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A new strategy to simultaneous microextraction of acidic and basic compounds

Morteza Moradi, Yadollah Yamini *, Jamal Kakehmam, Ali Esrafili, Mahnaz Ghambarian

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

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ABSTRACT

The simultaneous extraction of acidic and basic pollutants from water samples is an interesting and debatable work in sample preparation techniques. A novel and efficient method named ion pair based surfactant assisted microextraction (IP-SAME) was applied for extraction and preconcentration of five selected acidic and basic aromatic species as model compounds in water samples, followed by high performance liquid chromatography–ultraviolet detection. A mixture including 1 mL of ultra-pure water (containing ionic surfactant as emulsifier agent) and 60 μL 1-octanol (as extraction solvent) was rapidly injected using a syringe into a 10.0 mL water sample which formed an emulsified solution. IP-SAME mechanism can be interpreted by two types of molecular mass transfer into the organic solvent (partitioning and ion pairing for non-ionized and ionized compounds, respectively) during emulsification process. The effective parameters on the extraction efficiency such as the extraction solvent type and its volume, type of the surfactant and its concentration, sample pH and ionic strength of the sample were optimized. Under the optimum conditions (60 μL of 1-octanol; 1.5 mmol L^{-1} cethyltrimethyl ammonium bromide (CTAB) as emulsifier agent and sample pH 10.0), the preconcentration factors (PFs), detection limits and linear dynamic ranges (LDRs) were obtained in the range of 87–348, 0.07–0.6 μg L^{-1} and 0.1–200 μg L^{-1} respectively. All of natural water samples were successfully analyzed by the proposed method.

1. Introduction

Aromatic compounds such as aniline, phenol and their derivatives are of great importance in environmental chemistry due to their toxic nature and their suspected carcinogenic properties [1–3]. They are used in several manufacturing processes, particularly in dye industry [4]. Also with the recent development of aniline and phenol-based herbicides, there has been a great deal of attention on aniline, phenol and their derivatives as environmental pollutants. Due to their high solubility in water, anilines and phenols can easily permeate through soil and contaminate ground water. Aniline is highly toxic and readily absorbed through the skin in dangerous amounts and is fatal if swallowed or if the vapors are inhaled [5].

Chlorinated anilines (CAs) such as 3-chloroaniline, 4-chloroaniline and 3,4-dichloroaniline have also been found as degradation products and intermediates of various phenylurea and phenylcarbamate pesticides [6]. Regarding the importance of these compounds, a rapid and sensitive method of analysis is needed to detect them in the environment.

Nitrophenols (NPs) might be released due to the photochemical reaction of benzene with nitrogen monoxide in highly polluted air. Therefore, nitrophenols are found as contaminants in wastewater, rivers, groundwater, soil, and in the atmosphere. Concentrations in the range of 4.6–100 μg L^{-1} have been found in rain water and in the tropospheric atmosphere [7].

Several analytical methods have been reported for determination of anilines, phenols and their derivatives such as gas chromatography (GC) [8,9] and capillary zone electrophoresis (CZE) [10]. The most popular technique for the analysis of aromatic amines and phenols in environmental water is high-performance liquid chromatography (HPLC) [11].

Although the development of modern analytical instruments allows great enhancement in aspects of analysis, the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples in many cases. Sample preparation is still a bottleneck for overall throughput because the steps involved often employ large volumes of hazardous organic solvents, are time consuming and/or expensive. Besides, there might also be the problem of contamination and sample loss [12–16].

Recently, liquid phase microextraction (LPME) was developed as a novel and disposable method for sample preparation [17]. LPME is a solvent-minimized sample preparation procedure, in which only several μL of solvent are required to concentrate analytes from

* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.
E-mail address: yyamini@modares.ac.ir (Y. Yamini).

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various samples and also is compatible with GC, capillary electrophoresis (CE) and HPLC. In 2006 Assadi and co-workers [18] reported dispersive liquid–liquid microextraction (DLLME) as a new version of LPME technique which uses μL volumes of extraction solvent along with a few mL of disperser solvents. In this method, a cloudy solution is formed when a mixture of extraction and disperser solvents are injected into an aqueous sample containing the analytes of interest. Having formed the cloudy solution, the surface area between extraction solvent and aqueous sample is enlarged and equilibrium state is achieved quickly resulting in a short extraction time. In fact, this is the principal advantage of DLLME.

One of the major disadvantages of DLLME is the small partition coefficients of analytes between organic and aqueous phases due to presence of disperser solvent in the aqueous phase. A new format of DLLME based on surfactant, as disperser agent, was reported in 2010 [19,20]. In this method a mixture of aqueous solution including surfactant and extraction solvent is quickly injected into the sample solution so as to form an emulsified solution. The enriched analytes in the collected phase are determined by an appropriate analytical instrument after centrifugation. One of advantages of surfactant application is that it does not decrease the partition coefficient of the analytes considerably and also the toxicity of the surfactants is low.

