Simultaneous Determination of Three Phenolic Compounds in Water Samples by Pre-column Derivatization Coupled with Reversed-Phase High Performance Liquid Chromatography

Üç Fenolik Bileşiğin Kolon Öncesi Türevlendirme ile Ters-Faz Sıvı Kromatografisi Yöntemi Kullanılarak Su Örneklerinde Eşzamanlı Tayini

Research Article

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ABSTRACT

In this study, a sensitive and accurate method for simultaneous separation and determination of three phenolic compounds (phenol, m-cresol and resorcinol) in water by revesed-phase high performance liquid chromatography using uv-visible detection has been described. Pre-column derivatization with 4-aminoantipyrine is used for the seperation and determination phenol, m-cresol and resorcinol in water. The derivatives formed within 5 min were extracted with chloroform and then analyzed by liquid chromatography with UV-visible detection at 440 nm. Chromatographic separation was performed using a reversed-phase column and acetonitrile-water (45:55%, v/v) as the mobile phase. The three derivatives were elueted in 13 min. The detection limits of phenol, m-cresol and resorcinol in a standard water sample were between 0.07 and 0.09 $\mu g.L^{-1}$ for 100 mL respectively. The recoveries of the derivatives from pure water were betweeen 97.1-102.3% within relative standard deviations of 2.3-4.7%. The method was applied to the analysis of phenols in different water samples.

Key Words

Phenols, derivatization, reversed-phase liquid chromatography, 4-aminoantipyrine.

ÖZ

Bu çalışmada; suda üç fenolik bileşiğin (fenol, m-kresol ve resorsinol), UV-görünür detektör kullanılarak ters-faz yüksek performanslı sıvı kromatografisi ile ayrılması ve eş zamanlı tayini için hassas ve doğru bir yöntem geliştirildi. Fenol, m-krezol ve resorsinolün sudaki tayini ve ayrılması için kolon öncesi 4-aminoantipirin ile türevlendirilmiştir. 5 dakika içinde oluşan türevler kloroform ile ODS kolondan geri alınmıştır ve daha sonra 440 nm'de UV-görünür detektörde sıvı kromatografisi ile analiz edilmiştir. Kromatografik ayırım, ters-faz kolonda ve mobil faz olarak asetonitril-su (%45:55, v/v) karışımı kullanılarak gerçekleştirilmiştir. Üç fenol türevi 13 dakikada içerisinde başarıyla ayrılmıştır. Standart bir su numunesinde fenol, m-kresol ve resorsinolün tayin sınırı sırasıyla 100 mL için 0.07 ve 0.09 $\mu g.L^{-1}$ arasındadır. Türevlerin saf sudan geri kazanımı, %2.3-4.7'lik bağıl standart sapma ile %97.1-102.3 düzeylerinde bulundu. Yöntem, farklı su numunelerindeki fenollerin analizi için başarıyla uygulandı.

Anahtar Kelimeler

Fenoller; türevlendirme, ters faz sıvı kromatografisi; 4-aminoantipirin.

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INTRODUCTION

Phenolic compounds are toxic substances that occur naturally in the environment, in plants and food [1]. Therefore, these compounds are typically found in domestic and industrial products, natural waters and potable water supplies. Owing to their toxicity, persistence and unpleasant organoleptic properties [2,3], both the US Environmental Protection Agency (EPA) and the European Union (EU) have classified several phenols as priority pollutant [4].

They have also been employed as raw materials for drugs, pesticides, synthetics fibers, resins, and dyes. Thus, they are discharged from a variety of industrial plants to environmental water. Their input into the ecosystems results directly from human activity or indirectly from the transformation of natural or synthetic chemicals and they are found in waters from various sources [5-8]. Several methods have been reported for the determination of phenolic compounds in different samples including spectrophotometric methods [9], high-performance liquid chromatography (HPLC) [10-17] gas chromatography (GC) [18-23] and capillary electrophoresis [24,25]. Owing to the complex nature of samples (biological, water, etc) and low concentration of phenolic compounds in such samples, their isolation and preconcentration are commonly necessary prior to their quantitative determination. Liquid-liquid extraction [26] and solid-phase extraction [27] are the most usual techniques for this purpose.

