

# Micelle-Mediated Extraction and Cloud Point Pre-concentration for the Spectrophotometric Determination of Phenol in Water Samples

Ali Reza Zarei\*, Forouzan Gholamian and Soheila Chalavi

*Department of Chemistry, Faculty of Materials, Malek Ashtar University of Technology, Tehran, Iran.*

Received 6 September 2011, revised 15 October 2011, accepted 23 October 2011.

## ABSTRACT

In this paper, a cloud point extraction method for the determination of trace amounts of phenol by spectrophotometry is described. The method is based on the colour reaction of phenol with diazotized p-nitroaniline alkaline media and the cloud point extraction of azo dye product using of nonionic surfactant Triton X-114. The effects of reaction and extraction parameters were studied and optimum parameters were established. The calibration graph was linear in the range of 2.0–400 ng mL<sup>-1</sup> of phenol. Detection limit based on three times the standard deviation of the blank (3S<sub>b</sub>) was 1.0 ng mL<sup>-1</sup> and the relative standard deviation (RSD) for 50 ng mL<sup>-1</sup> of phenol was 1.73 % (*n* = 10). The proposed method was applied for the determination of phenol in water samples.

## KEYWORDS

Pre-concentration, cloud point extraction, phenol, spectrophotometry, water samples.

## 1. Introduction

Phenol and its derivatives are important industrial chemicals that have been extensively used as disinfectants, pesticides, herbicides, fungicides and synthetic fibres.<sup>1,2</sup> These compounds may occur in domestic and industrial wastewaters, natural waters and potable water supplies as a result of their wide use in numerous commercial products. The environmental concern posed by phenol pollution results from the high toxicity of phenol to mammals, fish and other aquatic organisms.<sup>3</sup> The highest volatile phenol limits are normally set at a few ng mL<sup>-1</sup>-sub-g mL<sup>-1</sup> range for different grades of environmental quality standards. These compounds appear in a list of dangerous substances of the Environmental Protection Agency (EPA) and European Community (EC) due to their toxicity, bioaccumulation, persistence in the environment and carcinogenic properties.<sup>4,5</sup> The importance of monitoring phenols in the aquatic environment is due to their toxicity to aquatic organisms even below the mg L<sup>-1</sup> level and the production of odorous and objectionable taste to drinking water supplies and edible aquatic species at the µg L<sup>-1</sup> level. Hence, the determination of trace phenol is very important for evaluating the total toxicity of water sample.

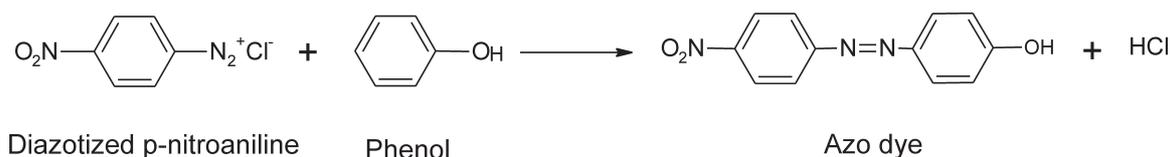
Several analytical procedures with different systems of detection such as spectrophotometry,<sup>6–12</sup> flow-injection analysis,<sup>13–18</sup> electrochemical biosensors,<sup>19–23</sup> gas chromatography,<sup>24–26</sup> high performance liquid chromatography<sup>27–32</sup> and electrophoresis,<sup>33–36</sup> have been developed to determine phenol. Despite the very sensitive analytical methods available, for direct determination of low levels of phenol in environmental science, a separation and pre-concentration step is required in order to improve their detectability and to eliminate interferences. For this purpose, various separation and pre-concentration methods, such as simultaneous steam distillation extraction (SDE),<sup>37</sup> supercritical fluid extraction (SFE),<sup>38</sup> solid phase extraction (SPE),<sup>39,40</sup> solid

phase microextraction (SPME),<sup>41,42</sup> immersed solvent microextraction (Immersed-SME),<sup>43</sup> single-drop microextraction (SDME),<sup>44</sup> stir bar sorption extraction (SBSE),<sup>45</sup> aqueous two-phase system (ATPS),<sup>46</sup> and dispersive liquid-liquid microextraction (DLLME)<sup>47</sup> have been developed.