The dispersion phenomenon can be qualitatively interpreted via the liquid–liquid interface chemistry. The interfacial tension is the parameter representing the uncompensated intermolecular forces acting in the bulk phase. The surfactants reduce interfacial tension (γ) between organic and aqueous phases making an increase in surface area during fine droplets formation as is described by the Young–Laplace equation

$$\Delta P = P_{\text{internal}} - P_{\text{external}} = \gamma \left(\frac{2}{R_{\text{sph}}} \right) \quad (1)$$

where R_{sph} is the radius of the spherical droplet and P_{internal} and P_{external} are the internal and external pressures of droplet, respectively. This simple form of the Young–Laplace equation shows that the interfacial tension reduction leads to a reduction in the droplet radius and forming finer droplets in a constant pressure difference.

In our previous study [19] cationic surfactant was used as emulsifier for microextraction of the chlorophenols in water samples. The chlorophenols are acidic compounds and are not extractable into organic solvents in alkaline medium. Occurring the ion-pair formation, chlorophenols can be extracted from alkaline solutions (containing cationic surfactants) into organic solvents. Therefore it is expected that the anionic surfactants is capable to form ion-pair with the protonated chloroanilines (CAs) in acidic medium resulting in CAs extraction into organic solvent.

In the present study, nitrophenols and chloroanilines are selected as acidic and basic model compounds, respectively, to consider their simultaneous extraction using ion pair based surfactant assisted microextraction (IP-SAME).

The eventual mechanism of IP-SAME to transfer protonated CAs by anionic surfactant in acidic medium and deprotonated NPs by cationic surfactant in alkaline medium to organic solvent is shown in Fig. 1. As can be seen, the mentioned equilibriums tend to right side of reaction, in (a) acidic, (b) alkaline medium and anionic surfactant-CA and cationic surfactant-NP ion pairs are formed, respectively. In the adjusted basic pH, CAs are in its neutral form and can be extracted into organic solvent, while, NPs are deprotonated and able to form ion pair with the cationic surfactant and extract into extraction solvent. Thus the mass transfer process occurs by a mechanism involving two parallel phenomena (partitioning and ion pairing) in proposed study.

The aim of the proposed study was to optimize various parameters, affecting the extraction efficiency of IP-SAME in simultaneous extraction of the CAs and NPs from water samples.

2. Experimental

2.1. Chemicals and reagents

3-Chloroaniline (3-CA, $pK_b = 10.48$, $\log K_{ow} = 1.88$), 4-chloroaniline (4-CA, $pK_b = 10.0$, $\log K_{ow} = 1.85$), 3,4-dichloroaniline (3,4-DCA, $pK_b = 11.1$, $\log K_{ow} = 2.8$), 4-nitrophenol (4-NP, $pK_a = 7.2$, $\log K_{ow} = 2.0$) and 3-nitrophenol (3-NP, $pK_a = 8.3$, $\log K_{ow} = 2.0$) [7,21–23] obtained from Sigma–Aldrich (Milwaukee, WI, USA). Cethyltrimethyl ammonium bromide (CTAB) was obtained from Merck (Darmstadt, Germany), and tetradecyl trimethyl ammonium bromide (TTAB), sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (STS) were purchased from Sigma–Aldrich. HPLC-grade methanol and acetonitrile were purchased from Caledon (Ontario, Canada). The ultra-pure water was prepared by a model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea). Toluene, 1-undecanol, 1-octanol and 1-dodecanol were purchased from Merck.

Stock standard solutions of analytes (1000 mg L^{-1}) were prepared by dissolving the proper amounts of them in HPLC grade methanol. Standard aqueous solutions were prepared by spiking ultra-pure water with 1.0, 10.0 and 50 mg L^{-1} of mixed standard solutions of analytes in methanol. All other chemicals used were of analytical grade.

2.2. Apparatus

An Agilent 1200 series liquid chromatograph (Centerville Road, Wilmington, USA) equipped with a UV–Vis diode array detector (DAD) was applied. The system was equipped with a Rheodyne 7125i injector with a 20-μL loop. An ODS-Zorbax column (250 cm × 4.6 mm, with 5 μm particle size) and an ODS-Zorbax guard column (4.6 mm × 1.25 cm) were applied to separate the analytes under gradient elution conditions. Firstly, a mixture of ultra-pure water and acetonitrile (50:50) for 15 min and then 100% acetonitrile for 10 min were used as mobile phase. The mobile phase flow rate was 1 mL min^{-1} and DAD monitoring wavelengths were chosen at 220, 220, 240, 240 and 240 nm for 4-NP, 3-NP, 4-CA, 3-CA and 3,4-DCA respectively. It is worthy to note that the optimization of the parameters were performed at fixed wave length of 230 nm and the figures of merit of the method were obtained at λ_{max} of each analyte by using DAD detector.