In this study, a sensitive and accurate method for simultaneous separation and determination of three phenolic compounds (phenol, m-cresol and resorcinol) in water by reversed-phase high performance liquid chromatography using UV-visible detection has been established. The main objective of this study is to develop and validate a selective and sensitive method for the simultaneous determination of phenolic compounds in water. A reversed-phase liquid chromatographic and UV-visible detection was accomplished based on pre-column the reaction between phenols and 4-aminoantipyrine (4-AA). 4-AA is a common reagent and that has been previously studied [28]. Although in the present study, the derivatization reaction between 4-AA and phenolic compounds were modified in the presence of potassium peroxydisulfate as oxidizer. Then obtained derivatives (quinoneimines) exhibited intense absorption at 440 nm were separated in RP-HPLC system and determined using visible spectrophotometric detector. Consequently, a simple pre-column derivatization plus reversed-phase liquid chromatographic procedure for the determination of phenolic compounds in water at ppb levels was obtained.

MATERIALS and METHODS

Reagents and Chemicals

The phenolic compounds (phenol, m-cresol and resorcinol) and the derivatization agent (4-aminoantipyrine) (4-AA) were obtained from Sigma-Aldrich. The tested extraction solvents were purchased from Merck. All other reagents were of analytical reagent grade and were used without further purification. Individual standard phenol stock solutions (500 $mg.L^{-1}$) were prepared by dissolving 50 mg of phenol in 100 mL of deionized water. Working standard solutions of various concentrations were prepared daily by diluting the stock solution with deionized water. Ultrapure Milli-Q water (Millipore) was used for the preparation of solutions. The stock solutions were stable for up to 2 week when stored in the dark at room temperature. The 4-aminoantipyrine stock solution (88 $mmol.L^{-1}$) was prepared by dissolving 1.8 g of 4-aminoantipyrine in 100 mL of deionized water.

The ammonia buffer solution was prepared by dissolving 6.75 g of ammonium chloride in 57 mL of ammonia and diluted to 100 mL with deionized water. An ammonium peroxodisulfate stock solution (88 $mmol.L^{-1}$) of pH 10 was prepared by dissolving 2.0 g of ammonium peroxodisulfate in 80 mL of water, while adjusting to pH 10 by the addition of a potassium hydroxide solution (2 $mol.L^{-1}$) and diluting to 100 ml of water.

The water samples (Borcka dam lake and Murgul stream) were collected (in 1-1 dark colored glass bottles) from the Artvin in Turkey. The area where the samples are taken was the place where

the garbage is laid and near to the mine site. The bottles were previously washed with 0.1 mol.L^{-1} HCl and repeatedly rinsed with deionized water. During sampling, the bottles were rinsed twice with the sample water, then filled and tightly capped. Samples were filtered through Millipore membrane filters (0.45-μm pore size, Millipore, Bedford, USA) and analyzed immediately.

Apparatus

Chromatographic analysis was performed using a Shimadzu liquid chromatograph LC-20AD (Kyoto, Japan), equipped with binary solvent delivery units (LC-20AD), UV-vis detector (SPD- M20A), LC solution Version 1.25 and an auto sampler (SIL-20 MT). The LC solution workstation software was used to control the gradient setting and data acquisition.

Absorbance measurements for phenol derivatives were performed using a UV-visible spectrophotometer (Shimatzu UV-1800, Tokyo, Japan). For pH measerements, the pH meter (WTW ino lab pH level 1) with a pH-electrode Sentix-41 was used.

A GL Sciences Inertsil ODS-2 C18 reversed-phase column (250 mm x 4.6 mm, 5 μm particle size) was used for the separation of the target analysts. Mobile phase composition that providing the best separation was a mixture acetonitrile and water (45:55%, v/v), which was filtered and degassed prior to use. The flow-rate was 1.0 mL/min, the sample injection volume was 20 μL, and the detection wavelength was 440 nm.

Derivatization and Extraction Procedure

The 4-aminoantipyrine (4-AA) derivatives of the phenols were prepared according to the procedure described by Morita and Nakamura [28], after a major modification. To a 100 mL 1x10^{-4} mol.L^{-1} each phenolic compound solution, 5x10^{-4} mol.L^{-1} of 4-AA and 5x10^{-4} mol.L^{-1} of potassium peroxydisulfate ($K_2S_2O_8$) were added.

