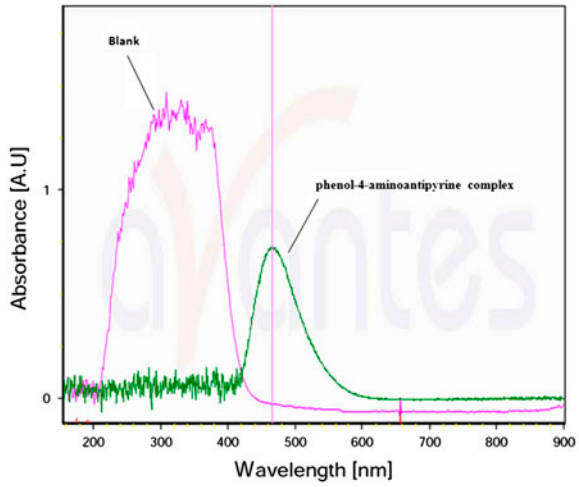

Fig. 1. Spectrums of phenol-4-AAP complex and blank.

2.5. Water samples

Different types of water samples (tap, mineral, river, and seawater) were collected for the investigation of the applicability of the proposed method. Tap water was collected in our laboratory from drinking water system of Tehran, the river water was sampled in the Tajan river (Mazandaran, Iran), the sea water samples were collected from the Caspian Sea (Iran), and the mineral water was purchased from a local supermarket (Damavand mineral water Co., Tehran, Iran). Samples were kept at 4°C and analyzed within 24 h after collection.

3. Results and discussion

In order to obtain the best conditions, effect of different parameters, including the type and volume of extraction and disperser solvents, type and volume of de-emulsifier, concentration of 4-AAP and potassium hexacyanoferrate, pH and concentration of salt, were investigated and optimized. In all optimization steps, concentration of phenol was 20 μg L^{-1}.

3.1. Effect of pH

The reaction of phenol with 4-AAP should be carried out in alkaline solutions with a high enough

pH to prevent the formation of antipyrine red [19], so the effect of pH on the extraction of phenol from water samples we studied was in the range of 8–12 with the use of ammonia buffers. The results showed pH 10.0 was the optimum value.

3.2. Effect of type and volume of extraction solvent

Phenolic materials react with 4-AAP in the presence of potassium hexacyanoferrate to form a stable reddish-brown-colored solution. In general, it was found that chlorinated hydrocarbons could be used to extract the dye from the reaction mixture [20]. Therefore, in this research, four chlorinated solvents including chloroform, carbon tetrachloride, dichloromethane, and dichlorobenzene were compared as extraction solvents. Due to different solubility of these extraction solvents in water, different volume of the selected extraction solvent was used to obtain the same volume (60 ± 3 μL) of the extractant phase at the bottom of the tube. The results showed that chloroform had the highest extraction efficiency among other solvents.

To examine the effect of the extraction solvent volume, in the same experimental conditions, different volumes of chloroform (100, 110, 120, 140, 160, 180, and 200 μL) were investigated in the presence of acetone as disperser solvent. In this work because of using a 50 μL quartz cylindrical microcell, the collected volume of the organic solvent should be more than 50 μL, and so volume smaller than 100 μL was not used. The results were shown in Fig. 2. As can be seen, at volume greater than 120 μL, absorbance decreased due to a decrease in enrichment factor but extraction recovery remained constant. So, 120 μL was selected as the optimum volume of the organic solvent.

3.3. Type and volume of disperser

Selection of the disperser solvent is based on its miscibility with both the extraction solvent and the aqueous phase. In order to obtain the best extraction condition, several solvents such as acetone, methanol, and acetonitrile were evaluated as disperser solvents. The effect of these solvents on the extraction efficiency was investigated using 0.5 mL of each solvent containing 120 μL of chloroform as the extraction solvent. The results showed that the best extraction efficiencies were obtained when acetone was used as a disperser solvent.

The volume of settled phase and the solubility of chloroform in water solution are directly related to the volume of disperser solvent. The influence of the disperser solvent volume was studied by using different volumes of acetone (300, 400, 500, 600, 700, and 800 μL) containing 120 μL chloroform. The results (Fig. 3) showed that the extraction efficiencies increased by increasing the volume of acetone first, and then decreased. At low volume of acetone, a cloudy state was not well formed and at high volume of acetone, the volume of settled phase and extraction efficiency decreased because of increasing solubility of chloroform in the aqueous sample. At volume greater than 800 μL, the settled volume was not sufficient to full the microcell. The results were shown in Fig. 3. Thus, 500 μL of acetone was chosen as the optimum value.