2.3. IP-SAME procedure

An aliquot of 10.0 mL water sample containing the analytes was poured into a 12 mL glass test tube which is designed for collection of low density solvents [24]. The pH of the solutions was adjusted to an appropriate level (pH 10.0). A mixture containing 1 mL CTAB (as emulsifier agent, 1.5 mmol L^{-1}) and 60 μL 1-octanol (as extraction solvent) was quickly injected into the sample solution using 1.0 mL gastight syringe. Cloudy solution was quickly formed as the fine droplet of the immiscible extraction solvent dispersed in the aqueous sample. This process greatly enlarged the contact area between the extraction solvent and aqueous phase, and the analytes were extracted into the formed fine droplets. The formed emulsion was centrifuged at 5000 rpm for 3 min to separate the phases. Twenty microliters of collected phase was taken using a 50 μL microsyringe and directly injected into the HPLC instrument.

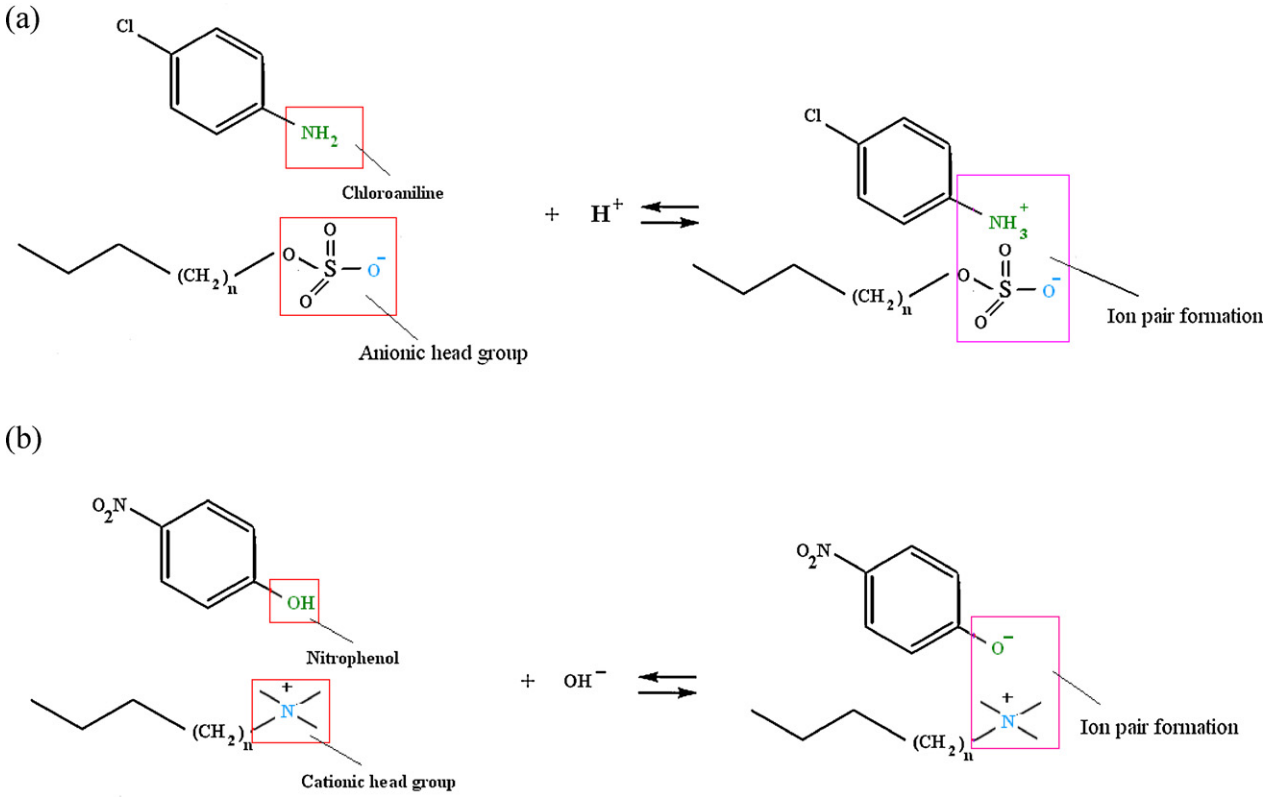

Fig. 1. Schematic representation of the ion pair formation of (a) protonated CAs by anionic surfactant in acidic medium and (b) deprotonated NPs by cationic surfactant in alkaline medium.