The mixture was alkalinized to pH 9 using 0.1 M ammonia/ammonium buffer solution which was added dropwise under vigorous shaking for 5 min. The reaction is as shown in Figure 1. The thus-prepared solution was left standing for 5 min at room temperature, and then both solid-liquid and liquid-liquid extraction procedures were applied to collect the quinoneimine derivatives obtained as a result of the reaction. The derivatization reaction is shown in Figure 1.

For the solid-phase extraction, the solution was passed through the ODS-functionalized silica cartridge (60x8 mm constructed in the laboratory), which was washed with 5 mL of methanol and 10 mL of deionized water subsequently before use. The adsorbed quinoneimine derivatives were eluted with 2 mL of different extraction solvents (chloroform, hexane, dichloromethane and diethyl ether). For the liquid-liquid extraction, extraction efficiencies were compared by adding different extraction solvents onto the phenol derivatives solution. The highest extraction yield was obtained using chloroform. The samples were extracted with 1x10 mL and 1x5 mL of chloroform. The water layer was saved and potassium chloride

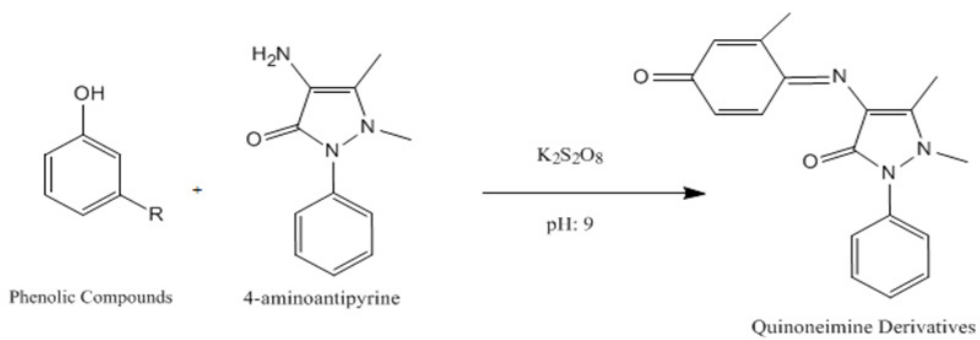

Figure 1. Derivatization reaction between phenol compounds and 4-aminoantipyrine.

(1.2 g) added to increase the ionic strength and promote the transfer of quinoneimine derivatives into the organic extract. For all extractions, separating funnels were shaken for 1 min and the phases were allowed to separate for 3 min. The extracts were evaporated to dryness at 40°C in a water bath. The precipitates were redissolved in 1 mL of mobil phase (acetonitrile and water, 45:55, v/v) and 20 μL of each sample was injected onto the RP-HPLC system. In applications of the method, a sample volume of a 100 mL was used for the extraction, since a reasonable linearity was obtained for all phenols studied. The phenols were identified from their retention times and quantitatively determined their peak areas.

RESULTS and DISCUSSION

Optimization of the derivatization reaction

As the derivatization reaction of phenolic compounds with 4-aminoantipyrine proceeded in a basic medium, the effect of the pH in the presence of ammonia/ammonium buffer solution was examined using a standard solution of the phenols at a concentration of $1x10^{-4}$ mol.L^{-1}. The peak heights of all compounds reached maxima at pH 8-10. The highest peak height was obtained at pH 9. For this reason, the pH value was 9 throughout the study. The effect of peak height with pH change is shown in Figure 2.