Separation and pre-concentration, based on cloud point extraction (CPE), is becoming important and practical applications in analytical chemistry, using surfactants, are being developed. CPE is a green method for the following reasons; (i) it uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generation of few laboratory residues, and (ii) surfactants are not toxic, not volatile, and not easily flammable.<sup>48</sup> Micelle-mediated extraction procedures have found wide applications in different areas of analytical chemistry, and their advantages over the conventional liquid-liquid extraction technique have been well documented in the literature.<sup>49–51</sup> The formation of micelles depends on the aggregation of a certain number of surfactant monomers.<sup>52</sup> Aqueous solutions containing a non-ionic or zwitterionic surfactant above its critical micellar concentration (CMC) become turbid, because the surfactant molecules associate spontaneously, forming aggregates of colloidal dimensions.<sup>53</sup> Any species that originally present associates and binds to these micellar aggregates can be extracted from the initial solution and preconcentrated in a small volume of the surfactant-rich phase. The small volume of the surfactant-rich phase obtained by using the cloud point methodology (generally between 100 and 400 µL) permits the design of extraction schemes that are simple, cheap, efficient and safe in comparison with liquid-liquid extraction methods.

Spectrophotometric methods offer many appealing characteristics, including simple instrumentation, rapid response times and easy operation. These properties are highly desirable to the future design and development of portable analytical devices capable of quickly responding to trace levels of hazardous compounds in the field. The most commonly used analytical

\*To whom correspondence should be addressed.  
E-mail: zarei1349@gmail.com



**Scheme 1**  
Coupling reaction of phenol with diazotized p-nitroaniline,

methods (e.g. those described in the Standard Methods for Examination of Water and Wastewater) are spectrophotometric methods based on the oxidative coupling of phenols with 4-aminoantipyrine (4-AAP) in buffer solution.<sup>54</sup> This procedure has many disadvantages, including (i) employment of large amounts of reagents, especially chloroform (50 mL), which is toxic and carcinogenic; and (ii) difficulty in finding suitable buffers, due to the reactive sensitivity to pH variations.

The aim of the present work was to develop a spectrophotometric determination of phenol in water samples after pre-concentration in a simple cloud point extraction (CPE) process. The method is based on the color reaction of phenol with diazotized p-nitroaniline in alkaline media and micelle mediated extraction of the azo dye product. A nonionic surfactant, Triton X-114, was chosen as the extraction agent without any need for a thermostated water bath.

## 2. Experimental

### 2.1. Instrumentation

A model 3310 UV-Vis spectrophotometer (Hitachi, Tokyo, Japan) with 1-cm quartz cells (1.0 mL) was used for recording absorbance spectra. All spectral measurements were performed by using the blank solution as a reference. A centrifuge with 10 mL calibrated centrifuge tubes (Hettich, Tuttlingen, Germany) was used to accelerate the phase separation process.

### 2.2. Reagents

All chemical reagents used were of analytical reagent grade, and distilled water was used throughout the experiments. A stock solution of 1000  $\mu\text{g mL}^{-1}$  of phenol was prepared by dissolving 0.100 g phenol in water and diluting to 100 mL in a volumetric flask. The diazotized p-nitroaniline reagent ( $2.5 \times 10^3 \text{ mol L}^{-1}$ ) was obtained daily first by dissolving 0.0348 g p-nitroaniline in 10 mL of  $1 \text{ mol L}^{-1}$  hydrochloric acid followed by a dropwise addition of the nitrite solution ( $1 \text{ mol L}^{-1}$ ) until the solution turned colourless. The solution was then diluted to the mark in a 100 mL volumetric flask. A 2.0 g portion of Triton X-114 was dissolved in 100 mL of distilled water to give a 2% (w/v) of surfactant solution. A  $1.2 \text{ mol L}^{-1}$  sodium carbonate solution was prepared by dissolving 12.72 g  $\text{Na}_2\text{CO}_3$  in distilled water and diluted to the mark in a 100 mL volumetric flask.