3. Results and discussion

The focus of the present work was to find the extraction conditions providing the highest extraction yields of CAs and NPs from water samples using an IP-SAME procedure compatible with low density solvents. In order to obtain the optimum IP-SAME conditions, the influence of different experimental parameters including the type and volume of the extraction solvent, type and concentration of surfactant, sample pH and the presence of salt on IP-SAME performance were investigated and optimized.

3.1. Selection of extraction solvent

Selection of an appropriate extraction solvent is of great importance in optimizing IP-SAME procedure. The extraction solvent should satisfy several requirements: (1) being immiscible with water and have low volatility in order to be stable during the extraction period, (2) to extract analytes well, (3) having a lower density than water and good chromatographic behavior. Therefore, toluene (density; 0.867 g mL^{-1}), 1-undecanol (density; 0.829 g mL^{-1}), 1-octanol (density; 0.824 g mL^{-1}) and 1-dodecanol (density; 0.830 g mL^{-1}) were examined in this research. The compatibility of these solvents with the IP-SAME technique was studied by adding a mixture of 1 mL ultrapure water (including 1 mmol L^{-1} SDS, as emulsifier agent) and 80 μL of each mentioned solvents into 10.0 mL aqueous solution (pH 2) containing 100 μg L^{-1} of analytes. After the extraction and centrifugation processes, twenty microliters of collected extraction solvent was injected into the HPLC–UV. As can be seen in Fig. 2, 1-octanol gives the highest overall extraction efficiency for the target analytes among the four solvents investigated. Therefore, 1-octanol was selected as the extraction solvent.

3.2. Synchronous effect of pH and type of surfactant

The emulsifier agent should be miscible with both water and the extraction solvent in IP-SAME method. The miscibility in both of organic and aqueous phase is a characteristic specificity of all amphiphilic materials like surfactants. In the present study, two cationic (CTAB and TTAB) and two anionic (SDS and STS) surfactants were used to investigate the influence of the surfactant type on the IP-SAME performance.

Generally, sample solution pH determines the state of analytes in aqueous solution which plays an important role in extraction of pollutants from environmental water samples. The donor phase was alkalized and acidified in different experiments to convert the CAs and NPs to their un-dissociated forms, respectively, in order

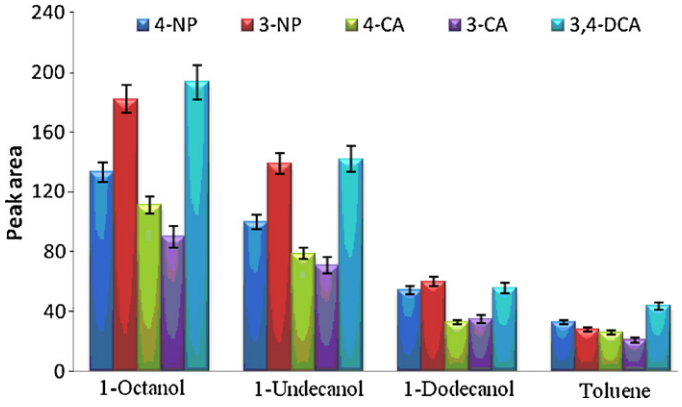

Fig. 2. Effect of organic solvent on the extraction efficiency. Extraction conditions: sample solution, 10.0 mL of 100 μg L^{-1} of each analyte; 1.0 mL of ultra-pure water containing SDS (1.0 mmol L^{-1}) as emulsifier agent; sample pH, 2.0; extraction solvent volume, 80 μL.

