Talanta 84 (2011) 587–592

Contents lists available at ScienceDirect

Talanta

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

Short communication

Determination of linear alkylbenzene sulfonates by ion-pair solid-phase extraction and high-performance liquid chromatography

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ARTICLE INFO

Article history:
Received 15 October 2010
Received in revised form
21 December 2010
Accepted 6 January 2011
Available online 15 January 2011

Keywords:
Ion-pair solid-phase extraction
Linear alkylbenzene sulfonates
Multiwalled carbon nanotubes
High-performance liquid chromatography

ABSTRACT

In this paper, the potential use of multiwalled carbon nanotubes (MWCNTs) as solid phase extraction (SPE) adsorbent was evaluated for preconcentration of linear alkylbenzene sulfonates (LAS) using ion-pair (IP)-SPE with tetrabutylammonium hydroxide (TBAH). The LAS homologues present in the aqueous sample were ion-paired with TBAH and the solution was passed through the MWCNT cartridges. The analytes retained in the cartridge were eluted with methanol and the concentrated methanol extract was analysed by HPLC-UV. In order to obtain the satisfactory recovery of LAS homologues, various parameters including the type and amount of the ion-pair reagents, the desorption and enrichment conditions such as the effect of eluent and its volume, pH, the flow rate, the ultrasonic time of sample, and the volume of sample solution were systematically optimized. Under the optimal conditions, LAS homologues could be easily extracted by the proposed SPE cartridge. The favorable limits of detection (LOD) for LAS homologues were in the range from 0.02 to 0.03 μg L^{-1}, and the relative standard deviations (RSDs) were 1.55–2.54% for 10 μg L^{-1} LAS ($n = 6$). The proposed method has been successfully applied for the analysis of LAS homologues in aqueous environmental samples. A comparison study with ion-pair solid extraction on MWCNTs, C8 and C18 as adsorbents for LAS demonstrated that ion pair-based solid extraction on MWCNTs adsorbent was advantageous over C8 and C18, the widely used traditional adsorbents.

1. Introduction

As the most widely used synthetic anionic surfactant with the global production of about 2.4×10^6 t year^{-1} [1], LAS is a ubiquitous water contaminant with concentration in the μg L^{-1} level ranging from low to 0.1 μg L^{-1} and high to above 100 μg L^{-1} in water column [2,3] due to its high-volume use in laundry and cleaning products. In the terrestrial environment, LAS also showed some biological effects [4,5], for example, it has been found that ammonia-oxidizers are thought to be more sensitive to LAS than other microorganisms [5], which may lead to disturbances of water ecology system.

Various analytical techniques have been developed for LAS determination such as enzyme-linked immunoassay [6] and chemiluminescence immunoassay [7], high-performance liquid chromatography (HPLC) combined with various types of detectors including fluorescence (FL)[8], diode array (DAD) [9], ultra-violet (UV) [10,11], and mass spectrometry [12–15].

In order to determine trace level of LAS, sample pretreatment is a needed step in the analytical procedure because sample pretreatment can lower the limit of detection and eliminate the matrix interference. Solid-phase extraction (SPE) is the most important and routinely used technique for sample enrichment among various pretreatment methods [16] and has been extensively used in sample pretreatment for LAS analysis at trace level [10,11,17].

In recent years, a novel SPE method using CNTs as adsorbent has attracted much attention [18–20]. The advantages of the carbon nanotubes-based SPE method are rapidity, low cost and high enrichment factors derived from their strong hydrophobicity and high surface area. Since the first work on CNTs as SPE adsorbents for the determination of bisphenol A, 4-n-nonylphenol, and 4-tert-octylphenol successfully [21], CNTs as SPE adsorbents have been investigated to extract various organic compounds and inorganic ions [22–29]. Very recent work demonstrated that SWCNTs (single-walled carbon nanotubes) possess intrinsic peroxidase-like activity [30]. All these achievements provide new insights into the application of this novel material in environmental analysis and biosensing. However, almost all above studies concerning MWCNTs as SPE adsorbents for enrichment of organic compounds were based on direct adsorption of the non-polar or weak polar targets onto surface of MWCNTs. There are some challenges to use pristine

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doi:10.1016/j.talanta.2011.01.014

MWCNTs for enrichment of highly polar targets due to their poor retention ability.

Ion-pair extraction is a method for partitioning of ionic compounds with the aid of counter-ions of opposite charge, and can be used to increase retention of highly polar compounds on non-polar or weak polar SPE adsorbents. Here, we report that pristine MWCNTs have a predominant ability to capture highly polar linear alkylbenzene sulfonates (LAS) when LAS was ion-paired with tetrabutylammonium hydroxide (TBAH, a typical ion-pair reagent) in environmental water samples, showing a high enrichment for LAS in a SPE-based format. Comparison studies with the traditional C8 and C18 adsorbents indicate that the proposed SPE adsorbent has higher enrichment ability to LAS than the C18 and C8 adsorbents. To the best of our knowledge, this is the first report of using ion-pair formation combined with pristine MWCNTs for enrichment of linear alkylbenzene sulfonates in environmental water samples.