### 2.3. Recommended Procedure

An aliquot of the solution containing 20–4000 ng of phenol, 1 mL of  $1.2 \text{ mol L}^{-1}$  carbonate solution and 1 mL of  $2.5 \times 10^3 \text{ mol L}^{-1}$  diazotized p-nitroaniline reagent was transferred into a 10-mL tube. The solution was diluted to ca. 9 mL with water and then 1.0 mL of 2.0% (w/v) of Triton X-114 solution was added. The solution was diluted to the mark with triply distilled water. For the separation of two phases of the turbid solution was accelerated by centrifugation for 3 min at 3500 rpm. The mixture was cooled in an ice-salt bath to increase the viscosity of the surfactant-rich phase, and the aqueous phase was easily decanted by simply inverting the tube. The surfactant rich phase of this procedure was dissolved and diluted to 1.0 mL with a

water-ethanol mixture (50:50) and transferred to a 1.0 mL quartz cell for absorbance measurement at 500 nm against a reagent blank as the reference. The blank solution was prepared in the same way as the sample solution except that distilled water was used instead of the phenol solution.

## 3. Results and Discussion

In the alkaline media, the coupling reaction of phenol with diazotized p-nitroaniline produces the coloured azo dye product (Scheme 1).<sup>55</sup>

The azo product is a non-ionic dye and that is extracted into the non-ionic surfactant, Triton X-114, hence this is a suitable method for the separation and pre-concentration of phenol by CPE. Figure 1 shows that the visible absorption spectrum of the azo product in the surfactant-rich phase exhibits a maximum absorbance at 500 nm and all absorbance measurements were performed at this wavelength.

### 3.1. Optimization of Conditions

Before proceeding with the analysis of standards and real samples, an optimization study was needed to ensure that the maximum extraction was attained.

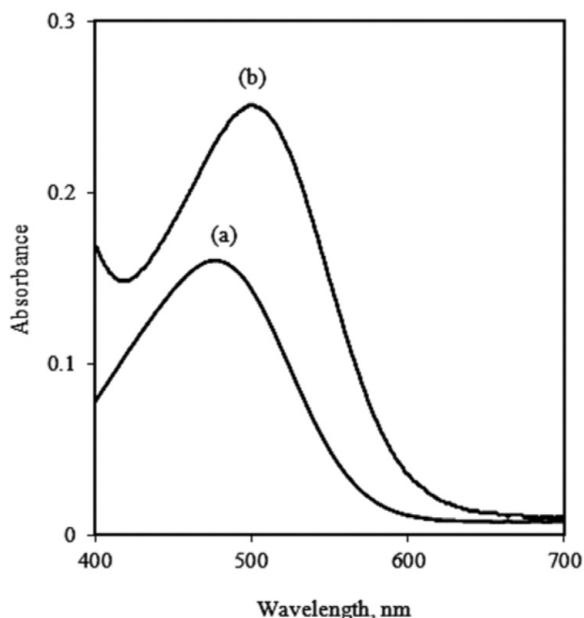
The effect of p-nitroaniline concentration (as diazotized) on the absorbance of the system was investigated within the range 50–500  $\mu\text{M}$ . The results revealed that the absorbance increased by increasing diazotized p-nitroaniline concentration up to 250  $\mu\text{M}$ , and decreased at higher concentrations (Fig. 2). Therefore, a concentration of 250  $\mu\text{M}$  of p-nitroaniline was applied in the proposed method.