3.4. Volume of de-emulsifier

The effect of volume of de-emulsifier was also investigated in the range of 600–1,600 μL. The results (Fig. 4) showed that higher extraction efficiency was

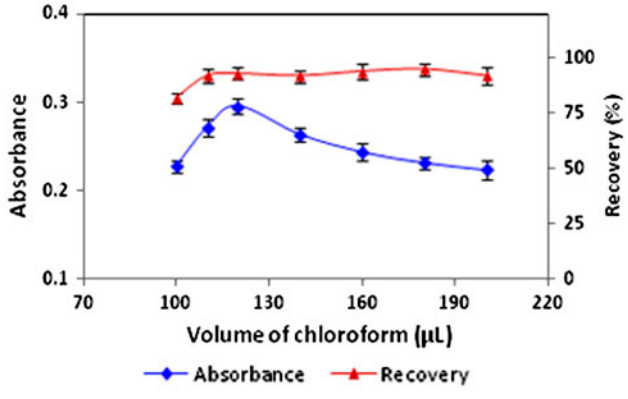

Fig. 2. Effect of volume of extraction solvent (chloroform). Conditions: 20 μg L^{-1} phenol, 70 μL 4-AAP (0.02 g mL^{-1}), 70 μL potassium hexacyanoferrate (0.08 g mL^{-1}), 10 mL sample, 500 μL acetone, 1,200 μL de-emulsifier, and pH 10.0.

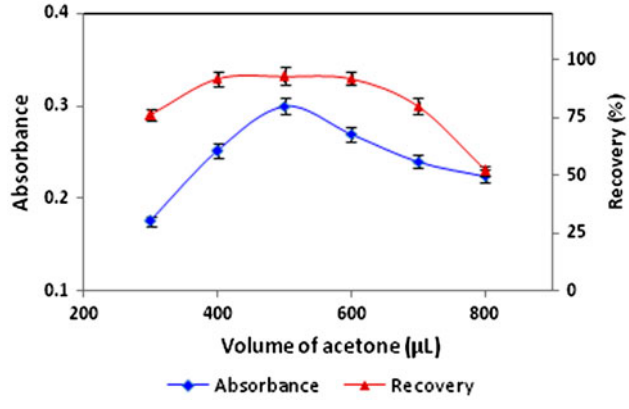

Fig. 3. Effect of volume of disperser solvent (acetone). Conditions: 20 μg L^{-1} phenol, 70 μL 4-AAP (0.02g mL^{-1}), 70 μL potassium hexacyanoferrate (0.08 g mL^{-1}), 10 mL sample, 120 μL chloroform, 1,200 μL de-emulsifier, and pH 10.0.

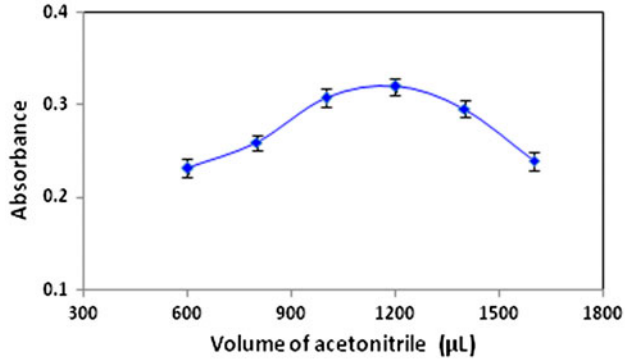

Fig. 4. Effect of volume of de-emulsifier. Conditions: 20 µg L^{-1} phenol, 70 µL 4-AAP (0.02g mL^{-1}), 70 µL potassium hexacyanoferrate (0.08 g mL^{-1}), 10 mL sample, 120 µL chloroform, 500 µL acetone, and pH 10.0.

obtained using 1,200 µL acetonitrile. At low volume of acetonitrile, de-emulsification was not complete and the cloudy solution did not clear totally. At higher volume of acetonitrile, some fraction of chloroform was dissolved in acetonitrile and led to the decrease of absorption. Therefore, 1,200 µL was selected as the optimum volume of the de-emulsifier solvent.