2. Experimental

2.1. Chemicals and reagents

Commercial LAS mixture (C_{10} (19.16%), C_{11} (30.1%), C_{12} (28.65%) and C_{13} (22.09%)) was supplied by Sigma–Aldrich. Acetonitrile and methanol were of the HPLC grade (Scharlau Chemie S.A., Spain). MWCNTs with purity of 95%, general outer diameters of about 30–50 nm, the length of about 20 μm, and the surface area of above 60 $m^2\,g^{-1}$ were purchased from R&D Center of Carbon Nanotubes, Chengdu Organic Chemicals Co., Chinese Academy of Sciences. Before use, MWCNTs were dried at 100 °C for 2 h. Tetrabutylammonium hydroxide (TBAH) solution (10.0%, v/v in water), tetrabutylammonium bromide (TBAB), cetyltrimethylammnonium bromide (CTAB), cetyltrimethylammnonium chloride (CTAC), sodium fluoride, acetone, and hydrochloric acid were purchased from Chongqing Chemical Reagents Co., Ltd. C8 and C18 Sep-Pak cartridges (500 mg) were supplied by Waters Cooperation, USA. Ultra pure water was prepared in the lab using a water treatment device. All other solvents and reagents used were of analytical reagent grade unless otherwise stated.

2.2. Instrumental analysis

The HPLC instrument (JASCO Corporation, Japan) used was composed of two JASCO PU-2080i plus intelligent HPLC inert pumps, JASCO CO-2060 plus intelligent column thermostat and a JASCO UV-2075 plus intelligent UV detector. Chromatographic separation was performed on a Symmetry C8 column (150 mm × 4.6 mm, 5 μm) (Waters Corporation, USA) with a guard column. The mobile phase used in the chromatographic separation consisted of a binary mixture of methanol and water (0.5 mmol L^{-1} sodium acetate was added into mobile phase in order to improve separation of LAS homologues [10]) with the ratio of 75:25 at a flow rate of 0.5 mL min^{-1}. The column temperature was 30 °C, and the chromatographic data were acquired at 224 nm. The injection volume of sample was 20 μL. JASCO Chrompass Chromatography Data System was used to control the chromatographic units, acquire and process chromatographic data.

2.3. SPE procedure

0.2 g MWCNTs were packed in an empty 6-mL polypropylene cartridge, which was purchased from SUPELCO Corporation, USA. Before extraction, 6 mL of methanol and 6 mL of ultra pure water were adopted, respectively, to pass through the MWCNTs packed cartridge for the purpose of precondition. Extraction of the target LAS compounds was carried out by adding 100 mL of the mixed solution of LAS standard (or 500 mL of sample solution) at the desired concentration and 40 mg L^{-1} TBAH to pass through the packed cartridge under vacuum at a certain flow rate, followed by a rinsing step using 10 mL of ultra pure water. And then the cartridge was dried under a certain negative pressure (20 mm Hg) for 10 min. The concentrated target LAS compounds were eluted with the optimal organic solvent (6 mL of methanol), and the eluates were evaporated to dryness by a stream of nitrogen gas, and the residue was dissolved with 0.5 mL of ultra pure water. Finally, a volume of 20 μL was injected into the HPLC. The recovery was used as criterion to optimize the parameters for ion-pair SPE. The recovery was calculated as the ratio of the amount of LAS with and without preconcentration.

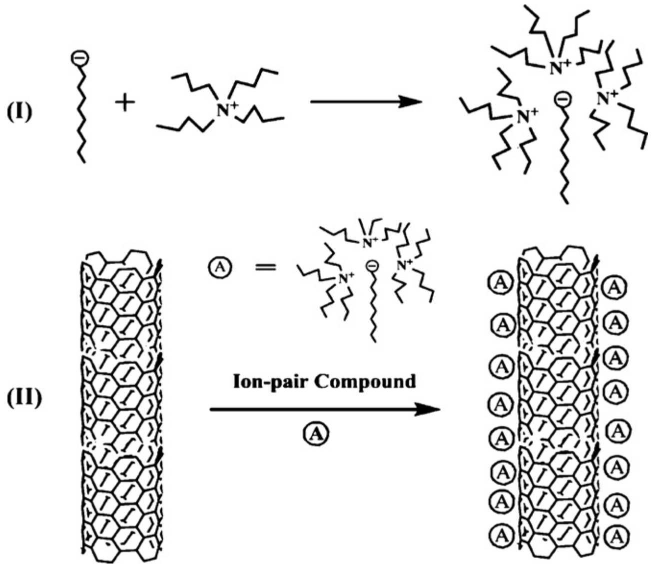
Breakthrough volumes of MWCNTs-based SPE column were evaluated by using different sample volumes (250, 500, 750, 1000 and 1500 mL) with the same LAS concentration of 50 μg L^{-1}.

2.4. Water samples

Tap water and river water samples were selected for investigation. The tap water sample was collected from our laboratory after flowing for 10 min and the river water sample from the Jialingjiang River in the area of central Chongqing. Before experiment, the environmental water samples were filtered through 0.45 μm micropore membrane (Tianjin Automatic Science Instrument Co., Ltd., China) and stored in brown glass bottles at 4 °C in a refrigerator. For real water sample analysis, 1 mL of 100 mmol L^{-1} sodium fluoride as masking agent was added to 500 mL (adjusted to pH 5) of the environmental water samples for eliminating the interference of metal ions. Note that if the precipitation takes place after addition of sodium fluoride, the sample should be filtered through 0.45 μm membrane filters, and then used for analysis of LAS homologues.

