Talanta 97 (2012) 279–284

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Rapid analysis of chlorinated anilines in environmental water samples using ultrasound assisted emulsification microextraction with solidification of floating organic droplet followed by HPLC-UV detection

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ARTICLE INFO

Article history:
Received 14 January 2012
Received in revised form
15 April 2012
Accepted 19 April 2012
Available online 3 May 2012

Keywords:
Ultrasonication-assisted emulsification microextraction
Solidification of floating organic droplet
HPLC-UV
Chlorinated anilines
Environmental water samples

ABSTRACT

The present study demonstrates a simple, rapid and efficient method for the determination of chlorinated anilines (CAs) in environmental water samples using ultrasonication assisted emulsification microextraction technique based on solidification of floating organic droplet (USAEME-SFO) coupled with high performance liquid chromatography-ultraviolet (HPLC-UV) detection. In this extraction method, 1-dodecanol was used as extraction solvent which is of lower density than water, low toxicity, low volatility, and low melting point (24 °C). After the USAEME, extraction solvent could be collected easily by keeping the extraction tube in ice bath for 2 min and the solidified organic droplet was scooped out using a spatula and transferred to another glass vial and allowed to thaw. Then, 10 μL of extraction solvent was diluted with mobile phase (1:1) and taken for HPLC-UV analysis. Parameters influencing the extraction efficiency, such as the kind and volume of extraction solvent, volume of sample, ultrasonication time, pH and salt concentration were thoroughly examined and optimized. Under the optimal conditions, the method showed good linearity in the concentration range of 0.05–500 ng mL^{-1} with correlation coefficients ranging from 0.9948 to 0.9957 for the three target CAs. The limit of detection based on signal to noise ratio of 3 ranged from 0.01 to 0.1 ng mL^{-1}. The relative standard deviations (RSDs) varied from 2.1 to 6.1% ($n=3$) and the enrichment factors ranged from 44 to 124. The proposed method has also been successfully applied to analyze real water samples and the relative recoveries of environmental water samples ranged from 81.1 to 116.9%.

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1. Introduction

Chlorinated anilines (CAs) are an important class of environmental water pollutants. They are used worldwide in different industries and could be released from the manufacturing of medicines, personal-care products, dyestuff, polymers and as by-products of energy technologies [1,2]. They can be easily discharged into rivers, lakes and soil by inappropriate waste disposal during their own production. Moreover, CAs are also formed from biodegradation of various phenylcarbamate, acylanilide and phenylurea herbicides [3,4]. Usually, this class of compounds is considered hazardous to human health and implicated in inducing damage to DNA and to cause cancer [5,6]. Especially, acute administration of 4-chloroaniline (4-CA) induced renal and hepatic toxicity and 2,6-dichloroaniline (2,6-DCA) has been identified as toxic to fish, crustaceans and mammals [7,8]. Dicloran or 2,6-dichloro-4-nitroaniline (DCNA) is a fungicide used for major crops including celery, lettuce and sweet potatoes. The toxicity of DCNA to organs include kidney, liver, spleen and hematopoietic system, particularly red blood cells [9,10]. As a result, these compounds have been included in the list of priority pollutants by the United States (US) Environmental Protection Agency (EPA) and also in European Union (EU) legislation. Accordingly, the surface water chronic estimated drinking water concentration (EDWC) is 2.76 ng mL^{-1} for 4-CA [11] and the EU predicted environmental concentration of 4-CA is 1 ng mL^{-1} [6]. The surface and ground water chronic EDWC for DCNA was estimated at 1.8 ng mL^{-1} and 1.3 ng mL^{-1} respectively [12]. Having known the highly toxic effects of the above mentioned pollutants in the environment and the complex environmental transformations that they undergo at the trace level, we aimed at developing a simple, rapid, reliable and sensitive analytical method for the determination of these compounds in environmental water samples.