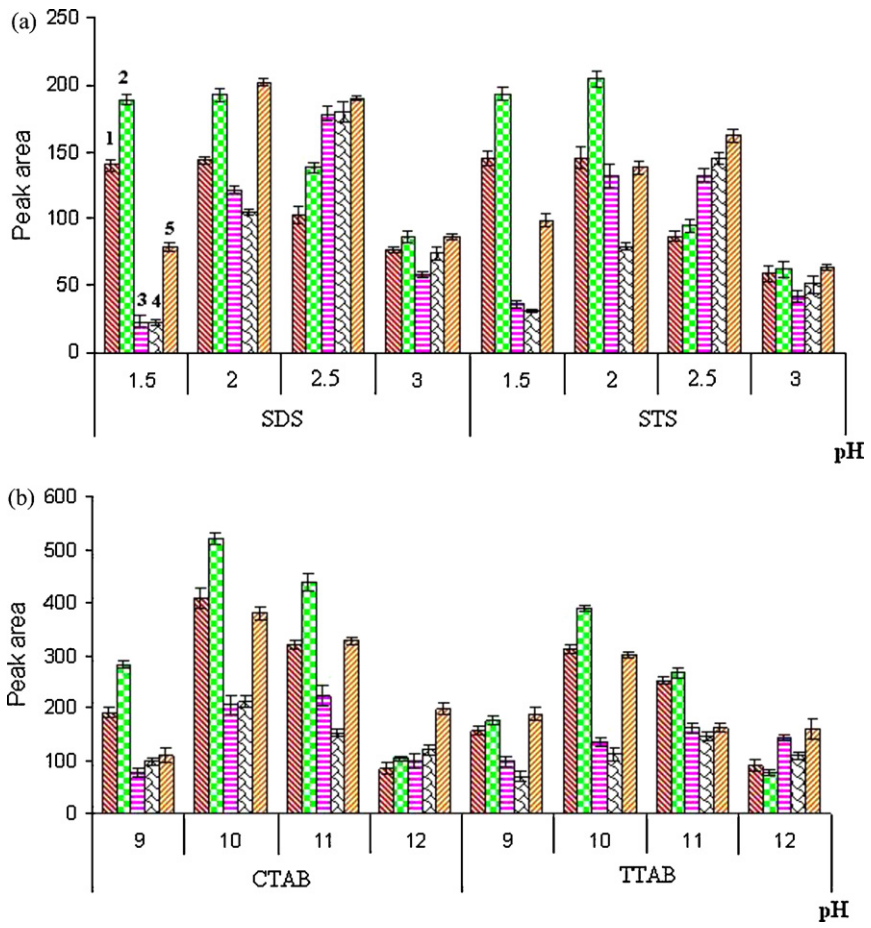

Fig. 3. Synchronous effect of pH and type of (a) anionic and (b) cationic surfactant on the extraction efficiency. Extraction conditions: sample solution, 10.0 mL of 100 μg L^{-1} of each analyte; extraction solvent, 80 μL of 1-octanol; surfactant concentration, 1.0 mmol L^{-1} (1.0 mL). (1) 4-NP, (2) 3-NP, (3) 4-CA, (4) 3-CA and (5) 3,4-DCA.

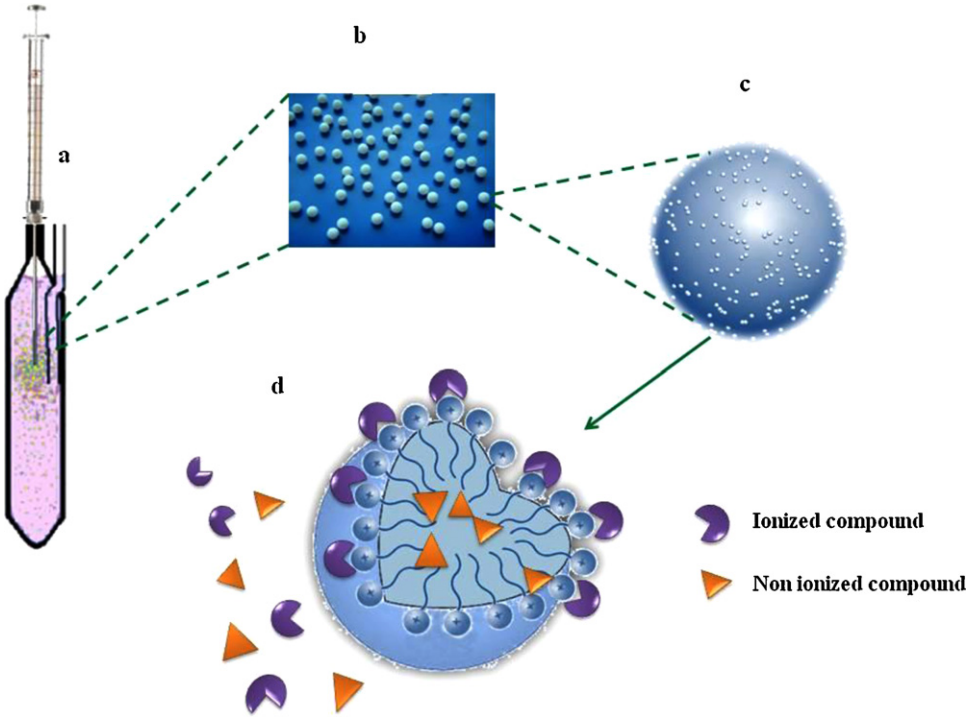

Fig. 4. A schematic representation of emulsification and ion pair formation that are two fundamental CTAB behaviors have been used to extraction of NPs and CAs, respectively. (a) Injection of CTAB/extraction solvent mixture into aqueous phase, (b) emulsified solution, (c) single organic droplet including CTAB and (d) a two-dimensional mechanism for mass transfer into the organic solvent.