3. Results and discussion

Our approach was based on hypothesis that formation of ion-pair between negatively charged LAS homologues and positively charged ion-pair reagent or surfactant through electrostatic interactions would decrease the polarity of LAS homologues, which might lead to enhanced adsorption of LAS onto MWCNTs. Scheme 1 presents an illustration for formation of the ion-pair and then adsorption by MWCNTs. In order to study this, different reagents



Scheme 1. An illustration for formation of the ion-pair between negatively charged LAS homologues and positively charged ion-pair reagent TBAH (I), and then adsorption by MWCNTs (II).

Table 1
Comparison of LAS recoveries using IP-SPE with different ion-pair reagents on MWCNTs.

Analyte	Recovery %[a]		
	TBAB	TBAH	Without IP
C10	48.7 ± 4.7	95.9 ± 1.8	19.2 ± 5.9
C11	49.7 ± 5.8	94.0 ± 1.7	19.5 ± 3.9
C12	55.2 ± 7.0	103.2 ± 5.9	13.0 ± 1.0
C13	54.6 ± 9.3	107.7 ± 3.6	14.0 ± 2.4

[a] Average ± standard deviation ($n = 3$). Conditions for LAS enrichment are as following. Sample solution volume: 100 mL (pH 5); LAS concentration in sample solution: 50 μg L^{-1}; eluent: 6 mL methanol; sonication time: 3 min; concentrations of ion-pair agents: 40 mg L^{-1}; sample flow rate: 6 mL min^{-1}.

such as ion-pair reagent TBAH, TBAB, positively charged surfactant CTAB, and CTAC were tested for recovery of LAS in water samples. Our experimental results suggested that there were no peaks of LAS homologues detected by HPLC-UV after enrichment by MWCNTs through ion-pair formation using 40 mg L^{-1} of CTAC or CTAB. However, quantitative recovery of LAS was obtained when TBAH was used as ion-pair reagent (Table 1). So, TBAH was selected for further study in the present work.

3.1. Optimization for the ion-pair solid-phase extraction

3.1.1. Effect of TBAH concentration

The effect of TBAH concentration on adsorption of the studied LAS homologues onto MWCNTs column was studied in the range from 0 to 40 mg L^{-1}. As can be seen from Fig. 1 that the recovery of LAS increased sharply when TBAH concentration was above 10 mg L^{-1}. No significant difference of recoveries was observed when the TBAH concentration ranged from 0 to 10 mg L^{-1}. When TBAH concentration reached 20 mg L^{-1}, great enhancement of LAS recovery was obtained. However, quantitative recovery for LAS homologues was obtained at 40 mg L^{-1} of TBAH concentration. In order to get better recoveries, 40 mg L^{-1} of TBAH concentration was recommended for further experiments.

3.1.2. Effect of the eluent

Desorption of the target analytes LAS homologues from the MWCNTs packed cartridge was investigated using different organic solvents such as methanol, acetonitrile, acetone, and dichloromethane. The experimental results demonstrated that all the above selected organic solvents could elute the target analytes, in which methanol and acetone gave the best elution ability. Considering that a binary mixture of methanol and water with the ratio of 75:25 was used as mobile phase in our case, it may have been more appropriate to use methanol as eluent. Then the volume of the methanol was investigated between 2 and 6 mL. The experimental results indicated that the recoveries increased with the increasing of methanol volume from 2 to 5 mL. It remained stable from 5 to 6 mL, being quantitative in this interval. In order to obtain a higher preconcentration factor and satisfactory recovery, finally, 6 mL methanol was selected as optimal eluent to obtain the quantitative results.

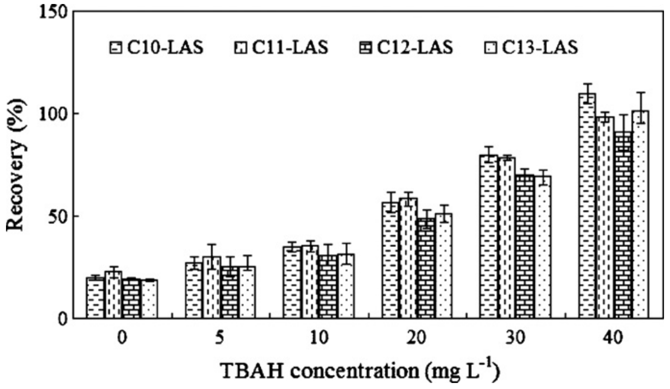


Fig. 1. Effect of TBAH concentration. MWCNTs: 200 mg; LAS concentration: 50 μg L^{-1}, sample solution volume: 100 mL (pH 5), sample flow rate: 2 mL min^{-1}; eluent: 6 mL methanol. Error bars represent one standard deviation for three measurements.