The azo dye formation reaction takes place in alkaline medium. Different alkaline salts were tested, and sodium carbonate was found to be the best one. The effect of the concentration of  $\text{Na}_2\text{CO}_3$  on the sensitivity of the method was studied in the range of 10–200 mM. As Fig. 3 shows, the absorbance increased with increasing  $\text{Na}_2\text{CO}_3$  up to 120 mM and remained nearly constant at higher concentrations. Consequently, 120 mM  $\text{Na}_2\text{CO}_3$  was employed as the optimum concentration to complete colour development. Therefore, an advantage over the 4-aminoantipyrine (4-AAP) method is that strict adjustment of pH solution is not necessary.

The concentration of the surfactant used for CPE is an important factor. Preliminary investigations showed that the azo dye product was completely extracted in Triton X-114. To obtain the optimal concentration of Triton X-114, the effect of its concentration was investigated on the absorbance of the extracted phase. The results, illustrated in Fig. 4, reveal that maximum extraction occurred at the surfactant concentration of 0.2% (w/v). This value was selected as the optimal concentration value.

The centrifugation time does not have a considerable effect on the analytical characteristics of the CPE method. This parameter was examined in the range of 2–10 min at 3500 rpm. A time of 3 min was selected as optimum, since complete phase separation occurs in this time and no appreciable improvements were observed for longer times.

Because the surfactant-rich phase was highly viscous, a



**Figure 1** Absorption spectra of the azo dye produced by (a) 500 ng mL<sup>-1</sup> phenol before CPE and (b) 50 ng mL<sup>-1</sup> phenol after CPE. Conditions: diazotized p-nitroaniline, 250 μM; Na<sub>2</sub>CO<sub>3</sub>, 120 mM; Triton X-114, 0.2 % (w/v).

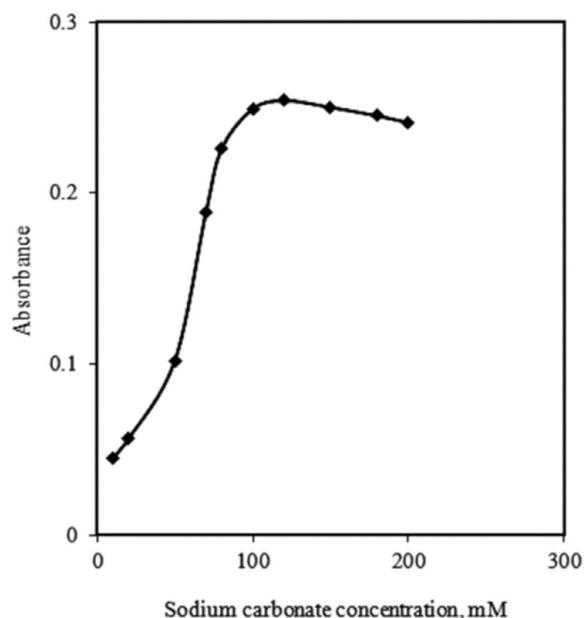
water-ethanol mixture (50:50) as solvent was added to the surfactant-rich phase after CPE to facilitate its transfer into the spectrophotometric cell. The extracted phase was diluted to 1 mL with solvent.

### 3.2. Analytical Figures of Merit

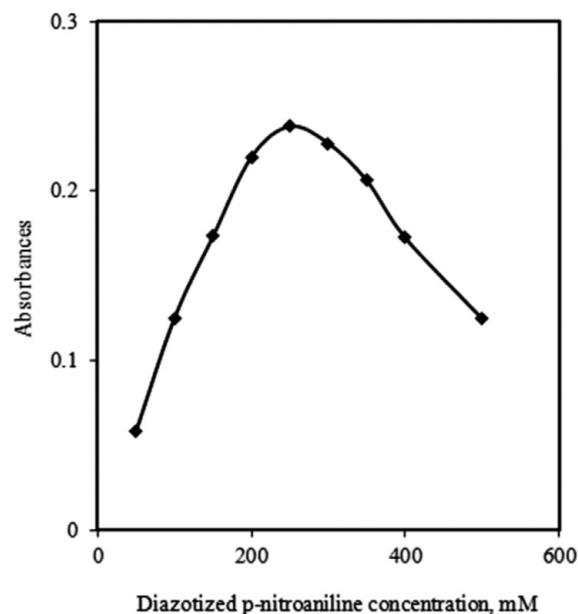
In this work, we studied the reaction of phenol and some phenol derivatives of p-nitroaniline, which the analytical characteristics of the optimized method, including regression equation, linear range, and limit of detection, reproducibility, and pre-concentration and improvement factors were summarized in Table 1. The limit of detection is defined as<sup>56</sup>