High performance liquid chromatography (HPLC) and gas chromatography (GC) are the most commonly employed methods for the determination of CAs [13]. According to method 8131 of US EPA [14] for the analysis of aniline and its derivatives in

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http://dx.doi.org/10.1016/j.talanta.2012.04.031

extracts prepared from environmental samples by GC method, the detection limits of 4-CA and DCNA are 0.6 ng mL^{-1} and 2.9 ng mL^{-1} respectively. However, owing to the polarity and thermal lability of these compounds, a derivatization step is essential for obtaining good GC performance [15]. Hence, HPLC analysis seems to be a good alternative to GC analysis since no derivatization step is required [16]. Generally, a sample preparation step should be performed to obtain accurate and sensitive results in most analytical procedures. Of the various sample preparation methods established for sample pretreatment and preconcentration of CAs, liquid–liquid extraction (LLE) [17] suffers from the disadvantages of being tedious, time and large amounts of organic solvents consuming. Followed by LLE, solid-phase extraction (SPE) method was developed by Patsias and Mourkidou [18] for the determination of various chlorinated anilines, but SPE is a relatively expensive and laborious technique. Later on, single drop microextraction (SDME) and different modes of liquid-phase microextraction (LPME) techniques were introduced [19,20]. However, long extraction time, instability of the microdrop, and sometimes low precision are the disadvantages of LPME techniques. In 2006, Assadi and coworkers [21] introduced dispersive liquid–liquid microextraction (DLLME) technique and Wang et al. [22] used this method for the determination of halogenated anilines. However, poor detection limits (>0.8 ng mL^{-1}), usage of dispersive solvents and toxic chlorinated solvents as extraction solvents which is non environment-friendly, are the disadvantages of this method. In general, the variety of solvents that can be used in DLLME is limited. In 2005, Jiang et al. [23] developed ionic liquid based headspace LPME for the determination of CAs, but the disadvantages of this method include long extraction time of 30 min, and poor detection limits (ranged between 0.5–1 ng mL^{-1}). Then, Zhu et al., (2008) [24] developed ionic liquid (IL) based DLLME for the determination of aromatic amines. But this procedure yielded poor sensitivity when compared to other LPME methods. Moreover, usage of high density, low volatile ionic liquids gives overscale peaks in HPLC and GC and also contributes to rapid column degradation.

Taking the above disadvantages into account, an approach of utilizing the cavitation phenomenon of ultrasonic radiation to achieve dispersion has been proposed recently [25]. A novel DLLME method coupled with ultrasound radiation was introduced by Regueiro et al. in 2008 [26] and was termed ultrasound-assisted emulsification microextraction (USAEME). In this method, a micro-liter amount of water-immiscible extraction solvent is dispersed into water sample by ultrasound-assisted emulsification without using any dispersive solvent [27]. This method is simple, efficient and contributes to fast analyte extraction. However, this method requires high-density or highly toxic extraction solvents, such as chlorobenzene, carbon tetrachloride, chloroform and tetrachloroethylene etc., all of which are toxic and non environment-friendly [28].

Solidification of floating organic droplet (SFO) technique was first introduced by Yamini et al. [29] and was coupled with LPME for the determination of polycyclic aromatic hydrocarbons in water samples using GC. This is one of the effective LPME techniques that has been explored in recent research papers [30,31]. One of the main conditions for SFO technique is that the organic solvent must have melting point near room temperature (in the range of 10–30 °C), so that the droplet could be collected easily by solidifying it in lower temperature after the USAEME procedure. However, the extraction time is longer, thereby failing to satisfy the demand of rapid analysis. More recently, in order to achieve the merits of both USAEME and LPME-SFO techniques, a combination technique was introduced, termed as USAEME-SFO, that includes the advantages of large contact surface between the aqueous solution and the droplets of extraction solvent, thus speeding up mass transfer, so that the method was as fast as USAEME and had shorter extraction time than LLME-SFO [32,33].

The goal of the present study was to explore the potential application of USAEME-SFO for the fast analysis of CAs in environmental water samples by HPLC-ultraviolet (HPLC-UV) detection. To the best of our knowledge, this may be the first report about the application of USAEME-SFO method for the determination of CAs using 1-dodecanol as the extraction solvent (melting point: 24 °C). Various parameters affecting the extraction efficiency were examined and optimized. The present method was proven to be simple and had good analytical performance in terms of accuracy, linearity, repeatability, and limits of detection (LODs).