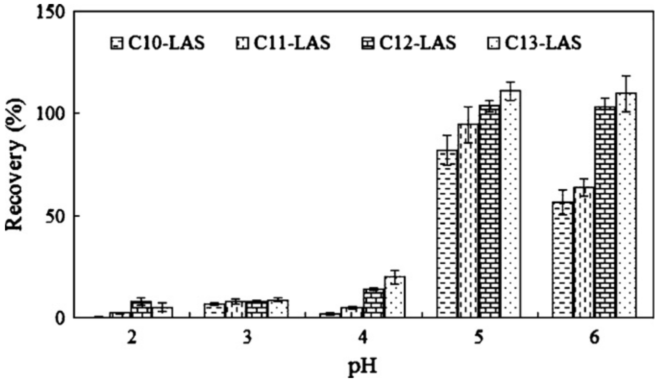


Fig. 2. Effect of sample pH. TBAH concentration: 40 mg L^{-1}; ultrasonic time: 3 min; other conditions were same as in Fig. 1. Error bars represent one standard deviation for three measurements.

3.1.3. Effect of the ultrasonic treatment

The experimental results demonstrated that the ultrasonic treatment of the mixture of sample solution and TBAH could enhance the retention of LAS homologues on MWCNTs probably because of the reduction in surface tension of the surfactant solution under ultrasonic condition. Similar enhancement effect was also observed in our previous work [11]. The recovery of LAS increased with ultrasonic time of the mixture of sample solution and TBAH in the range from 1 to 3 min for LAS homologues at 50 ng mL^{-1} concentration level. When the ultrasonic time exceeded 4 min, the recoveries decreased. Therefore, 3 min was chosen to get the better recoveries.

3.1.4. Effect of pH

The influence of solution pH on the recoveries of analytes is shown in Fig. 2. As can be seen that the studied LAS homologues could hardly be recovered in the highly acidic medium. With increase of solution pH, the retention of all analytes on MWCNTs increased. And the highest retention for all analytes was obtained at pH of 5, which was consistent with previous work by Akyüz [31]. The effect of solution pH on retention of LAS homologues is related to the degree of ionization of the sorbates and on the ability to form ion-pairs with the cationic ion-pair agent. The pK_a of alkylsulfonates range in values between 2.0 and 3.0 depending on the substituents on the alkyl group [32]. So, at the pH value less than 3, LAS existed mainly in the molecular forms. The ion-pair complex between LAS molecular and the TBAH with positive charge was hardly formed, leading to low recoveries of LAS homologues. In addition, it is highly possible that the rapid conversion of TBAH to its corresponding hydrochloride salt in the highly acidic medium, and hence the ion pairing ability becomes poor due to this rapid salt equilibrium [33]. When the pH value of solution was above 3, the increase on the retention of LAS homologues can be ascribed to the ion pair formation between the negatively charge LAS anion due to deprotonation and the cationic TBA$^+$. At a pH value of 5.0, quantitative recoveries of LAS homologues could be obtained. When the surfaces of most LAS molecules were negatively charged, leading to formation of ion-pair complex with the cationic TBAH with quantitative recoveries of LAS homologues. Consequently, a pH value

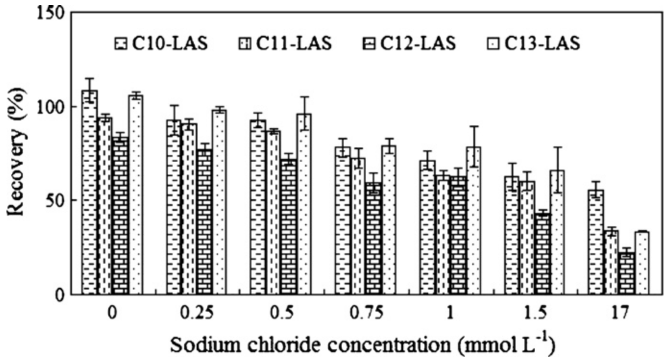


Fig. 3. Effect of sodium chloride concentration. TBAH concentration: 40 mg L^{-1}; ultrasonic time: 3 min; other conditions were same as in Fig. 1. Error bars represent one standard deviation for three measurements.

of 5.0 was chosen for the optimum retention of the target compounds.

3.1.5. *Effects of ionic strength*

Further experiments were conducted to investigate the effect of ionic strength on the extraction of LAS homologues. Sodium chloride was selected to investigate ionic strength effect in this study. The examined NaCl amount ranged from 0 to 17 mmol L^{-1}. As shown in Fig. 3 that addition of sodium chloride decreased retention of all analytes on MWCNTs rather than enhancing them. The effect of electrolytes on retention of LAS homologues is related to the effects of NaCl addition to the sample solution. Generally, addition of NaCl to the sample solution increases the ionic strength of solution as well as changes the physical properties of the Nernst diffusion layer. It is well known that addition of salt can decrease the solubility of analytes in the aqueous sample [34,35], and hence is benefit to extraction of target analytes. However, addition of sodium chloride also reduces mass transfer by changing the Nernst diffusion layer, probably leading to the decreased rate of the formation of ion pairs of the analytes [36,37], therefore decreasing the extraction efficiency. Results shown in Fig. 3 clearly suggest that the higher the concentration of NaCl is, the lower the rate of formation of ion pairs of LAS homologues in the aqueous sample is. On the basis of above experimental results, sodium chloride was not added to the aqueous sample in the subsequent experiments.