$$C_L = 3S_b/m, \quad (1)$$

where  $C_L$ ,  $S_b$ , and  $m$  are the limit of detection, standard deviation



**Figure 3** Effect of sodium carbonate on the absorbance system after CPE. Conditions: phenol, 50 ng mL<sup>-1</sup>; diazotized p-nitroaniline, 250 μM; Triton X-114, 0.2 % (w/v).



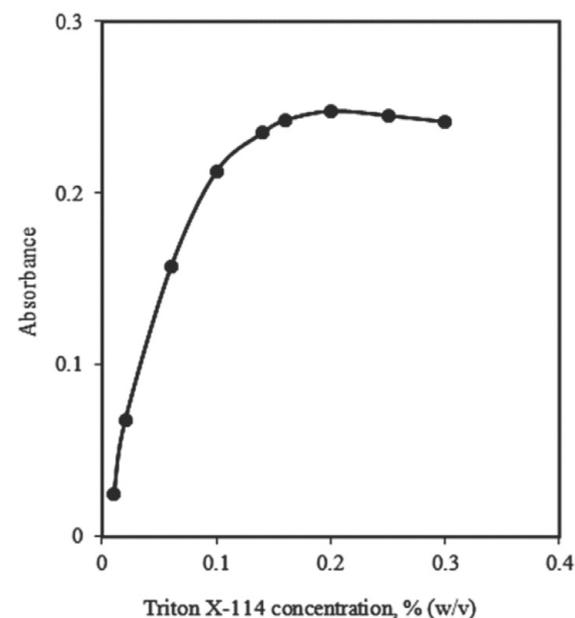
**Figure 2** Effect of diazotized p-nitroaniline concentration on the CPE pre-concentration and determination of phenol. Conditions: phenol, 50 ng mL<sup>-1</sup>; Na<sub>2</sub>CO<sub>3</sub>, 120 mM; Triton X-114, 0.2 % (w/v).

of the blank, and slope of the calibration equation, respectively.

Since the amount of phenol in 10 mL of sample solution was measured after pre-concentration by CPE in a final volume of nearly 1 mL, the solution was concentrated by a factor of 10. The enrichment improvement factor was calculated as the ratio of slope of pre-concentrated samples to that obtained without pre-concentration. According to this concept, an enrichment improvement of 15.7 was obtained for phenol.

### 3.3. Interference Studies

The influence of foreign ions on the determination of phenol was studied and an error of ±5 % in the absorbance reading was considered tolerable. Sample solutions containing 50 ng mL<sup>-1</sup> of phenol and different concentration of other ions or compounds



**Figure 4** Effect of Triton X-114 concentration on the CPE pre-concentration performance of the system. Conditions: phenol, 50 ng mL<sup>-1</sup>; diazotized p-nitroaniline, 250 μM; Na<sub>2</sub>CO<sub>3</sub>, 120 mM.

**Table 1** Analytical characteristics of the proposed method

Regression equation ( $n = 10$ )	$A = 0.0047C + 0.0109, R^2 = 0.998$
Regression equation ( $n = 10$ ) before pre-concentration	$A = 0.0003C + 0.0095, R^2 = 0.999$
Linear range /ng mL <sup>-1</sup> )	2.0–400 (100–4000) <sup>a</sup>
Limit of detection /ng mL <sup>-1</sup> )	1.0 (30) <sup>a</sup>
Reproducibility (R.S.D./ %)	1.73 (1.49) <sup>a</sup>
Pre-concentration factor	10
Enrichment factor	15.7

<sup>a</sup> For before pre-concentration.

were prepared and the developed procedure was applied. The results showed that the ions Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ba<sup>2+</sup>, As<sup>3+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, ClO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, F<sup>-</sup> do not interfere even when present at 1000-fold excess over phenol.