2. Experimental

2.1. Reagents and solutions

4-chloroaniline (98%) and 2,6-dichloroaniline (98%) were obtained from ACROS Organics, (New Jersey, USA) and dicloran (2,6-dichloro-4-nitroaniline, 95%) was purchased from Fluka Chemika, (Buchs, Switzerland). 1-dodecanol (density, 0.83 g/mL) and undecanol (density, 0.82 g/mL), were obtained from Merck (Hohenbrunn, Germany). HPLC-grade acetonitrile (ACN), acetone, ethanol, hydrochloric acid (HCl), methanol and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). All chemicals used in this work were of ACS reagent grade. Ultrapure water for all aqueous solutions was produced in the laboratory using Barnstead Nanopure water system (Barnstead, New York, USA). Stock solutions (1 mg/L of each analyte) were prepared by dissolving the CAs in methanol and stored in brown glass bottles with PTFE-lined caps and kept at 4 °C. Working standard solutions were obtained daily by diluting the stock solutions with ultrapure water.

2.2. Instrumentation

A liquid chromatograph (Knauer, Germany) with a UV/vis detector system (Knauer, Germany), was used for separation and determination of CAs. Extraction solvent collection and injections were carried out using a 50 μL HPLC microsyringe (SGE, Ringwood, Australia). Chromatographic separations were accomplished using a LiChrospher 100RP-18 (5 μm, 125 mm × 4 mm ID) column (Merck, Darmstadt, Germany) and all injections were performed manually with a 10 μL sample loop. Data acquisition and process were accomplished with a Euro-chrom Workstation (Knauer, Germany). The mobile phase was water and acetonitrile (30:70, v/v) at a flow rate of 0.7 mL/min. Detection was set at 240 nm. Under these chromatographic conditions, baseline separation could be obtained for the target compounds.

2.3. USAEME-SFO procedure

10 mL of aqueous sample was placed in a 15 mL screw-cap glass test tube with conical bottom. Then, 60 μL of 1-dodecanol (as extraction solvent) was rapidly injected into the above mentioned aqueous sample by a 0.5 mL syringe (SGE, Australia, Ringwood, Australia) and the resulting mixture was immersed in an ultrasonic bath (model D80, Delta, Taiwan) at 43 KHz frequency (80 W power) for 2 min (at 25 °C), following which a turbid cloudy solution was formed in the test tube. In this step, the analytes in aqueous sample were extracted into the fine droplets of 1-dodecanol. The formed emulsion was centrifuged for 6 min at 4000 rpm and the dispersed fine particles of the extraction phase were collected at the top of conical test tube which

was then kept in ice bath for 2 min. The solidified organic droplet was scooped out using a spatula and transferred to another glass vial and let to thaw. Then, the collected extraction solvent was measured and only 10 μL of extraction solvent was diluted with mobile phase (1:1) and taken for HPLC-UV analysis.

2.4. Calculation of extraction recovery and relative recovery

Extraction recovery (ER) [32] was calculated based on the following equation.

$$ER(\%) = (C_{fo}V_{fo})/(C_0V_{aq}) \times 100$$

where C_{fo} and C_0 are the concentration of analyte in the floating phase and initial concentration of the analyte in the aqueous sample; V_{fo} and V_{aq} are the volumes of the floating phase and aqueous sample, respectively.

Relative recoveries (RR) [32] of the CAs were calculated by subtracting the measured quantity of spiked sample (C_{real}), from the measured quantity of sample (C_{found}), divided by the spiked quantity (C_{spike}).

$$RR(\%) = C_{found} - C_{real}/C_{spike} \times 100$$

3. Results and discussion

In this study, a USAEME-SFO technique using 1-dodecanol as the extraction solvent combined with HPLC-UV was developed for the determination of CAs in water samples. In order to obtain better extraction recovery, the effect of different extraction parameters such as kind and volume of extraction solvent, ultrasonication time, pH and salt addition were thoroughly examined and the optimum conditions were selected.

3.1. Selection of extraction solvent

The selection of an appropriate extraction solvent plays vital role in the USAEME-SFO process. In the present study, solvents were selected based on density lower than water, low solubility in water, low volatility, low melting point, extraction capability of the interested compounds, and a good chromatographic behavior [29–33]. 1-dodecanol, 2-dodecanol, and 1-undecanol were selected and examined as extraction solvents for the extraction of CAs. A series of experiments were performed using 60 μL of extraction solvents. Fig. 1 demonstrates the extraction recoveries using these extraction solvents for the extraction of 100 ng mL^{-1} of three target CAs in 10 mL water sample under USAEME-SFO conditions, as described in Section 2.3. Results revealed that 1-dodecanol gave the highest extraction recoveries for all CAs compared to other extraction solvents. Therefore, 1-dodecanol was chosen for subsequent experiments.