3.1.6. *Effect of sample flow rate and volume*

The effect of the sample flow rate was investigated over the range from 2 to 10 mL min^{-1} (the maximum flow rate of the vacuum pump). The experimental results demonstrated that when the flow rate of sample solutions was below 6 mL min^{-1}, the recoveries of LAS homologues remain stable over 99%. For flow rate above 6 mL min^{-1}, the increase in flow rate induced a general decrease in recovery. Considering the sensitivity and the analytical time in this study, 6 mL min^{-1} was chose as the optimal flow rate for further experiment.

Breakthrough volumes and optimal sample volume were investigated in order to obtain an enrichment factor as high as possible. Breakthrough was considered to occur when the recovery was below 95%. As can be seen form Fig. 4 that the good recoveries of the LAS homologues were obtained with no significant difference when the sample volumes ranged from 250 to 1000 mL. However, the recoveries were lower than 40% for LAS homologues when the sample volume increased to 1500 mL, so the breakthrough volumes for LAS homologues on MWCNTs SPE cartridges through ion-pair formation were 1000 mL. Considering the enrichment factor, the packed amount of MWCNTs in cartridge (about 200 mg) used in present study and the experimental time, finally, sample volume of 500 mL was selected for further investigation to achieve the reliable experimental results and a high enrichment factor because the recoveries for all the analytes were satisfactory.

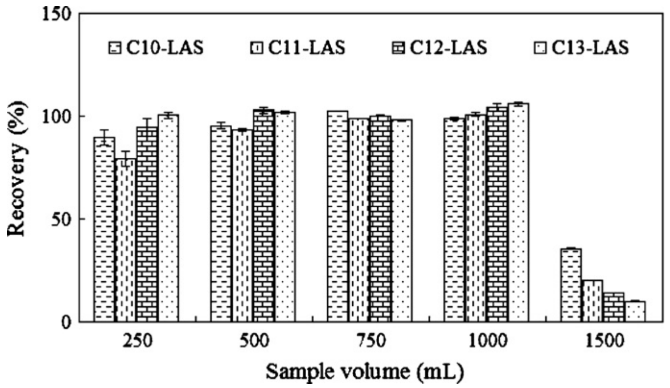


Fig. 4. Effect of sample volume. The sample flow rate: 6 mL min^{-1}; TBAH concentration: 40 mg L^{-1}; ultrasonic time: 3 min; other conditions were same as in Fig. 1. Error bars represent one standard deviation for three measurements.

3.2. *Method performance evaluation*

Calibration curves were run for LAS homologues in the range 0.2–30 μg L^{-1} by the proposed method. As can be seen from Table 2 that the correlation coefficients were between 0.9945 and 0.9997. The detection limits of the LAS homologues ranged from 0.02 to 0.03 μg L^{-1} (S/N = 3). The precision of the overall procedure, expressed as relative standard deviations (RSDs), was evaluated by extracting eleven consecutive ultra pure water samples which diluted from a standard solution. The RSDs ranged from 1.55 to 2.54% (n = 6) at the 10 μg L^{-1} level of LAS homologues, demonstrating good precision of the method. When 500 mL of water sample was used, the enrichment factors of LAS C10, C11, C12 and C13 were 953, 932, 995, 999, respectively. In order to check the validation of the proposed method, the recovery tests were carried out using MWCNTs, C8, and C18 SPE cartridge for enrichment of 10 or 30 μg L^{-1} LAS in ultra-pure water samples. As illustrated in Table 3, the proposed method can be satisfactory applied to the determination of LAS in environmental water samples.

3.3. *Application to environmental water samples and comparison study*

As an illustration of analytical application, the proposed method was used to determine LAS homologues in the environmental water samples under the optimal experimental conditions shown above using MWCNTs as SPE cartridge and TBAH as the ion-pair agent. Fig. 5 depicts the chromatograms of river water sample and spiked river water sample. The results for LAS determination for unspiked and spiked water samples were shown in Table 3. Also, the commercial C8 cartridge (500 mg) and C18 cartridge (500 mg) as SPE adsorbents for LAS enrichment were tested. The results of target analysis in water samples enriched by the MWCNTs as SPE cartridge (200 mg) and TBAH as the ion-pair agent, C8 cartridge (500 mg) and

Table 2
Linear range, correlation coefficients, relative standard deviation, and limits of detection.

Compound	Linear range (μg L^{-1})	R^2	RSD (%) (n = 6)	LOD (μg L^{-1})
C10-LAS	0.1916–19.16	0.9997	2.18	0.02
C11-LAS	0.3010–30.01	0.9993	2.54	0.03
C12-LAS	0.2865–28.65	0.9984	2.16	0.03
C13-LAS	0.2209–22.09	0.9945	1.55	0.02

Table 3
The results of LAS determination in Jialingjiang River water and tap water samples.