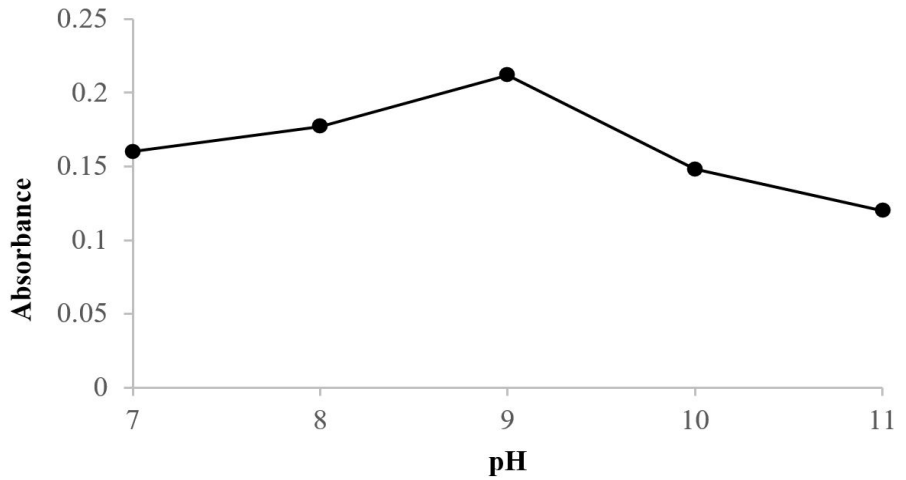

Figure 2. Effect of pH on the derivatization reaction between phenol compounds and 4-aminoantipyrine (phenol: $1x10^{-4}$ M; peroxydisulfate: $5x10^{-4}$ M; 4-aminoantipyrine: $5x10^{-4}$ M).

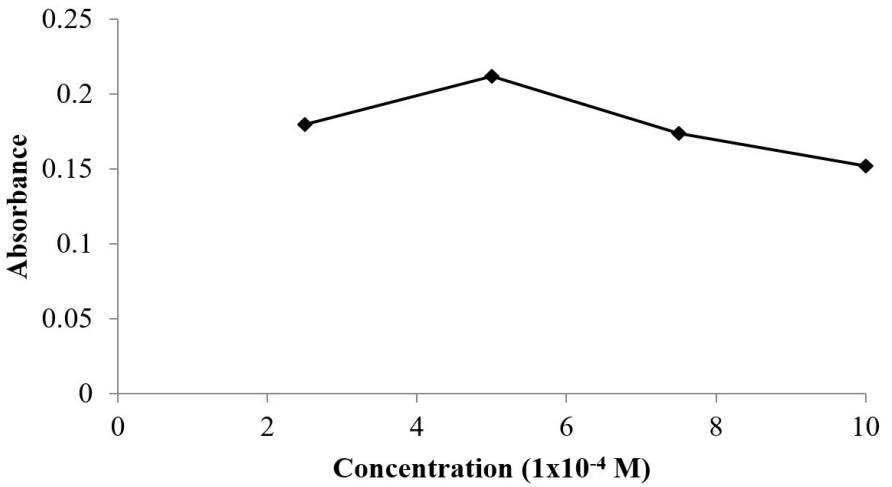

Figure 3. Effect of 4-aminoantipyrine concentration on the derivatization reaction (phenol: $1x10^{-4}$ M; peroxydisulfate: $5x10^{-4}$ M).

The effect of 4-aminoantipyrine concentrations on the reaction was tested. The highest absorption value was obtained when 4-aminoantipyrine was used at a concentration of $5x10^{-4}$ mol.L^{-1}. The effect of absorption with 4-aminoantipyrine concentration change is shown in Figure 3.

The amount of peroxydisulfate ($K_2S_2O_8$) used as oxidant in the reaction was tested. It was determined that the optimum amount of peroxydisulfate for the derivatization reaction was $5x10^{-4}$ mol.L^{-1}. The effect of absorption with peroxydisulfate concentration change is shown in Figure 4.

Temperatures of 30, 40 and 50°C were tested. All peak heights reached a maximum after a reaction time 10 min at all temperatures. For this reason, the work was done at room temperature. Figure 5 shows the effect of temperature on peak height. As a result, all the parameters in the reaction are optimized.