3.2. Effect of volume of extraction solvent

To examine the effect of extraction solvent volume, 10 mL of aqueous sample solutions (100 ng mL^{-1} of three target CAs) containing different volumes of 1-dodecanol (40, 50, 60, 70, and 80 μL) were subjected to USAEME-SFO procedure. Fig. 2 shows the variation of extraction recoveries versus volume of the extraction solvent. By increasing the volume of 1-dodecanol from 40 to 80 μL, volume of the floating organic phase was increased from 20 to 70 μL (amount of measured organic phase after USAEME-SFO process). Accordingly, extraction recoveries of the target CAs increased till 60 μL and then decreased which might be because concentration of the analytes in the floating organic phase reached maximum when 60 μL of the extraction solvent was used and any further increase in the volume of extraction solvent lead to dilution of the analytes in the floating organic phase, thus decreasing the value of C_{fo}, thereby decreasing extraction recovery [31]. Hence, at 60 μL, high extraction recoveries with maximum extraction efficiency were obtained for all target CAs. Thus 60 μL was selected as the optimum volume of extraction solvent.

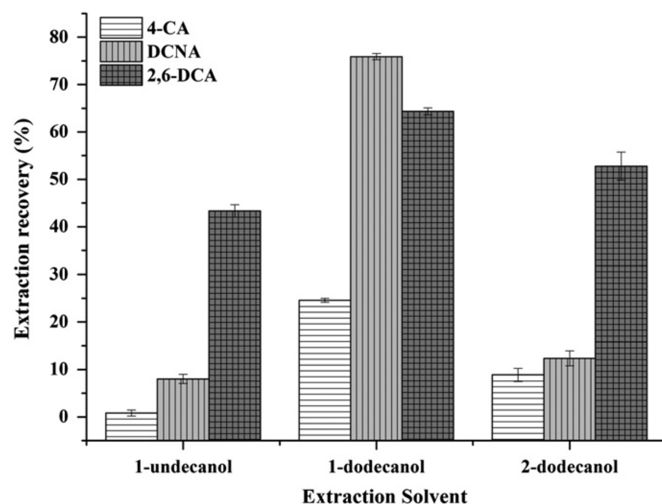

Fig. 1. Effect of extraction solvent on the extraction recovery. Sample: 10 mL of water sample (100 ng mL^{-1} of three target CAs) at pH 11. Volume of extraction solvent: 60 μL, Ultrasonication time: 2 min, $n=3$.

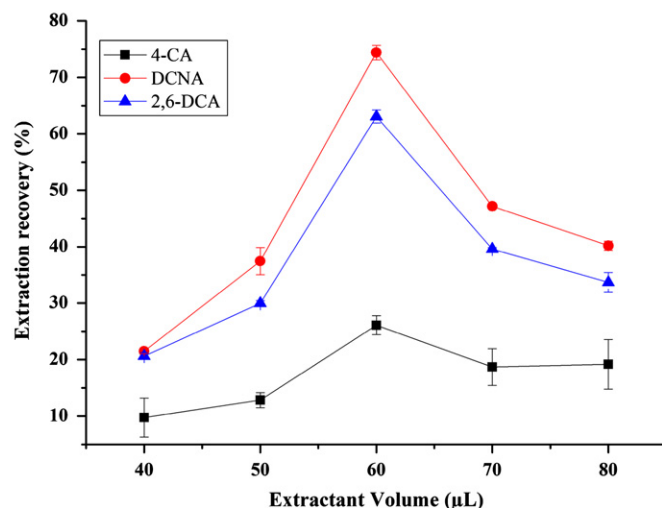

Fig. 2. Effect of volume of extraction solvent on extraction recovery. Extraction solvent: 1-dodecanol, Sample and extraction conditions: as in Fig. 1 except volume of extraction solvent.