Compound	Added (μg L^{-1})	Found[a] (μg L^{-1})			Recovery[a] (%)		
		MWCNTs	C8	C18	MWCNTs	C8	C18
(A) Ultra-pure water sample							
C10-LAS	1.46	1.45 ± 0.03	1.18 ± 0.20	1.33 ± 0.09	99.5 ± 1.8	88.4 ± 1.8	90.8 ± 6.0
	4.37	4.44 ± 0.13	3.82 ± 0.23	3.75 ± 0.10	101.7 ± 3.0	87.2 ± 5.2	85.7 ± 2.5
C11-LAS	3.80	4.02 ± 0.26	3.33 ± 0.15	3.43 ± 0.08	105.6 ± 6.9	85.7 ± 3.5	90.5 ± 2.2
	11.40	12.52 ± 0.34	10.62 ± 0.33	10.31 ± 0.31	109.8 ± 3.0	93.1 ± 2.9	90.4 ± 2.7
C12-LAS	3.02	3.03 ± 0.11	2.64 ± 0.22	2.68 ± 0.12	100.4 ± 3.7	85.8 ± 4.3	88.7 ± 4.0
	9.06	9.84 ± 0.35	7.81 ± 0.65	7.69 ± 0.57	108.7 ± 3.8	86.2 ± 7.2	84.9 ± 6.3
C13-LAS	1.73	1.70 ± 0.13	1.53 ± 0.20	1.48 ± 0.03	98.7 ± 7.6	92.4 ± 4.5	85.5 ± 1.9
	5.16	5.65 ± 0.12	4.22 ± 0.31	4.22 ± 0.16	109.3 ± 2.3	81.4 ± 5.9	81.3 ± 3.2
(B) Tap water sample							
C10-LAS	0.00	0.38 ± 0.07	0.52 ± 0.09	0.32 ± 0.06			
	1.46	1.76 ± 0.02	1.72 ± 0.04	1.46 ± 0.03	94.2 ± 1.1	82.3 ± 2.8	77.3 ± 2.0
	4.37	4.91 ± 0.03	4.32 ± 0.04	3.31 ± 0.06	103.5 ± 0.6	87.0 ± 0.8	68.5 ± 1.5
C11-LAS	0.00	0.89 ± 0.02	0.61 ± 0.04	0.64 ± 0.17			
	3.80	4.01 ± 0.03	3.91 ± 0.08	2.59 ± 0.07	82.3 ± 0.9	87.0 ± 2.2	52.1 ± 1.8
	11.40	12.25 ± 0.45	9.15 ± 0.10	4.90 ± 0.45	99.7 ± 3.9	75.0 ± 0.9	37.4 ± 3.9
C12-LAS	0.00	0.90 ± 0.01	0.64 ± 0.01	0.76 ± 0.16			
	3.02	3.37 ± 0.09	2.97 ± 0.12	3.21 ± 0.14	81.7 ± 3.0	77.2 ± 4.1	81.2 ± 4.7
	9.06	9.93 ± 0.10	6.91 ± 0.37	7.28 ± 0.38	99.7 ± 1.1	69.2 ± 4.1	72.1 ± 9.2
C13-LAS	0.00	0.50 ± 0.07	0.73 ± 0.10	0.55 ± 0.07			
	1.73	1.96 ± 0.08	1.87 ± 0.13	1.78 ± 0.06	84.9 ± 4.6	65.5 ± 7.6	71.1 ± 3.3
	5.18	5.96 ± 0.06	4.79 ± 0.18	4.80 ± 0.24	105.6 ± 1.2	78.3 ± 3.5	82.1 ± 4.7
(C) Jialingjiang River water sample							
C10-LAS	0.00	0.27 ± 0.03	0.16 ± 0.02	0.14 ± 0.01			
	1.46	1.49 ± 0.06	1.17 ± 0.06	1.13 ± 0.12	87.7 ± 3.9	69.6 ± 3.5	68.5 ± 6.1
	4.37	4.72 ± 0.05	4.11 ± 0.19	3.02 ± 0.13	103.2 ± 1.2	90.6 ± 6.7	66.0 ± 5.8
C11-LAS	0.00	0.18 ± 0.01	0.12 ± 0.01	0.31 ± 0.03			
	3.80	3.51 ± 0.28	2.41 ± 0.13	1.39 ± 0.01	87.8 ± 6.8	60.1 ± 3.4	28.4 ± 0.1
	11.40	10.95 ± 0.41	7.10 ± 0.34	7.48 ± 0.01	94.5 ± 3.6	61.2 ± 2.7	62.9 ± 2.6
C12-LAS	0.00	0.19 ± 0.01	0.11 ± 0.01	0.11 ± 0.01			
	3.02	3.34 ± 0.14	1.85 ± 0.10	1.72 ± 0.06	104.4 ± 4.7	57.5 ± 3.4	53.1 ± 2.1
	9.06	8.67 ± 0.08	7.02 ± 0.43	6.28 ± 0.35	93.6 ± 0.9	76.3 ± 4.7	68.1 ± 3.9
C13-LAS	0.00	0.27 ± 0.01	0.21 ± 0.02	0.10 ± 0.01			
	1.73	2.00 ± 0.09	1.69 ± 0.08	1.12 ± 0.04	100.3 ± 5.4	85.1 ± 4.4	58.6 ± 2.3
	5.18	5.62 ± 0.24	3.06 ± 0.24	3.86 ± 0.31	103.5 ± 4.6	55.0 ± 4.7	72.6 ± 6.0

[a] Average ± standard deviation (n = 3).