### 3.4. Responses of other Phenolic Compounds

Under the experimental conditions, many phenolic compounds can give the colour reaction. These compounds include 2-chlorophenol, m- and o-cresol, and 3-aminophenol. Therefore, the total concentration of phenol and its derivatives that react with diazotized p-nitroaniline that is defined as 'phenols' or 'phenol index' is preferred in the routine analytical monitoring of the quality of water.

### 3.5. Applications

In order to test the reliability of the proposed method, it was applied to the determination of the total concentration of phenols in several water samples. The results are presented in Table 2. The results are in good agreement with those obtained by standard methods.<sup>54</sup> The results indicate that the proposed method is helpful for the determination of phenols in the natural water samples.

## 4. Conclusion

The proposed method describes a very rapid, simple, sensitive, and low-cost spectrophotometric procedure with wide dynamic range, for the determination of phenols in water-samples. A more user-friendly surfactant with a moderate health effect has been used for pre-concentration of phenol, and thus toxic solvent extraction has been avoided. A nonionic micelle of Triton X-114 was chosen for the formation of the surfactant rich phase at room temperature. A comparison of the proposed

method with the previously reported methods for spectrophotometric determination of phenol (Table 3) indicates that the proposed method is faster and simpler than the existing methods and that it provides a wider dynamic range and a lower limit of detection. The proposed method is simple, rapid, low cost, safe, and nontoxic and can be applied to the determination of phenol in water samples.

## References

- National Research Council of Canada, NRC, Associate Committee on Scientific Criteria for Environmental Quality, *Chlorinated Phenols: Criteria for Environmental Quality*, Public No. 18578, Ottawa, 1982.
- D. Martinez, E. Pocurull, R.M. Marce, F. Borrull, M. Calull, *J. Chromatogr. A*, 1996, **734**, 367–373.
- J.W. Moore, S. Ramamourthy, *Organic Chemicals in Natural Waters Applied Monitoring and Impact Assessment*, Springer-Verlag, New York, 1984
- United States Environmental Protection Authority, *Toxic Substances Control Act (TSCA)*, USEPA, Washington, DC, 1979.
- Commission of the European Communities, *Drinking Water Directive, 80/778/EEC*, Brussels, 1980.
- J.P. Rawat, K.P.S. Muktawat, *Microchem. J.*, 1984, **30**, 289–296.
- L.P. Eksperianidova, I.I. Fokina, A.B. Blank, T.I. Ivkova, B.P. Soukhomlinov, *Anal. Chim. Acta*, 1999, **396**, 317–320.
- C. Kang, Y. Wang, R. Li, Y. Du, J. Li, B. Zhang, L. Zhou, Y. Du, *Microchem. J.*, 2000, **64**, 161–171.
- Y.C. Fiamegos, C.D. Stalikas, G.A. Pilidis, M.I. Karayannis, *Anal. Chim. Acta*, 2000, **403**, 315–323.
- I. Nukatsuka, S. Nakamura, K. Watanabe, K. Ohzeki, *Anal. Sci.*, 2000, **16**, 269–273.
- Y. Fiamegos, C. Stalikas, G. Pilidis, *Anal. Chim. Acta*, 2002, **467**, 105–114.
- M. Hasani, M. Moloudi, *J. Hazard. Mater.*, 2008, **157**, 161–169.
- W. Frenzel, J. Oleksy-Frenzel, J. Morlen, *Anal. Chim. Acta*, 1992, **261**, 253–259.