3.3. Effect of sample pH and salt addition

pH plays a significant role in the extraction of ionizable compounds such as anilines, therefore the influence of pH in this USAEME-SFO method was evaluated. CAs are weak basic substances and pKa values for the deprotonation of protonated salts of 4-CA, 2,6-DCA and DCNA are 4.15, 2.97, and 3.31 respectively; hence they must be extracted in alkaline medium [34]. Therefore, the effect of pH was examined in the range of 3.0–13.0. The pH values of aqueous sample solutions were adjusted using 1 M NaOH for alkaline samples and 1 M HCl for acidic samples prior to spiking the target analytes. As shown in Fig. 3, when pH value was in the range of 7–11, the extraction efficiency of all the CAs

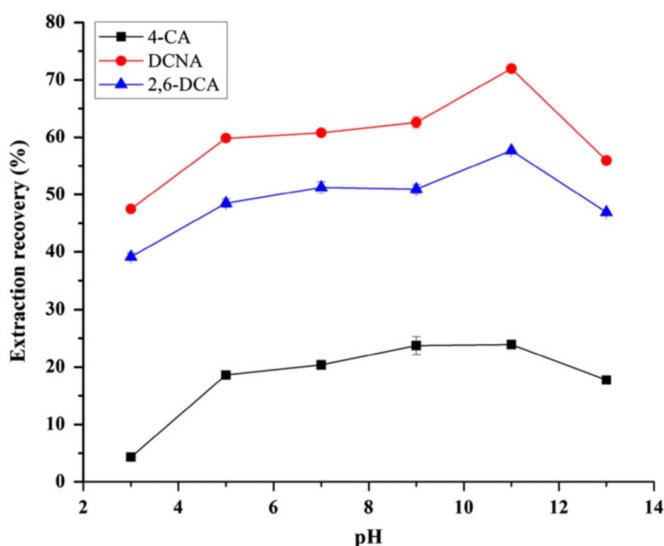

Fig. 3. Effect of sample pH on extraction efficiency. Sample and extraction conditions: as in Fig. 1 except sample pH.

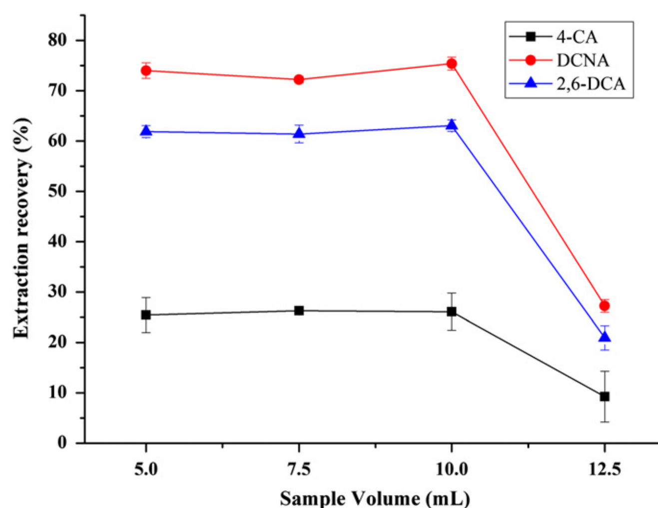

Fig. 4. Effect of sample volume on extraction recovery. Sample and extraction conditions: as in Fig. 1 except sample volume.

increased gradually. However, pH 13 resulted in a significant decrease of extraction efficiency. The reason could be the low stability of target CAs in highly alkaline environment probably because of sonochemical degradation at pH 13 condition, thereby decreasing extraction efficiency and hence the extraction recovery [35]. Hence, pH 11 was selected for the following experiments.

On the other hand, influence of ionic strength on the efficiency of USAEME-SFO was examined by adding NaCl (0–2.5% w/v) into the aqueous sample solution, while other experimental conditions were the same as described before. The obtained results exhibit that increasing the NaCl concentration from 0 to 2.5% showed no significant increase of extraction efficiency, but had an adverse effect (volume of the floating organic phase increased from 60 to 80 μL because of decreased solubility of extraction solvent in aqueous sample solution in the presence of salt) on the extraction of CAs. Also, results showed that salt addition has no considerable effect on the extraction recoveries. Therefore, salt was not added to the aqueous samples in the proposed method.

3.4. Effect of sample volume

Sample volume plays an important role in USAEME-SFO procedure [36]. Various sample volumes were investigated for this experiment from 2.5 to 12.5 mL of aqueous sample solution spiked with 100 ng mL^{-1} of the target CAs and the results revealed (Fig. 4) that 10 mL of sample solution showed maximum extraction recoveries for all the target analytes. Extraction recoveries increased very slightly as sample volume increased from 7.5 to 10 mL and it gradually decreased beyond 10 mL for all the three CAs, due to considerable decrease in the amount of extraction solvent recovery under ultrasonication (thereby decrease in extraction recovery) when the sample volume was increased beyond 10 mL. Thus, 10 mL of aqueous sample solution was taken as the optimum sample volume for subsequent analysis.