C18 cartridge (500 mg) were compared; the recoveries were shown in Table 3. As can be seen, the ion-pair SPE on MWCNTs as cartridge showed stronger retention ability than C8 cartridge (500 mg) and C18 cartridge (500 mg) for target compounds. The recoveries of LAS homologues in the spiked environmental water samples ranged from 82 to 106% when 500 mL water sample at two spiked concentration levels (10 and 30 μg L^{-1} LAS) was tested. However, the recoveries obtained by using C8 cartridge (500 mg) and C18 cartridge (500 mg) as SPE adsorbents changed from 55% to 91% and 28% to 82%, respectively. Apparently, it was proved that the MWCNTs as SPE cartridge and TBAH as the ion-pair agent can be an excellent SPE format for LAS pretreatment and enrichment from real water samples. It should be indicated that when performing LAS analysis for real water samples, NaF was added to the water samples to

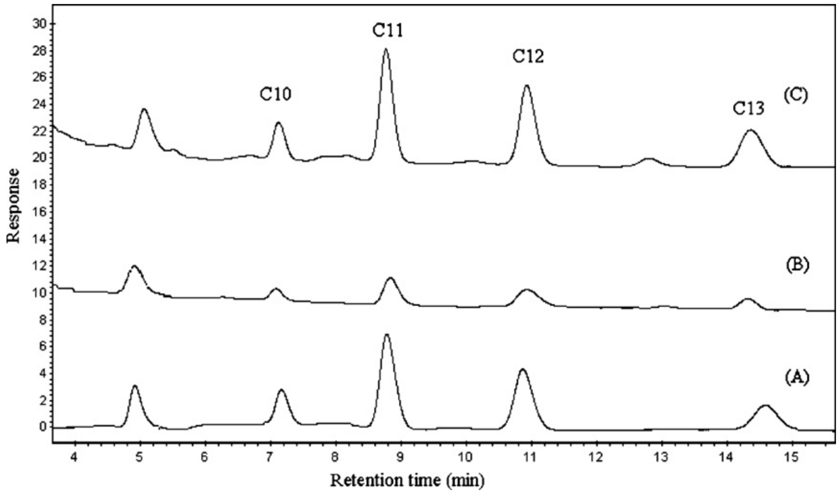


Fig. 5. HPLC-UV chromatograms of 10 μg L^{-1} standard and Jialingjiang River water sample after pretreatment by IP-SPE with MWCNTs as adsorbent. (A) 10 μg L^{-1} of LAS standard; (B) water sample; (C) water sample spiked 10 μg L^{-1} of LAS; volume of sample solution: 500 mL (pH 5); other conditions were same as in Fig. 4.

eliminate the possible interference from the metal ions in the environmental samples. It has been demonstrated that calcium ion had significant effect on LAS extraction [38]. In fact, only 15–70% and 19–69% recoveries were obtained for LAS homologues at 10 μg L^{-1} and 30 μg L^{-1} levels when performing direct LAS preconcentration without considering the elimination of cation ions. In order to eliminate the interferences derived from Ca and other coexisting metals, NaF was selected and tested. Experimental results indicated that quantitative recoveries of LAS homologues were obtained when NaF was added to the water samples. Hence, for real sample analysis for LAS homologues, NaF was selected.

4. Conclusion

The formation of ion-pair through electrostatic interactions between negatively charged LAS homologues and positively charged ion-pair reagent TBAH decreased the polarity of LAS homologues and meanwhile quantitative adsorption of LAS by MWCNTs was achieved. On this basis, a simple sample preparation and analysis method by HPLC-UV for LAS, a widely used surfactant in large quantities and a ubiquitous contaminant in water environment, has been developed in present study. Our results suggested that the ion-pair SPE on MWCNTs as cartridge showed stronger retention ability than C8 cartridge (500 mg) and C18 cartridge (500 mg) for target compounds. The recoveries of LAS homologues in the spiked environmental water samples ranged from 82 to 106% when 500 mL water sample at two spiked concentration levels (10 and 30 μg L^{-1} LAS) was tested. Nevertheness, the recoveries obtained by using C8 cartridge (500 mg) and C18 cartridge (500 mg) as SPE adsorbents changed from 55% to 91% and 28% to 82%, respectively. Hence, the MWCNTs as SPE cartridge and TBAH as the ion-pair agent can be an excellent SPE format for LAS pretreatment and enrichment from real water samples. The proposed method was successfully used for LAS enrichment in environmental water samples with good recoveries and precision, and the compounds can be detected in low microgram per liter quantities.

Acknowledgements

The authors thank Key Technologies R&D Programme from Ministry of Science and Technology (No. 2008AA06Z312), the Key Technologies R&D Programme from Chongqing Science and Technology Commission (No. 2006AA7003), the 211 Project of Southwest University (the Third Term), and Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education) for their financial supports.