3.5. Effect of amount of 4-AAP and potassium hexacyanoferrate

The color of the blank is directly related to the amount of 4-AAP. Therefore, in order to achieve best extraction efficiencies, the effect of volume of 4-AAP added has been studied. The results of this study (Fig. 5) demonstrated that higher absorbance was obtained when the volume of 4-AAP (0.02 g mL^{-1}) in the sample was 70 µL. As shown, further increase in

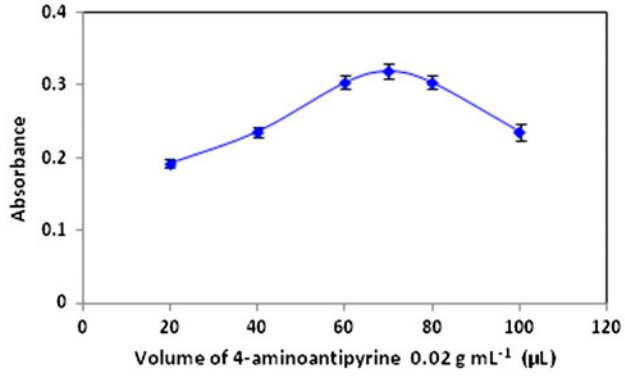

Fig. 5. Effect of volume of 4-AAP. Conditions: 20 µg L^{-1} phenol, 70 µL potassium hexacyanoferrate (0.08 g mL^{-1}), 10 mL sample, 120 µL chloroform, 500 µL acetone, 1,200 µL de-emulsifier, and pH 10.0.

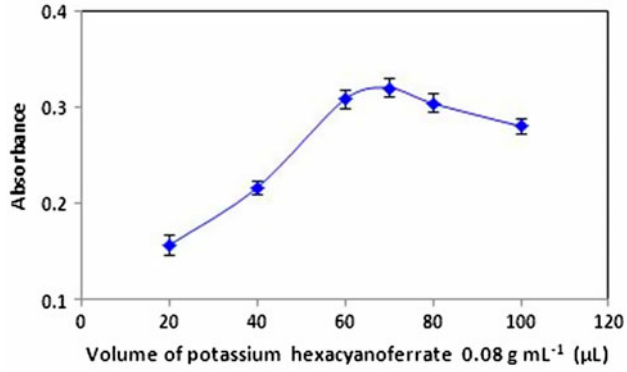

Fig. 6. Effect of volume of potassium hexacyanoferrate. 20 µg L^{-1} phenol, 70 µL 4-AAP (0.02 g mL^{-1}), 10 mL sample, 120 µL chloroform, 500 µL acetone, 1,200 µL de-emulsifier, and pH 10.0.

the 4-AAP content substantially lowers the absorbance at the measurement wavelength.

To investigate the effect of the amount of potassium hexacyanoferrate, it was tested in different volumes (20, 40, 60, 70, 80, and 100 µL). Too high concentrations of hexacyanoferrate can cause high blank values due to oxidation of the amine reagent, while low concentrations were insufficient for driving the reaction to completion [21]. The results were shown in Fig. 6. As can be seen, at volume greater than 70 µL, absorbance decreased. So, 70 µL was selected as the optimum volume of potassium hexacyanoferrate.

3.6. Effect of salt content

The influence of ionic strength was examined by studying the absorbance in the presence of various concentrations of $NaNO_3$ from 0.1 to 10% w/w. According to the obtained results (Fig. 7), as the ionic strength increased, the extraction efficiency decreased because some effects, such as changing the physical properties of the Nernst diffusion film and reducing the rate of diffusion of analytes into the organic phase, decrease the solubility of the extraction solvent in the aqueous phase and hence decrease the efficiency of emulsification. So, the rest of this study performed without salt addition.