Calibration, Detection Limits and Repeatability

Calibration graphs were performed using the external standard technique following.Linear regression analysis by plotting concentration (μg.L^{-1}) against peak area. Table 1 shows the

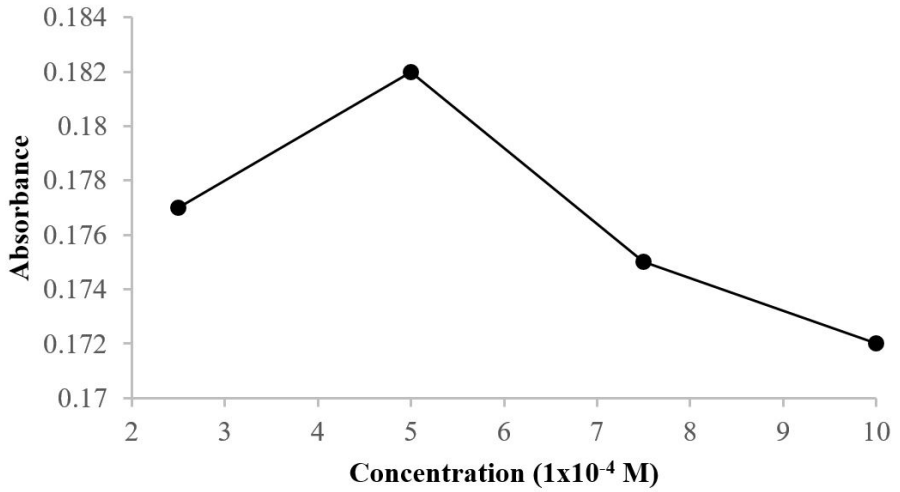

Figure 4. Effect of peroxydisulfate concentration on derivatization reaction (phenol: $1x10^{-4}$ M; 4-aminoantipyrine: $5x10^{-4}$ M).

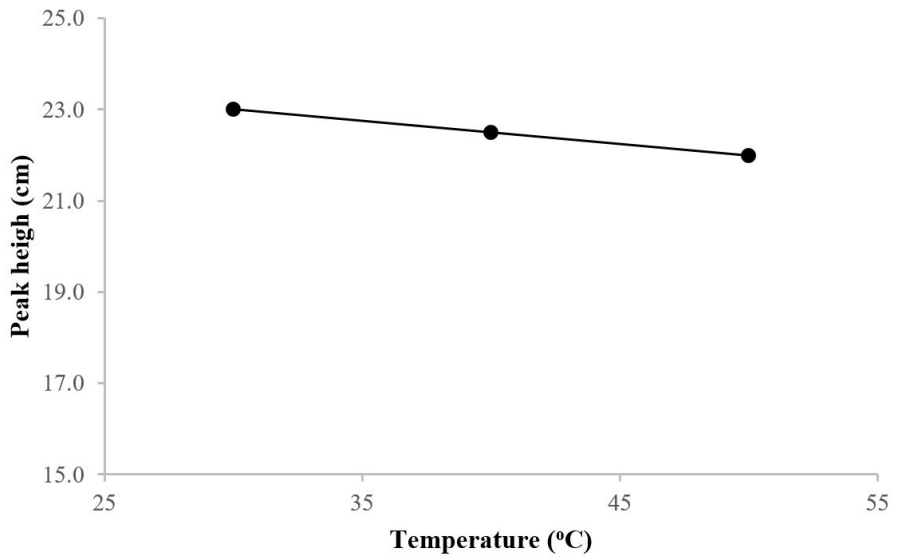

Figure 5. Effect of temperature on peak height.

equations obtained fort the calibration graphs and the regression coefficients. The repeatability of the method was calculated using the average relative standard deviation (RSD) for 10 replicate injections of the same sample at 10 μg.L^{-1}. The reproducibility was calculated using the RSD. For 10 injections of the same sample (10 μg.L^{-1}) on different days. The LOD and LOQ were calculated using the standard deviation (s) of response and the slope (m) of the calibration curve as LOD= 3.3 s/m; LOQ= 10 s/m [29-31]. All values obtained are given in Table 1. precision and accuracy for intra-day and inter-day assays of these derivatives are shown in Table 2. In the intra-day assay, the range of standard deviation for retention time was within 0.23 to 0.39% and standard deviation for peak area was within 2.17 to 3.73. In the inter-day assay, the range of standard deviation for retention time was within 0.26 to 0.41% and standard deviation for peak area was within 2.66 to 3.68%. Figure 6 shows the standard chromatogram of derivatives of phenol compounds.