Table 1
The performance characteristics of the proposed method.

Analyte	LDR ($\mu g\,L^{-1}$)	Linearity (R^2)	[a]RSD% ($n=5$)		LOD ($\mu g\,L^{-1}$)	[a]PF
			Intra-day	Inter-day		
4-NP	0.2–75	0.9925	12.7	3.4	0.1	293
3-NP	0.1–75	0.9976	8.4	5.8	0.07	348
4-CA	1.0–200	0.9930	7.9	5.0	0.6	87
3-CA	1.0–200	0.9942	10.8	7.7	0.5	94
3,4-DCA	0.6–150	0.9986	11.9	6.9	0.2	230

[a] Data were calculated based on extraction of 20 $\mu g\,L^{-1}$ of each analyte.

Table 2
Analytical results for extraction of the analytes from natural waters using the proposed method.[a]

Sample		4-NP	3-NP	4-CA	3-CA	3,4-DCA
Tap water	Initial concentration	nd[c]	nd	nd	nd	nd
	Found[b]	4.74	4.67	5.15	5.01	4.83
	Relative recovery (%)	94.8	93.4	103	100.2	96.6
	RSD% ($n=3$)	6.3	12.5	4.1	7.8	3.3
Mineral water	Initial concentration	nd	nd	nd	nd	nd
	Found	4.91	4.52	4.68	5.39	5.26
	Relative recovery (%)	98.2	90.4	93.6	107.8	105.2
	RSD%	4.5	8.2	6.7	8.6	10.3
Rain water	Initial concentration	3.1	4.2	nd	nd	nd
	Found	7.89	9.70	4.63	5.27	4.89
	Relative recovery (%)	95.8	110	92.6	105.4	97.8
	RSD%	2.6	6.5	9.8	6.4	3.9

[a] All concentrations are in $\mu g\,L^{-1}$.
[b] Five $\mu g\,L^{-1}$ of each analyte was added to calculate relative recovery (%).
[c] nd, not detected.

to extract them into the organic phase in traditional liquid phase microextraction. In the present work, the sample pH was selected in a range that the surfactant form ion pair with ionized compounds, in addition form an emulsified medium to extract neutral components. Regarding the mentioned above, the extraction efficiency of cationic and anionic surfactants was investigated in four acidic and alkaline pH levels, respectively.

The compatibility of these surfactants with the IP-SAME technique was studied by adding each mentioned surfactants (1.0 mL) and 80 μL 1-octanol to a 10.0 mL aqueous solution containing 100 $\mu g\,L^{-1}$ of each analyte. Based on Fig. 3, CTAB presented the highest extraction efficiency at pH 10.0 compared with the other surfactants. Aromatic phenols are acidic compounds and exist in deprotonated form at pH 10.0. CTAB molecule consisting a cationic head group and hydrophobic hydrocarbon chain is an appropriate agents to form ion pair with deprotonated phenols. As shown in Fig. 4, CTAB has two fundamental functions; (1) the formation of an emulsified phase because of interfacial tension reduction between the water and extraction solvent interfaces which makes the droplets finer, resulting in extraction of non ionized CAs into organic solvent (partition mechanism), (2) the ion pair formation with ionized NPs and making it extractable into organic phase. Thus, CTAB and pH 10.0 were selected as an appropriate surfactant and optimum pH for further experiments, respectively.

3.3. Surfactant concentration and ionic strength

The concentration of surfactant in IP-SAME is a critical factor. The variation of extraction efficiency upon the surfactant concentration was studied within the range of 0.25–5.0 mmol L^{-1} of CTAB. The signals at various surfactant concentrations are shown in Fig. 5. As can be seen, the quantitative extraction was observed at CTAB concentration of 1.5 mmol L^{-1}. As the CTAB concentration increased from 0.25 to 1.5 mmol L^{-1}, the extraction efficiency (especially for NPs) was increased due to making finer droplets causing an improved mass transfer into organic phase and well ion pair formation. The pre-micelles are formed as the surfactant concentration reaches critical micelle concentration (CMC) which causes a reduction in extraction efficiency probably due to interaction between analytes with pre-micelles. To achieve maximum preconcentration factor, CTAB concentration of 1.5 mmol L^{-1} was selected in further experiments.

In general, the addition of salt improves the extraction efficiency of analytes from the aqueous to the organic phase in liquid–liquid

Table 3
Comparison of the proposed method with other developed methods to determination of CAs and NPs.