**Table 2** Determination of phenol in water samples by proposed method.

Sample	Phenol/ng mL <sup>-1</sup>		Recovery/%	Standard method
	Added	Found <sup>a</sup>		
Drinking water	–	Not detected	–	Not detected
	10	9.60 ± 1.9	96.0	
	50	51.8 ± 2.1	103.4	
	100	97.3 ± 1.6	97.3	
Well water	–	47.9 ± 1.9	–	48.5 ± 1.2
	10	58.4 ± 1.4	105	
	50	95.7 ± 1.8	95.6	
	100	144.9 ± 1.5	97.0	
River water	–	78.2 ± 1.4	–	76.4 ± 1.7
	10	88.4 ± 1.3	102	
	50	130 ± 2.6	103.6	
	100	174.9 ± 2.2	96.7	

<sup>a</sup> Average of three determination ± standard deviation

**Table 3** Comparison of the performance of the proposed method with that of other reported methods for the spectrophotometric determination of phenol in water samples.

Analytical method	Linear range /ng mL <sup>-1</sup>	Detection limit /ng mL <sup>-1</sup>	Relative standard deviation, RSD /%	Reference
Spectrophotometry by using nitroprusside and hydroxylamine	50–5000	–	1.30	8
Chemiluminescence combined with C <sub>18</sub> -modified silica gel solid phase extraction	4.7–470	0.66	1.50	40
Spectrophotometry by using 4-aminopyrazolone derivatives	5–500	3.0	<3.5	9
Flow injection chemiluminescence using potassium permanganate and formaldehyde system	5–1000	3.0	1.20	18
Flow injection photometric determination after solvent extraction pre-concentration	1–10	–	≤25	17
Solid-phase spectrophotometry using anion-exchange resin extraction	0–20	0.50	1.9	10
Flow-injection spectrophotometry using amberlite XAD resin solid-phase extraction	10–1000	4	2.4	15
Cloud point extraction-spectrophotometry	1.0–400	0.50	1.73	Proposed method