Recovery

Both liquid-solid and liquid-liquid extraction were carried out for the extraction of quinoneimine derivatives. It was determined that the best extraction method for these derivatives was liquid-liquid extraction. For this reason, liquid-liquid extraction method was used for isolating the derivatives. Different solvents (chloroform, hexane, dichloromethane and diethyl ether) were used for extraction. Chloroform was chosen as the best among them. Extraction of quinoneimine derivatives with chloroform resulted a substantial improvement enabling a high recovery for the phenolic compounds from Murgul stream water and Borcka Dam Lake.

The efficiency of the extraction procedure and the recovery of phenols from 100 mL of Murgul stream water and Borcka Dam Lake are shown in Table 3 and Table 4. At the same time, Tables also show repeatability and reproducibility. For the Murgul stream water, the quantities of phenols were spiked to different concentrations and over 97.1-102.3% of the phenols was recovered from water with relative standard deviations 2.3-4.7% and also Borcka Dam Lake, the quantities of phenols were spiked to different concentration and over 97.4-103.1% of the phenols was recovered from water with relative standard deviations 2.3-4.1%.

Applications

The described method was used to determine phenol, m-cresol and resorcinol in tap water and water samples. As shown in Table 5, the level of phenol, m-cresol and resorcinol in tap water was below the lower limit of quantification. In Table 5,

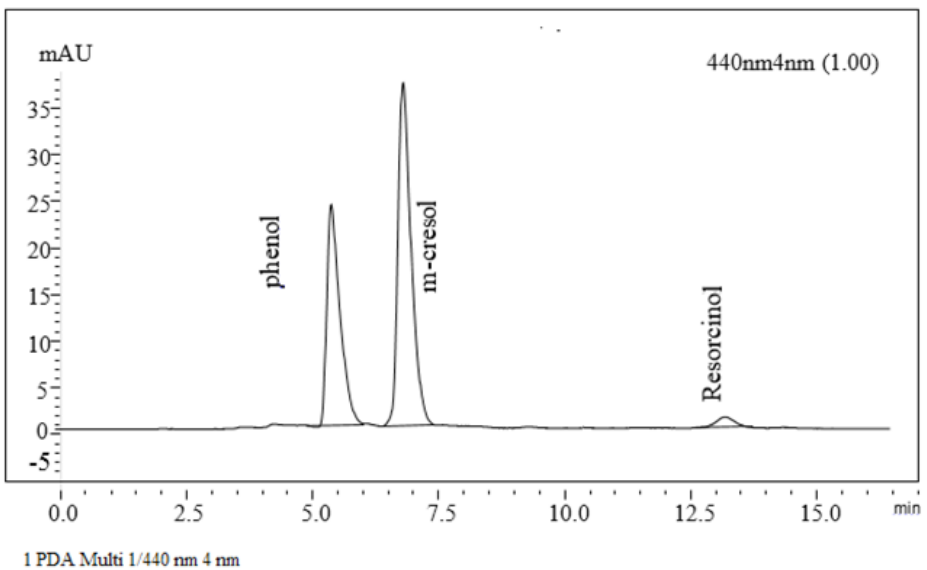

Figure 6. Reversed-phase HPLC-UV-vis. chromatograms of quinoneimine derivatives of phenols. Phenol, 6.0 ng; m-cresol, 7.4 ng; resorcinol, 2.0 ng. Column: GL Science Inertsil C_{18} RP (5μm, 250mm x 4.6 mm ID). Mobil phase: aceto-nitrile-water (45:55%, v/v); Flow-rate: 1.0 mL min^{-1}.

Table 1. Retention time (t_R) and linear regression parameters, LOD and LOQ, of the determined phenolic compounds.

Analyte	t_R (min)	Calibration curve	r^2	Linearity range ($\mu g.L^{-1}$)	LOD ($\mu g.L^{-1}$)	LOQ ($\mu g.L^{-1}$)
phenol	6.1	y= 62.821x+7067	0.9968	5.0-250	0.07	0.31
m-cresol	7.2	y= 58.374x+5535	0.9995	10-300	0.08	0.35
resorcinol	12.6	y= 73.811x-3052	0.9988	2.0-100	0.09	0.38

Table 2. Precision of three phenolics for retention time (t_R) and peak area (pa) (n= 5).