References

[1] M. Villar, M. Callejon, J.C. Jimenez, E. Alonso, A. Guiraum, Anal. Chim. Acta 634 (2009) 267–271.
[2] C.F. Tabor, L.B. Barber, Environ. Sci. Technol. 30 (1996) 161–171.
[3] P. Eichhorn, M.E. Flavier, M.L. Paje, T.P. Knepper, Sci. Total Environ. 269 (2001) 75–85.
[4] K.K. Brandt, M. Hesselsøe, P. Roslev, K. Henriksen, J. Soyrensen, Appl. Environ. Microbiol. 67 (2001) 2489–2498.
[5] H. Urakawa, J. Matsumoto, K. Inaba, S. Tsuneda, FEMS Microbiol. Lett. 282 (2008) 166–173.
[6] J. Ramón-Azcón, R. Galve, F. Sánchez-Baeza, M.P. Marco, Anal. Chem. 78 (2006) 71–81.
[7] R. Zhang, K. Hirakawa, D. Seto, N. Soh, K. Nakano, T. Masadome, K. Nagata, K. Sakamoto, T. Imato, Talanta 68 (2005) 231–238.
[8] J. Fernández, J. Riu, E. Garcıĭa-Calvo, A. Rodrguez, A.R. Fernández-Alba, D. Barceló, Talanta 64 (2004) 69–79.
[9] M. Villar, M. Callejón, J.C. Jiménez, E. Alonso, A. Guiráum, Anal. Chim. Acta 599 (2007) 92–97.
[10] S. Wangkarn, P. Soisungnoen, M. Rayanakorn, K. Grudpan, Talanta 67 (2005) 686–695.
[11] Z. Guan, Y.M. Huang, W.D. Wang, Anal. Chim. Acta 627 (2008) 225–231.
[12] P.A. Lara-Martin, A. Gomez-Parra, E. Gonzalez-Mazo, J. Chromatogr. A 1114 (2006) 205–210.
[13] F. Merino, S. Rubio, D. Perez-Bendito, Anal. Chem. 76 (2004) 3878–3886.
[14] M. Petrovic, D. Barcelo, Fresenius J. Anal. Chem. 368 (2000) 676–683.
[15] S. González, M. Petrovic, D. Barceló, J. Chromatogr. A 1052 (2004) 111–120.
[16] V. Pichon, J. Chromatogr. A 1152 (2007) 41–53.
[17] L. Sarrazin, A. Arnoux, P. Rebouillon, J. Chromatogr. A 760 (1997) 285–291.
[18] A.H. El-Sheikh, J.A. Sweileh, Y.S. Al-Degs, A.A. Insisi, N. Al-Rabady, Talanta 74 (2008) 1675–1680.
[19] M. Abdel Salam, R. Burk, Anal. Bioanal. Chem. 390 (2008) 2159–2170.
[20] Q.L. Li, D.X. Yuan, Q.M. Lin, J. Chromatogr. A 1026 (2004) 283–288.
[21] Y. Cai, G. Jiang, J. Liu, Q. Zhou, Anal. Chem. 75 (2003) 2517–2521.
[22] S. Wang, P. Zhao, G. Min, G. Fang, J. Chromatogr. A 1165 (2007) 166–171.
[23] H. Niu, Y. Cai, Y. Shi, F. Wei, J. Liu, S. Mou, G. Jiang, Anal. Chim. Acta 594 (2007) 81–92.
[24] Q.X. Zhou, W.D. Wang, J.P. Xiao, Anal. Chim. Acta 559 (2006) 200–206.
[25] Y. Cai, G. Jiang, J. Liu, Q. Zhou, Anal. Chim. Acta 494 (2003) 149–156.
[26] J.X. Wang, D.Q. Jiang, Z.Y. Gu, X.P. Yan, J. Chromatogr. A 1137 (2006) 8–14.
[27] J.M. Jiménez-Soto, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1216 (2009) 5626–5633.
[28] L. Li, Y.M. Huang, Y. Wang, W.D. Wang, Anal. Chim. Acta 631 (2009) 182–188.
[29] K. Pyrzynska, Trends Anal. Chem. 29 (2010) 718–727.
[30] Y.J. Song, X.H. Wang, C. Zhao, K.G. Qu, J.S. Ren, X.G. Qu, Chem. Eur. J. 16 (2010) 3617–3621.
[31] M. Akyüz, Talanta 71 (2007) 471–478.
[32] http://www.chem.wisc.edu/areas/reich/pkatable/index.htm.
[33] U.V.R. Vijaya Saradhi, S. Prabhakar, T. Jagadeshwar Reddy, M.R.V.S. Murty, J. Chromatogr. A 1157 (2007) 391–398.
[34] L. Pan, M. Adams, J. Pawliszyn, Anal. Chem. 67 (1995) 4396–4403.
[35] Z. Zhang, H. Duan, L. Zhang, X. Chen, W. Liu, G. Chen, Talanta 78 (2009) 1083–1089.
[36] J.M. Wu, H.K. Lee, Anal. Chem. 78 (2006) 7292–7301.
[37] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211–219.
[38] J. Tolls, M. Haller, W. Seinen, Environ. Sci. Technol. 34 (2000) 304–310.