3.7. Effect of sample volume

The main advantage of the HSD-DLLME method is its capability to handle large sample volume. In this study, sample volume up to 40 mL was submitted to the method without any decrease in the extraction recovery (with changing chloroform, acetone, and acetonitrile content proportionally). At volumes

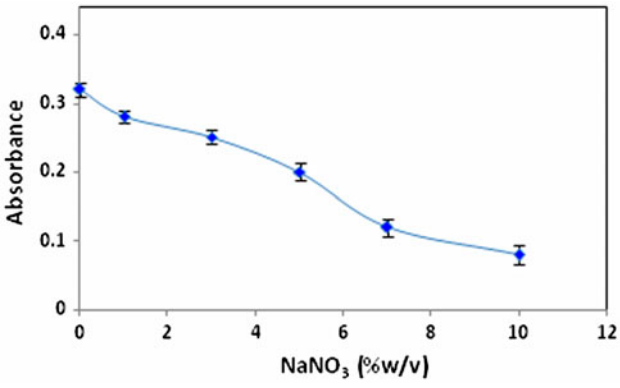

Fig. 7. Effect of salt concentration on the absorbance. Conditions: 20 μg L^{-1} phenol, 70 μL 4-AAP (0.02g mL^{-1}), 70 μL potassium hexacyanoferrate (0.08 g mL^{-1}), 10 mL sample, 120 mL chloroform, 500 mL acetone, 1,200 mL de-emulsifier, and pH 10.0.

Table 1
Analytical characteristics of the method

Parameter	Analytical feature
Linear range (μg L^{-1})	2–60
Correlation coefficient (r^2)	0.9991
LOD (μg L^{-1}) (3σ)	0.6
RSD (%) ($n = 5$, 50.0 μg L^{-1})	2.0
RSD (%) ($n = 5$, 10.0 μg L^{-1})	3.2
Enhancement factor	140
Sample volume (mL)	10

greater than 40 mL, extraction efficiency decreased due to an incomplete dispersion of extraction solvent.

3.8. Analytical figures of merit

Table 1 shows the analytical features of the method, including limit of detection (LOD), reproducibility, and enhancement factor. The LOD was calculated as $3s_b/m$ where s_b is the standard deviation of the blank signals and m is the slope of calibration curve after extraction. A good correlation coefficient ($r = 0.9991$) was obtained. The calibration curve was investigated up to 60 μg L^{-1} which was linear. The relative standard deviation (RSD) was calculated for five replicates measurements of 10 and 50 μg L^{-1} phenol. Enhancement factor was calculated as the ratio of the slope of preconcentrated samples to that obtained without preconcentration.

Comparison results of the presented method with the some other preconcentration methods used for the determination of trace levels of phenol were shown in Table 2. As can be seen, the proposed method has low LOD and good enrichment factor and is comparable with other methods; even with methods in which sensitive instruments such as GC–MS and HPLC were used.

3.9. Accuracy of the method

The validation of the presented procedure was performed by the analysis of samples according to the ASTM D1783 standard method (test method A: chloroform extraction). The results obtained by the proposed method were in good agreement with those obtained by the ASTM method (Table 3); no

Table 2
Comparison of analytical features of the methods with some of other methods

Method	LOD (μg L^{-1})	Enrichment factor	Matrix	Extraction time (min)	Reference
SPME-(GC-FID)	1.65	–	Wastewater	15	[22]
LLME-HPLC-DAD	1.3	30	Industrial wastewater	15	[23]
SPME-HPLC-UV	3.67	–	River water and wastewater	30	[24]
DLLME-HPLC-DAD	29	55.3	Tap, lake, fishpond waters, sewage and industrial wastewaters	5.5	[25]
DLLME -spectrophotometer	0.8	700	Tap, mineral, river waters and wastewater	10	[9]
LGLME-CE-DAD[a]	2	15	Industrial wastewater	10	[26]
USA-CIAME[b]	0.86	75	Tap, sea, river and mineral waters	5	[8]
LPME-GC–MS	0.68	–	Tap, mineral and river waters	15	[27]
HSD-DLLME[c] FOLADS[d]	0.6	140	Tap, well, river and mineral waters	3	This work

[a]Liquid–gas–liquid microextraction capillary electrophoresis diode array detection. [b]Ultrasound-assisted cold-induced aggregation microextraction. [c]High-density extraction solvent-based solvent de-emulsification dispersive liquid–liquid microextraction. [d]Fiber optic-linear array detection spectrophotometer.