3.5. Effect of ultrasonication time

In USAEME-SFO, ultrasonication time is defined as the time interval between injecting the extraction solvent, and the time starting to centrifuge (similar to DLLME procedure) [27,30]. After the addition of 1-dodecanol, the sample solution was ultrasonically extracted at different time durations. In this study, a series of

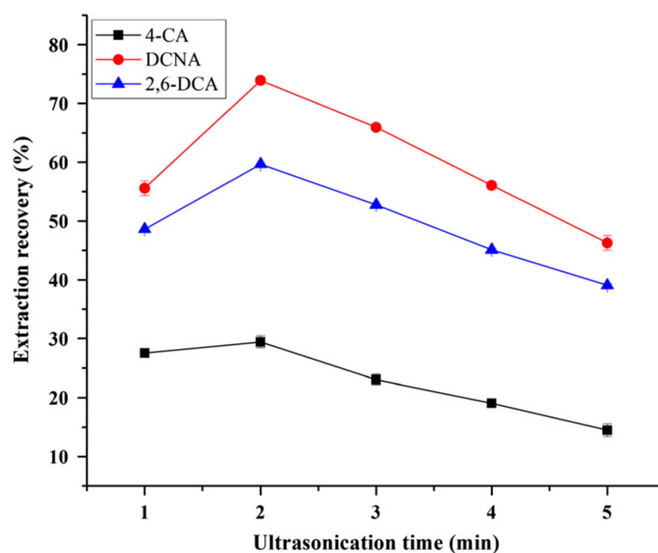

Fig. 5. Effect of ultrasonication time on extraction efficiency. Sample and extraction conditions: as in Fig. 1 except ultrasonication time.

ultrasonication times (1–5 min) were examined with same experimental conditions as mentioned in the previous section. Fig. 5 indicates that 2 min of ultrasonication provides the maximum extraction efficiency, after which a slight decrease in extraction efficiency could be seen. Maximum extraction could be achieved in a very short span because of the large contact surface area between extraction solvent and aqueous solution phase under ultrasonication, thus leading to fast extraction of target CAs from aqueous phase to extraction solvent, and the slight decrease in extraction efficiency after 2 min could be attributed to the fact that emulsion solution was unstable and it would delaminate in the course of over-extension of ultrasonication time, which could break the equilibrium and lead to lower extraction efficiency. Thus, 2 min of ultrasonication time was used for further experiments.

3.6. Evaluation of method performance

Under the above mentioned optimized conditions, linear dynamic ranges, correlation coefficients, LODs, relative standard

Table 1
Analytical performance of the proposed method.

Analyte	Linear range (ng mL^{-1})	Correlation coefficient (r^2)	LOD (ng mL^{-1})	RSD (%) (n=3)	Enrichment factor
4-CA	0.5–500	0.9954	0.1	2.1–6.1	44
DCNA	0.1–500	0.9948	0.07	2.5–5.5	124
2,6-DCA	0.05–500	0.9957	0.01	2.8–5.9	96

deviations (RSDs) and enrichment factors were investigated and summarized in Table 1. All the analytes showed good linearity, which ranged from 0.5–500 ng mL^{-1} for 4-CA, 0.1–500 ng mL^{-1} for DCNA and 0.05–500 ng mL^{-1} for 2,6-DCA respectively. The concentration levels used for calibration were 500, 250, 100, 75, 25, 1 and 0.5 ng mL^{-1} for 4-CA and for DCNA, the concentration levels used were 500, 250, 100, 75, 25, 1, 0.5 and 0.1 ng mL^{-1}. For 2,6-DCA, the concentration levels used were 500, 250, 100, 75, 25, 1, 0.5, 0.1 and 0.05 ng mL^{-1}. Correlation coefficients ranged from 0.9948 to 0.9957 for the target CAs. LODs were calculated as the analyte concentration equal to 3 times the standard deviation of the blank signal divided by the slope of the calibration curve. The LODs were in the range of 0.1–0.01 ng mL^{-1}. Precisions were also important for the proposed method, and it was obtained by performing three reduplicate extractions of spiked water samples with the concentrations used for calibration under optimal conditions, and they were achieved in the range of 2.1–6.1%. Enrichment factors were calculated as the ratio of final concentration of the analyte in the organic phase to its concentration in the original solution (which is 100 ng mL^{-1} of each analyte) under optimal conditions and it ranged from 44 to 124.