Analytes	Method	LOD ($\mu g\,L^{-1}$)	LDR ($\mu g\,L^{-1}$)	RSD%	Ref.
2-NP, 3-NP, 4-NP	[a]HF-cLC	0.5–1	1–200	≤6.23	[25]
2-NP, 4-NP	SPME-HPLC–UV	1.6–4.1	5–30,000	≤11.3	[26]
2-NP, 3-NP, 4-NP	[b]SLMME-HPLC–UV	0.0005–0.001	–	≤4.2	[7]
4-CA, 3,4-DCA	[c]HT-HS-LPME-HPLC-DAD	0.5–1	1–150	≤7.0	[27]
4-CA, 3,4-DCA	HF-LPME-MEEKC	2.8–3.3	5–240	≤4.7	[28]
3-CA	[d]LLLME-HPLC–UV	1.6	4–1000	5.5	[29]
4-NP, 3-NP, 4-CA, 3-CA, 3,4-DCA	IP-SAME-HPLC-DAD	0.07–0.6	0.1–200	≤7.7	Proposed method

[a] Hollow fiber liquid phase microextraction.
[b] Supported liquid membrane microextraction.
[c] High temperature head space liquid phase microextraction.
[d] Liquid–liquid–liquid microextraction.

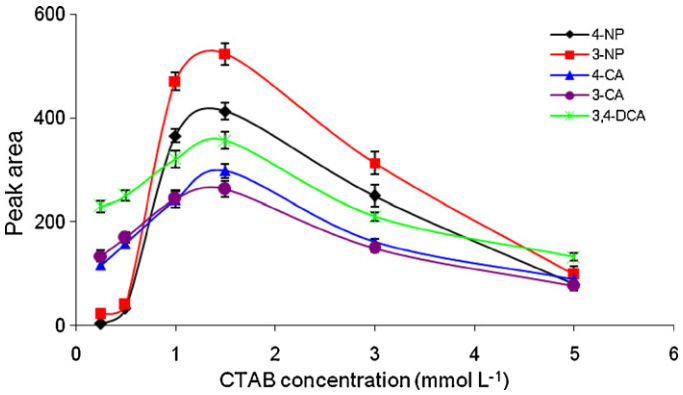

Fig. 5. The effect of CTAB concentration on the extraction efficiency. Extraction conditions: sample solution, 10.0 mL of 100 μg L^{-1} of each analyte; 1.0 mL of ultra-pure water containing CTAB as emulsifier agent; sample pH, 10.0; extraction solvent, 80 μL of 1-octanol.

extraction (LLE) and LPME due to the salting-out effect. Studying the influence of ionic strength on the extraction efficiency of IP-SAME, concentrations of NaCl in aqueous solutions were varied in the range of 0–20% (w/v) while other experimental conditions were kept constant. The results showed that the salt concentration has the positive significant effect on the extraction efficiency from 0 to 10.0% (w/v) NaCl for CAs. The addition of salt changes the activity coefficients of the analytes in the aqueous phase and, in this way; improves CAs extraction efficiency via salting out effect. The results however showed that, by increasing concentration of NaCl, the extraction efficiency of the NPs was decreased. One possible interpretation is that the salt addition increases the chloride concentration and prevents the ion pair forming between the ionized NPs and CTAB. Hence, NaCl was not added in all subsequent experiments.

3.4. 1-Octanol volume

Additional experiments were performed using different volumes of 1-octanol in the range of 40–100 μL. In order to evaluate the effect of extraction solvent volume on extraction efficiency.

The collected volumes of 1-octanol increased from 10 to 80 (±3 μL). However, it was observed that not enough extraction solvent was collected on the top of the vial (volume of HPLC loop is 20 μL) when the volumes lower than 60 μL were used. The results showed that an increase in extraction solvent volume from 60 to 100 μL will result in a decrease in the analyte recovery. The volume of collected phase is increased as the extraction solvent volume increases while the preconcentration factor of the analytes is decreased. Thus 60 μL was selected as the optimum extraction solvent volume.

3.5. Quantitative analysis

Quantitative parameters of the IP-SAME method were calculated under the optimized conditions (volume of 1-octanol, 60 μL; emulsifier agent, 1.5 mmol L^{-1} CTAB; pH, 10.0; and without salt addition). The calculated figures of merit are summarized in Table 1.