Table 3
Determination of phenol index in water samples by the proposed method

Sample	Added ($\mu g\,L^{-1}$)	Found ± SD ($\mu g\,L^{-1}$)[a]	Relative recovery (%)	ASTM method
Tap water[b]	0	<LOD	–	<3.0
	20.0	19.2 ± 0.6	96.0	20.7 ± 0.8
Mineral water[c]	0	<LOD	–	<3.0
	20.0	20.5 ± 0.7	102.5	19.6 ± 0.7
River water[d]	0	<LOD	–	<3.0
	20.0	20.8 ± 0.7	104	21.3 ± 0.6
Well water	0	<LOD	–	<3.0
	20.0	19.0 ± 0.9	95.0	19.8 ± 0.7

[a]Mean of three experiments ± standard deviation. [b]From drinking water system of Tehran, Iran. [c]From mineral water system of Damavand Co. of Iran. [d]From Tajan river.

significant differences have been observed at the 95% confidence levels.

For further the verification of the accuracy of the method, spiking recovery method was also used. For the spiking study, samples were split into two portions and a known amount of a standard solution of phenol was added to one portion. The concentration of the analytes was determined in both the spiked, C_1, and unspiked portions, C_2. The relative recovery, $\%R$, was calculated as "Eq. (1)":

$$R\,\% = \frac{C_1 - C_2}{C_3} \times 100\% \quad (1)$$

where C_3 is the concentration of the analytes added to the spiked portion. As can be seen in Table 3, the recovery values are acceptable.

4. Conclusions

In this work, solvent-based de-emulsification DLLME with high-density solvent (HSD-DLLME) combined with FO-LADS has been described for the preconcentration and determination of phenol index in water samples at sub-$\mu g\,L^{-1}$ level. The high sensitivity of FO-LADS for phenol-4-AAP complex and high enrichment factor obtained made this method an excellent, inexpensive, and fast method for the determination of phenol index. Moreover, because no centrifugation step is needed, this method could be used to handle large-volume samples. Using FO-LADS, a microcell made it possible to couple itself with HSD-DLLME so that the applied method significantly enlarged the FO-LADS application and led to the LOD value equal to, or better than, those obtained with other microextraction methods. Compared to the ASTM (D 1783), HSD-DLLME coupled with FO-LADS displays better LOD and the shortest extraction time with lower consumption of organic solvent. The results showed good agreement with those obtained by the ASTM method. The results indicated that the developed method is an excellent alternative for the routine attempts to turn green the determination of phenols.

References

[1] A.L. Moskvin, A.V. Mozzhukhin, E.A. Mukhina, L.N. Moskvin, Flow-injection photometric determination of the phenol index of natural waters in the presence of humic acids, J. Anal. Chem. 60 (2005) 70–74.
[2] D. Martínez, E. Pocurull, R.M. Marcé, F. Borrull, M. Calull, Separation of eleven priority phenols by capillary zone electrophoresis with ultraviolet detection, J. Chromatogr. A 734 (1996) 367–373.
[3] M. Czaplicka, Sources and transformations of chlorophenols in the natural environment, Sci. Total Environ. 322 (2004) 21–39.
[4] W. Frenzel, S. Krekler, Spectrophotometric determination of total phenolics by solvent extraction and sorbent extraction optosensing using flow injection methodology, Anal. Chim. Acta 310 (1995) 437–446.
[5] W. Frenzel, J. Oleksy-Frenzel, J. Mörlen, Spectrophotmetric determination of phenolic compounds by flow-injection analysis, Anal. Chim. Acta 261 (1992) 253–259.
[6] J. Vuković, S. Matsuoka, K. Yoshimura, V. Grdinić, R.J. Grubešić, Development and prevalidation of a method for phenol determination by solid-phase spectrophotometry, Microchim. Acta 159 (2007) 277–285.
[7] E. Ródenas-Torralba, A. Morales-Rubio, M. De La Guardia, Determination of phenols in waters using micro-pumped multicommutation and spectrophotometric detection: An automated alternative to the standard procedure, Anal. Bioanal. Chem. 383 (2005) 138–144.
[8] M. Eisapour, F. Shemirani, B. Majidi, M. Baghdadi, Ultrasound assisted cold-induced aggregation: An improved method for trace determination of volatile phenol, Microchim. Acta 177 (2012) 349–355.
[9] I. Lavilla, S. Gil, M. Costas, C. Bendicho, Dispersive liquid–liquid microextraction combined with microvolume spectrophotometry to turn green the 5530 APHA standard method for determining phenols in water and wastewater, Talanta 98 (2012) 197–202.
[10] B. Horstkotte, F. Maya, C. Duarte, V. Cerdà, Determination of ppb-level phenol index using in-syringe dispersive liquid–liquid microextraction and liquid waveguide capillary cell spectrophotometry, Microchim. Acta 179 (2012) 91–98.