Analyte	Intra-day variations		Inter-day variations	
	RSD for t_R (%)	RSD for pa (%)	RSD for t_R (%)	RSD for pa (%)
phenol	0.23	2.17	0.26	3.56
m-cresol	0.33	2.67	0.38	2.66
resorcinol	0.39	3.73	0.41	3.68

Table 3. Summary of results from analysis of phenols in spiked 100 mL of Murgul stream water (n= 5).

Analyte	Amount added (ng)	Recovery (%)	RSD (%)	Repeatability RSD (%)	Reproducibility RSD (%)
phenol	10	98.7	2.4	1.7	2.3
	100	97.1	3.7		
	200	102.3	2.3		
m-cresol	20	99.3	3.5	1.9	2.5
	150	98.1	2.9		
	250	101.2	3.2		
resorcinol	5	98.3	3.1	2.5	2.9
	50	97.3	4.7		
	75	102.1	3.8		

the results for the water samples are given. The concentration of phenolic compounds in different water samples were successfully determined. In Figure 7 and 8 typical chromatograms of phenols in 100 mL of Murgul stream and Borcka Dam Lake water samples are shown. Obviously, low $ng.mL^{-1}$ levels of phenols can be successfully determined in environmental samples. As Table 5 shows, phenolic compounds could not be assigned to tap water. The maximum amount of m-cresol was found in the Borcka Dam Lake water. On the other hand, the amount of resorcinol is the most in the Murgul stream water.

The comparison of the new method and reported methods (published over the period 2001-2016) is presented in Table 6. The proposed method without complex pre-treatment offered the linear range is 2-300 $\mu g.L^{-1}$ and LOD is 0.07 $\mu g.L^{-1}$ for phenolic compounds, which were significantly lower than the reported methods in Table 6.

Table 4. Summary of results from analysis of phenols in spiked 100 mL of Borcka dam lake water (n= 5).

Analyte	Amount added (ng)	Recovery (%)	RSD (%)	Repeatability RSD (%)	Reproducibility RSD (%)
phenol	10	97.7	2.3	1.9	2.1
	100	98.6	2.7		
	200	102.9	2.6		
m-cresol	20	97.8	3.1	1.4	2.3
	150	99.1	2.8		
	250	102.5	3.4		
resorcinol	5	97.4	2.9	2.1	2.8
	50	99.2	4.1		
	75	103.1	3.6		

Table 5. Analytical results of water samples from different locations*.

Analyte	Tap water	Borcka dam water**		Murgul stream water**	
		$\bar{X}$	ts	$\bar{X}$	ts
phenol	ND	7.6	2.3	9.8	2.9
m-cresol	ND	11.2	3.8	12.9	4.1
resorcinol	ND	8.5	2.9	17.3	3.2

*Samples were collected at Artvin, Turkey.

**Values represent the average (= μg.L^{-1}), standard deviation (ts= %), for n = 5 with a confidence of 95%.

ND: Not detected

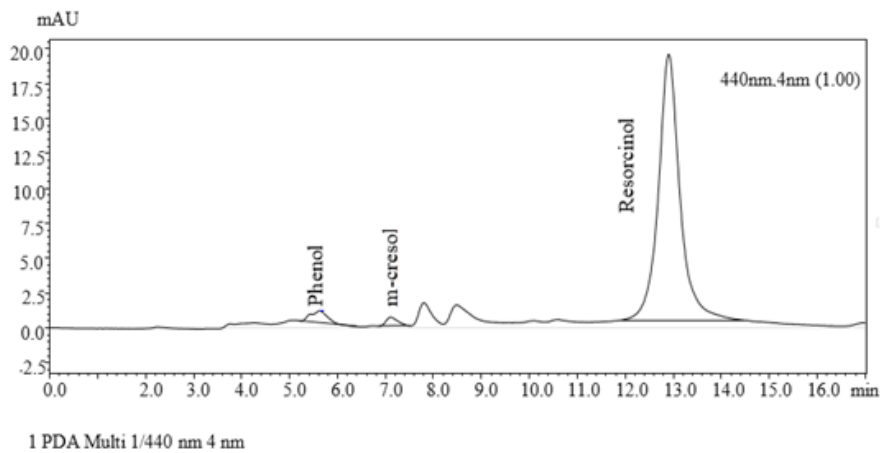

Figure 7. Reversed-phase HPLC-UV-vis. chromatograms of quinoneimine derivatives of phenols obtained from 100 mL of Murgul stream water. For conditions and peak assignment, see Figure 2.