- 14 M.J. Christophersen, T.J. Cardwell, *Anal. Chim. Acta*, 1996, **323**, 39–46.
- 15 W. Song, Z. Zhi, L. Wang, *Talanta*, 1997, **44**, 1423–1433.
- 16 H.Vieira, O. Fatibello-Filho, *Anal. Chim. Acta*, 1998, **366**, 111–118.
- 17 A.L. Moskvina, A.V. Mozzhukhin, E.A. Mukhina, L.N. Moskvina, *J. Anal. Chem.*, 2005, **60**, 70–74.
- 18 W. Cao, X. Mu, J. Yang, W. Shi, Y. Zheng, *Spectrochim. Acta A*, 2007, **66**, 58–62.
- 19 J. Metzger, M. Reiss, W. Hartmeier, *Biosens. Bioelectron.*, 1998, **13**, 1077–1082.
- 20 J.J. Roy, T. Emili Abraham, K.S. Abhijith, P.V. Sujith Kumar, M.S. Thakur, *Biosens. Bioelectron.*, 2005, **21**, 206–211.
- 21 S. Tingry, C. Innocent, S. Touila, A. Deratani, P. Seta, *Mat. Sci. Eng.*, 2006, **26**, 222–226.
- 22 S. Korkuta, B. Keskinler, E. Erhan, *Talanta*, 2008, **76**, 1147–1152.
- 23 P. Wang, M. Liu, J. Kan, *Sens. Actuators B*, 2009, **40**, 577–584.
- 24 L. Montero, S. Conradi, H. Weiss, P. Popp, *J. Chromatogr. A*, 2005, **1071**, 163–169.
- 25 A. Kovacs, A. Kende, M. Mortl, G. Volk, T. Rikker, K. Torkos, *J. Chromatogr. A*, 2008, **1194**, 139–142.
- 26 S. Vichi, A. Romero, J. Tous, E. Lopez Tamames, S. Buxaderas, *J. Chromatogr. A*, 2008, **1211**, 1–7.
- 27 G. Blo, F. Dondi, A. Betti, C. Bighi, *J. Chromatogr. A*, 1983, **257**, 69–79.
- 28 F.P. Bigley, R.L. Grob, *J. Chromatogr. A*, 1985, **350**, 407–416.
- 29 B. Makuch, K. Gazda, M. Kaminski, *Anal. Chim. Acta*, 1993, **284**, 53–58.
- 30 M. Teresa Galceran, O. Jauregui, *Anal. Chim. Acta*, 1995, **304**, 75–84.
- 31 P. Vinas, C. Lopez-Erroz, J. Jose Marin-Hernandez, M. Hernandez-Cordoba, *J. Chromatogr. A*, 2000, **871**, 85–93.
- 32 E. Herrero-Hernandez, R. Carabias-Martinez, E. Rodriguez-Gonzalo, *Anal. Chim. Acta*, 2009, **650**, 195–201.
- 33 Y.C. Chao, C.W. Whang, *Anal. Chim. Acta*, 1994, **663**, 229–237.
- 34 S. Morales, R. Cela, *J. Chromatogr. A*, 1999, **846**, 401–411.
- 35 K. Tsukagoshi, T. Kameda, M. Yamamoto, R. Nakajima, *J. Chromatogr. A*, 2002, **978**, 213–220.
- 36 T. Li, Q. Jia, L. Song, R. Su, Y. Lei, W. Zhou, H. Li, *Talanta*, 2009, **78**, 1497–1502.
- 37 P. Bartak, P. Frnkova, L. Cap, *J. Chromatogr. A*, 2000, **867**, 281–287.
- 38 Y.S. Fung, Y.H. Long, *J. Chromatogr. A*, 2001, **907**, 301–311.
- 39 M.A. Crespín, M. Gallego, M. Valcarcel, *J. Chromatogr. B*, 2002, **773**, 89–96.
- 40 H. Qi, J. Lv, B. Li, *Spectrochim. Acta A*, 2007, **66**, 874–878.
- 41 T. Serot, C. Lafficher, *Food Chemistry*, 2003, **82**, 513–519.
- 42 X. Liua, Y. Jia, Y. Zhanga, H. Zhang, M. Liua, *J. Chromatogr. A*, 2007, **1165**, 10–17.
- 43 H. Bagheri, A.S. Saber, R. Mousavi, *J. Chromatogr. A*, 2004, **1046**, 27–33.
- 44 M. Saraji, M. Bakhshi, *J. Chromatogr. A*, 2005, **1098**, 30–36.
- 45 X. Huang, N. Qiu, D. Yuan, *J. Chromatogr. A*, 2008, **1194**, 134–138.
- 46 G.D. Rodrigues, L.R. Lemos, L.H.M. Silva, M.C.H. Silva, L.A. Minim, J.S.R. Coimbra, *Talanta*, 2010, **80**, 1139–1144.
- 47 L. Farina, E. Boido, F. Carrau, E. Dellacassa, *J. Chromatogr. A*, 2007, **1157**, 46–50.
- 48 M.A. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, *Appl. Spectrosc. Rev.*, 2005, **40**, 269–299.
- 49 J.L. Manzoori, G. Karim-nezhad, *Anal. Chim. Acta*, 2004, **521**, 173–177.
- 50 V.A. Lemos, J.S. Santos, P.X. Baliza, *J. Braz. Chem. Soc.*, 2006, **17**, 30–35.
- 51 A.R. Zarei, *J. Anal. Chem.*, 2009, **64**, 896–902.
- 52 J.L. Burguera, M. Burguera, *Talanta*, 2004, **64**, 1099–1108.
- 53 M.F. Silva, E.S. Cerutti, L.D. Martinnez, *Microchim. Acta*, 2006, **155**, 349–364.
- 54 American Public Health Association, *Standard Methods for Examination of Water and Wastewater*, 5530, Phenols, 21st edn, 2005.
- 55 W. Fresenius, K.E. Quentin, W. Schneider, *Water Analysis*, Springer-Verlag, New York, 1988, p. 537.
- 56 J.D. Ingle Jr., S.R. Crouch, *Spectrochemical Analysis*, Prentice-Hall, USA, 1988.