3.7. Application to environmental water samples

Applicability of the proposed method and the effect of matrix upon extraction efficiency were evaluated for the extraction of target CAs in real water samples. The developed method was employed in conjunction with the external standard calibration method (using standard addition procedure) [37,38] to quantitate the concentration of target analytes in river water samples. Two river water samples (sample 1 and sample 2) collected from two different parts of a river in the agriculture district of Dali (Taichung City, Taiwan) were filtered with 0.45 μm cellulose acetate membrane filters in order to eliminate any fine particulates and debris in the water samples. Then, pH of the samples was adjusted to 11 and stored at 4 °C till analysis time. Blanks of the river water samples were run to determine the presence of target analytes. Experimental results exhibited that no significant quantities of interested CAs were detected from two river water samples. As can be seen in Fig. 6b, typical chromatogram of the blank (non-spiked) river water sample 1 obtained by the USAEME-SFO-HPLC-UV method did not contain any of the tested analytes, nor did it have any interfering peaks. The external standard calibration plots were built with various concentration levels (concentration ranges of CAs as given in Table 1 were used) of CAs by spiking the standard solutions to river water sample 1 blanks. LODs obtained were 0.16 ng mL^{-1} (4-CA), 0.08 ng mL^{-1} (DCNA), and 0.02 ng mL^{-1} (2,6-DCA) and correlation coefficients of the external standard calibration curves were obtained in the range of 0.9946–0.9955. Table 2 lists the correlation coefficients of the external standard calibration curves of the river water sample 1 and the spiked recoveries and RSDs of CAs for two river water samples at the two spiked concentration levels (75 ng mL^{-1} and 1 ng mL^{-1} of all target analytes) under optimal experimental conditions. Fig. 6a shows the chromatogram of the

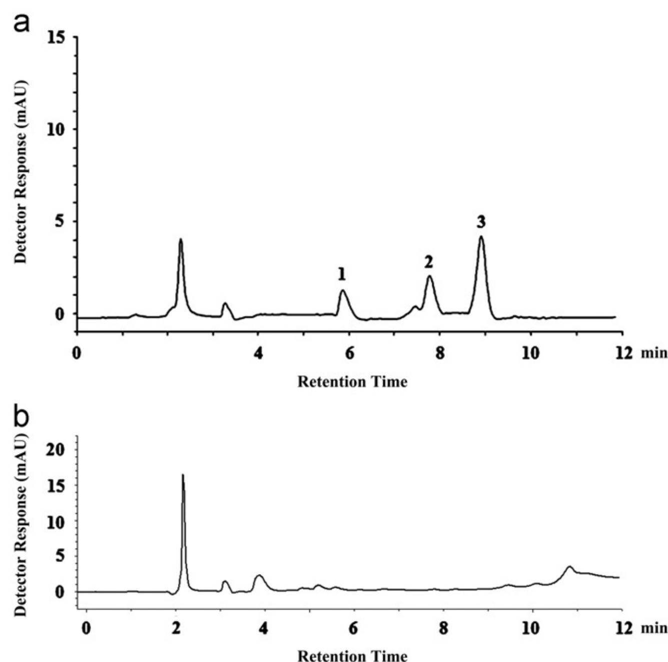

Fig. 6. Chromatogram of CAs in (a) spiked sample in river water and (b) non-spiked river water 1, by the proposed method. Spiked sample: 1 ng mL^{-1} of three target CAs. Peaks 1–3 refers to 4-CA, DCNA and 2,6-DCA respectively.

Table 2
Correlation coefficients, precisions and recoveries of CAs with the proposed method in spiked river water samples.