[11] T.-T. Liang, Z.-H. Lv, T.-F. Jiang, Y.-H. Wang, High-density extraction solvent-based solvent de-emulsification dispersive liquid–liquid microextraction combined with MEKC for detection of chlorophenols in water samples, Electrophoresis 34 (2013) 345–352.
[12] H. Chen, R. Chen, S. Li, Low-density extraction solvent-based solvent terminated dispersive liquid–liquid microextraction combined with gas chromatography-tandem mass spectrometry for the determination of carbamate pesticides in water samples, J. Chromatogr. A 1217 (2010) 1244–1248.
[13] C.K. Zacharis, P.D. Tzanavaras, K. Roubos, K. Dhima, Solvent-based de-emulsification dispersive liquid–liquid microextraction combined with gas chromatography–mass spectrometry for determination of trace organochlorine pesticides in environmental water samples, J. Chromatogr. A 1217 (2010) 5896–5900.
[14] B. Majidi, F. Shemirani, Solvent-based de-emulsification dispersive liquid–liquid microextraction of palladium in environmental samples and determination by electrothermal atomic absorption spectrometry, Talanta 93 (2012) 245–251.
[15] J. Johansson, M. Cauchi, M. Sundgren, Multiple fiber-optic dual-beam UV/Vis system with application to dissolution testing, J. Pharm. Biomed. Anal. 29 (2002) 469–476.
[16] T.K. Gangopadhyay, Prospects for fibre bragg gratings and fabry-perot interferometers in fibre-optic vibration sensing, Sens. Actuators, A 113 (2004) 20–38.
[17] B. Lee, Review of the present status of optical fiber sensors, Opt. Fiber Technol. 9 (2003) 57–79.
[18] N. Shokoufi, F. Shemirani, F. Memarzadeh, Fiber optic-linear array detection spectrophotometry in combination with cloud point extraction for simultaneous preconcentration and determination of cobalt and nickel, Anal. Chim. Acta 601 (2007) 204–211.
[19] M. Ettinger, C. Ruchhoft, R. Lishka, Sensitive 4-aminoantipyrine method for phenolic compounds, Anal. Chem. 23 (1951) 1783–1788.
[20] J.M. Martin, Jr., C.B. Kincannon, C.R. Orr, J.L. Bishop, Ultraviolet determination of total phenols, J. Water Pollut. Control Fed. 39 (1967) 21–32.
[21] Y.C. Fiamegos, C.D. Stalikas, G.A. Pilidis, M.I. Karayannis, Synthesis and analytical applications of 4-aminopyrazolone derivatives as chromogenic agents for the spectrophotometric determination of phenols, Anal. Chim. Acta 403 (2000) 315–323.
[22] F. Zhou, X. Li, Z. Zeng, Determination of phenolic compounds in wastewater samples using a novel fiber by solid-phase microextraction coupled to gas chromatography, Anal. Chim. Acta 538 (2005) 63–70.
[23] M. Saraji, M. Marzban, Determination of 11 priority pollutant phenols in wastewater using dispersive liquid—liquid microextraction followed by high-performance liquid chromatography—diode-array detection, Anal. Bioanal. Chem. 396 (2010) 2685–2693.
[24] X. Liu, Y. Ji, Y. Zhang, H. Zhang, M. Liu, Oxidized multi-walled carbon nanotubes as a novel solid-phase microextraction fiber for determination of phenols in aqueous samples, J. Chromatogr. A 1165 (2007) 10–17.
[25] X.-Z. Hu, J.-H. Wu, Y.-Q. Feng, Molecular complex-based dispersive liquid–liquid microextraction: Analysis of polar compounds in aqueous solution, J. Chromatogr. A 1217 (2010) 7010–7016.
[26] J. Zhang, T. Su, H.K. Lee, Development and application of microporous hollow fiber protected liquid-phase microextraction via gaseous diffusion to the determination of phenols in water, J. Chromatogr. A 1121 (2006) 10–15.
[27] H. Faraji, M.S. Tehrani, S.W. Husain, Pre-concentration of phenolic compounds in water samples by novel liquid–liquid microextraction and determination by gas chromatography–mass spectrometry, J. Chromatogr. A 1216 (2009) 8569–8574.