A linear calibration graph for the analytes was obtained over the range of 0.1–200 μg L^{-1} (14 concentration levels analyzed) using the proposed extraction method, the correlation of determinations (R^2) was between 0.9925 and 0.9986 and limits of detection (LODs) for the analytes based on a signal to noise ratio (S/N) of 3, varied in the range of 0.07–0.6 μg L^{-1}. Intra-day precision was obtained from five consecutive replicates and expressed as relative standard deviations (RSDs%) were between 3.4 and 7.7% and obtained inter-day RSDs% at five different days were in the range of 7.9–12.7%. The preconcentration factors (PFs) were calculated based on the following equation

$$PF = \frac{C_{\text{org, final}}}{C_{\text{aq, initial}}} \quad (2)$$

where $C_{\text{org, final}}$ and $C_{\text{aq, initial}}$ are the final and initial concentrations of the analyte in 1-octanol and aqueous solution, respectively. $C_{\text{org, final}}$ of each extracted analyte was calculated using the calibration graph obtained from direct injections of standard solutions of each analyte in 1-octanol in concentration range of 1–20 mg L^{-1}. The obtained PFs were in the range of 87–348.

3.6. Analysis of real samples

Investigating the applicability of IP-SAME in water samples, the proposed method was applied for analysis of the analytes in several types of natural water samples collected from the tap water of Tabiat Modares University (Tehran, Iran), rain water (Tehran, Iran) and the mineral water (Koohdasht, Iran). Neither dilution nor further treatment was applied in the samples before extraction. No target analytes were found in these samples (this was anticipated

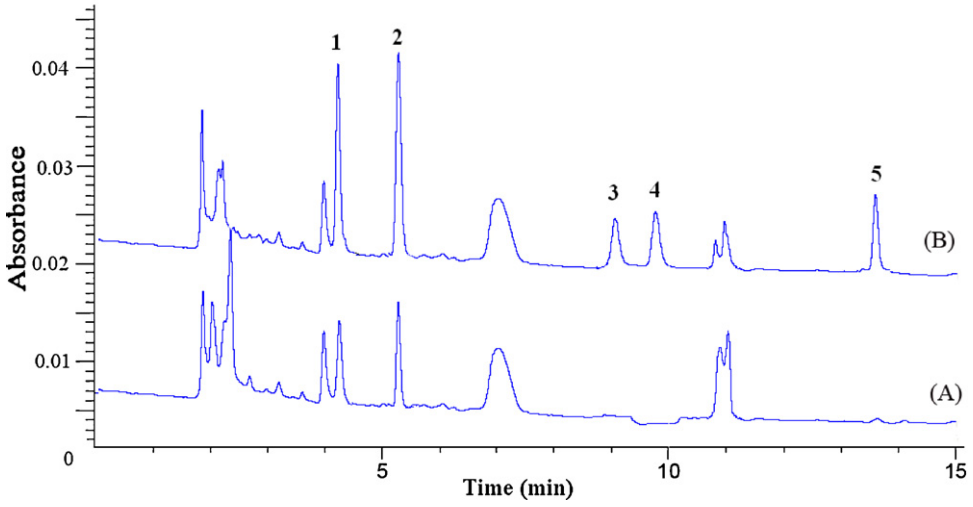

Fig. 6. HPLC–UV chromatograms of the (A) non-spiked and (B) spiked rain water by 5 μg L^{-1} of the target analytes, after IP-SAME. (1) 4-NP, (2) 3-NP, (3) 4-CA, (4) 3-CA and (5) 3,4-DCA. Suitable wavelength to detect each analyte was inserted in Section 2.2.

since CAs and NPs are not heavily used in the country). Determining the accuracy of the method, these samples were spiked with 5.0 $\mu g\,L^{-1}$ of each analyte. Relative recovery (%) and relative standard deviations (RSD%) for the analysis of target analytes in real water samples based on three replicate extractions are shown in Table 2. The obtained results demonstrated a good accuracy in all of the analyzed water samples. Fig. 6 shows IP-SAME-HPLC-DAD chromatograms of non-spiked and spiked rain water at the concentration level of 5.0 $\mu g\,L^{-1}$.

4. Conclusion

In the present study, a novel idea for simultaneous analysis of acidic and basic pollutants in natural waters was developed and validated. The proposed method is particularly time-saving, environmentally friendly, precise, reproducible and linear over a broad concentration range and also provides high preconcentration factor.

A comparison between the IP-SAME technique and the published values for extraction of selected NPs and CAs using SPME, LLLME, HF-LPME and other methods are shown in Table 3. The LOD, LDR and RSD% of analytes determination by the presented method are comparable with the other microextraction methods. The extraction time in IP-SAME is very short, approximately a few second, and the extraction equilibrium is attained very quickly. In addition to these advantages, it requires no extra approaches and is very simple, rapid, easy to use and environmentally benign. It is worthy to note that due to very high obtained PFs (87–348) for the analytes in the proposed method, by using sensitive detectors such as mass spectrometry very small LODs can be obtained.

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