Analyte	Correlation coefficients (r^2)[a]	Spiked Conc.[b] (ng mL^{-1})	River water sample 1		River water sample 2	
			Recovery (%)	RSD (%) (n=3)	Recovery (%)	RSD (%) (n=3)
4-CA	0.9947	75	116.9	4.4	115.4	5.1
		1	81.1	7.9	83.9	7.2
DCNA	0.9946	75	105.4	2.8	103.7	3.6
		1	96.8	4.5	90.6	4.2
2,6-DCA	0.9955	75	104.5	5.3	108.7	3.3
		1	94.1	6.7	96.6	4.6

[a] Correlation coefficients (r^2) of the external standard calibration curves of river water sample; LODs are 0.16 ng mL^{-1} (4-CA), 0.08 ng mL^{-1} (DCNA), and 0.02 ng mL^{-1} (2,6-DCA).
[b] Spiked concentrations in river water samples.

spiked river water sample 1 obtained by the proposed method. Relative recoveries of the CAs ranged from 81.1 to 116.9 % for river water sample 1 and from 83.9 to 115.4 % for river water sample 2. The RSDs ranged from 2.8 to 7.9 % for river water sample 1 and from 3.3 to 7.2 % for river water sample 2. Moreover, we also studied the effect of matrix on extraction efficiency by adding 10, 50, 100, 250 and 500 ppm humic acid in real water sample [13]. Experimental results indicated that increasing the humic acid concentration from 0 to 10 ppm showed no significant increase of extraction efficiency and beyond the addition of 10 ppm humic acid, there was decrease in extraction efficiency. Since the concentration of humic acid does not exceed 10 ppm in natural waters [39,40], it can be said that the matrices of real water samples do not have obvious effect on the proposed USAEME-SFO-HPLC-UV method for the extraction of target CAs. These merits show that this improved method could be a creative development for the fast determination of CAs in analytical and environmental fields.

Table 3
Comparison of the proposed USAEME-SFO method with other methods.

Method	*Total extraction time (min)	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	RSD (%)	Reference
IL-HS[a] LPME–HPLC	30	1–150	0.5–1	5–7	[23]
HF[b] LLLME–HPLC	30	0.5–500	0.05–0.1	4.89–7.26	[13]
HF-LPME–HPLC	80	5–200	0.5–1.5	–	[41]
LLLME[c] HPLC	15	2.5–250 × 10^3	0.85–1.8	2.07–10.9	[42]
IL-DLLME–HPLC	2	2–200	0.45–2.6	6.2–9.8	[24]
USA-IL-DLPME[d] HPLC	50	1.5–100	0.17–0.49	2–6.1	[43]
DLLME–HPLC	2	5–5000	0.8–1.8	4.1–5.3	[22]
USAEME-SFO–HPLC	10	0.05–500	0.01–0.1	2.1–6.1	This method

* Total extraction time refers to the overall time taken for the extraction procedure, including ultrasonication, centrifugation and solidification, wherever applicable.
[a] HS—Headspace.
[b] HF—Hollow fiber.
[c] LLLME—Liquid–liquid–liquid microextraction.
[d] DLPME—Dispersive liquid phase microextraction.

3.8. Comparison of USAEME-SFO with other methods

The analytical performance of the represented USAEME-SFO method combined with HPLC-UV for the analysis of CAs in water samples was compared with the corresponding performance of other methods [13,22–24,41–43] for the extraction and determination of three target CAs from water samples. As can be seen from Table 3, superiorities over the other methods include lowest LODs in comparison with other methods, good linear ranges and precisions. Moreover, 1-dodecanol is used as the extraction solvent, thus preventing the use of toxic chlorinated solvents. Therefore, the present method can be used as an alternative method for the determination of CAs in environmental water samples.

4. Conclusion

In this study, a fast and sensitive USAEME-SFO method combined with HPLC-UV has been developed for the analysis of trace levels of CAs in environmental water samples. When compared with other reported methods, the present method avoids derivatization process and can be performed with a much shorter extraction time. Moreover, the method requires only small volume of low toxicity extraction solvent. From the results of the applicability test for the analysis of CAs in aqueous samples, the present approach showed good linearities and satisfactory relative recoveries, thus proving to be an efficient, convenient, inexpensive and environment-friendly method. Thus, the present technique possesses great potential in the rapid preconcentration and analysis of CAs from environmental water samples and represents an attractive alternative to both traditional and recently developed methods.

Acknowledgments

The authors thank the National Science Council of Taiwan under grants of NSC-96-2113-M-005-0021-MY3, NSC-98-2113-M-005-016-MY3 and National Chung Hsing University for financial supports.

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