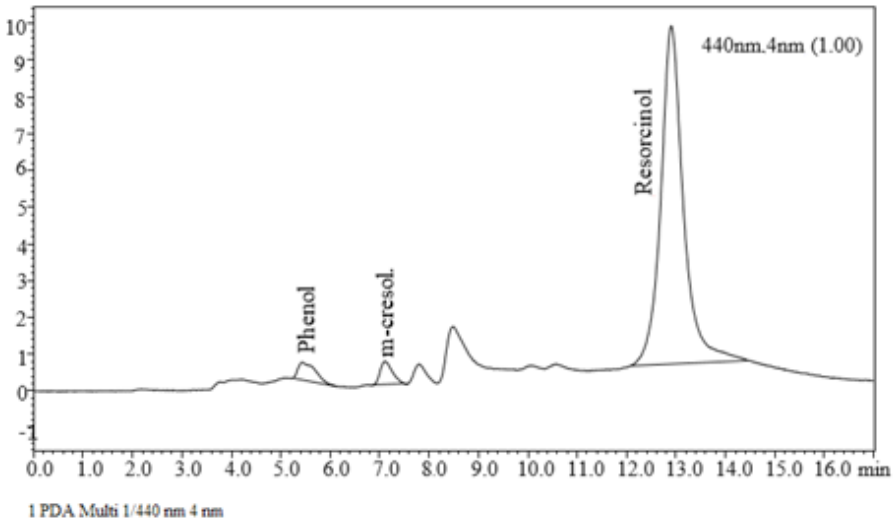

Figure 8. Reversed-phase HPLC-UV-vis. chromatograms of quinoneimine derivatives of phenols obtained from 100 mL of Borcka dam lake water. For conditions and peak assignment, see Figure 2.

Table 6. Comparison of literature HPLC methods (published over the period 2001-2016) for proposed method and some reported procedures for phenolic compound determination.

Method	Sample	Linear renge	Limit of detection	Reference
HPLC-UV	Aqueous sample	0.5-2.5 $\mu g.L^{-1}$	0.05 $\mu g.L^{-1}$	Zhao and Lee, 2001. [11]
HPLC-UV	Tap water, River water	0.2-5 $\mu g.L^{-1}$	0.06 $\mu g.L^{-1}$	H. Bagheri et al., 2004. [12]
HPLC-FD	Human urine	0.5-50 $mg.L^{-1}$	0.05 $mg.L^{-1}$	G. Marrubini et al., 2005. [13]
HPLC-UV	Bambo pulp	0.01-10 $mg.L^{-1}$	1.5 $\mu g.L^{-1}$	N. Sharma et al., 2011. [14]
HPLC-UV	River water, Tap water	100-500 $ng.L^{-1}$	82.1 $ng.L^{-1}$	M. C. Alcudia et al., 2011. [15]
HPLC-UV	Rice wines	0.5-50 $\mu g.L^{-1}$	0.02 $\mu g.L^{-1}$	Y. Huang et al., 2015. [16]
HPLC-UV	Soil extract, Sea water, River water, Tap water, Ground water	1.2-11.6 $\mu g.L^{-1}$	0.5 $\mu g.L^{-1}$	R. G. Dolatto et al., 2016. [17]
HPLC-UV	Tap water, Stream water, Dam lake water	2-300 $\mu g.L^{-1}$	0.07 $\mu g.L^{-1}$	This work

CONCLUSION

We have developed a pre-column RP-HPLC UV-visible method for simultaneous determination of phenol, m-cresol and resorcinol in water by using 4-aminoantipyrine as a labeling reagent, without complicated sample cleanup. The results showed that this new method was simple, rapid, practicable and feasible with high precision, sensitivity and repeatability, and could also provide a good resolution of the phenolic compounds in water samples. Thus, this procedure can be used to determine the basic phenolic compounds in various type of environmental samples.

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