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Rapid and high-throughput determination of cationic surfactants in environmental water samples by automated on-line polymer monolith microextraction coupled to high performance liquid chromatography–mass spectrometry

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ABSTRACT

A rapid, high throughput and sensitive method was presented for automated determination of cationic surfactants in environmental water samples. The method was based on an automated analysis platform that was composed of on-line polymer monolith microextraction (PMME) and high performance liquid chromatography–mass spectrum (HPLC–MS) with an autosampler. A poly(methacrylic acid-co-ethylene dimethacrylate) (MAA-co-EDMA) monolith was selected as the sorbent for purification and enrichment of cationic surfactants in environmental water samples while a new mixed-mode chromatographic column packed with octyl and sulfonic acid co-bonded silica (OSS) was employed for separation and quantitative determination of cationic surfactants in water samples. By integrating sample preparation, chromatographic separation and MS detection into one automated platform, it makes the whole analysis procedure simple, accurate, and time and labor-saving. Several parameters affecting the extraction performance were investigated. Under the optimized conditions, the proposed method was applied to the analysis of seven cationic surfactants in environmental water samples. Good linearities were obtained for all cationic surfactants with R^2 larger than 0.9895. The limits of detection were found to be in the range of 15–24 ng/L. The method recoveries of the cationic surfactants spiked in water samples were from 80.5% to 115.1%, with relative standard deviations less than 12.4%.

1. Introduction

Cationic surfactants (CSs) are widely used as fabric softeners, disinfectants, auxiliary agents and medical additives [1–4]. In most cases, the CSs are exposed directly to environment after usage [1]. Unfortunately, it is proved that CSs can disturb the ecological balance due to their toxicity to aquatic organisms even the concentration of them is very low [2,4,5]. As a result, it is important to develop a rapid, sensitive and effective method for trace analysis of CSs in environmental samples.

Since CSs are generally present in environment at very low concentration and are accompanied by complex sample matrices, direct analysis of them is problematic. As a result, sample pretreatment is unavoidable prior to instrumental analysis [6]. Liquid–liquid extraction (LLE) [2,7,8], solid-phase extraction (SPE) [1,6,9], acid-induced cloud-point extraction [5], supercritical fluid extraction (SFE) [3], accelerated solvent extraction (ASE) [10], and some other sample preparation techniques have been proposed to enrich and purify CSs from sample matrices. They are proved to be quite successful. However, those methods usually involved tedious extraction steps and are generally operated in off-line mode, which makes the whole determination time-consuming and labor-intensive. Development of new sample pretreatment method for the determination of CSs would be necessary.

After enrichment of CSs, detection of them on conventional ultraviolet or fluorescent detectors is also problematic since most of them lack a chromophore [5]. To achieve their determination on these detectors, post-column derivatization is generally necessary, which is tedious and troublesome [11]. Recently, mass spectrometry (MS) detection of CSs has received great attention due to several advantages over other detectors, such as increased sensitivity, specificity and direct analysis without derivatization [4,6,10–13].

For complex samples, separation of individual ingredients is generally necessary prior to their detection. To date, several methods, including high-performance liquid chromatography (HPLC) [2,3,6,7,10–14], capillary electrophoresis (CE) [15,16], gas chromatography (GC) [17] and thin layer chromatography (TLC) [18,19],

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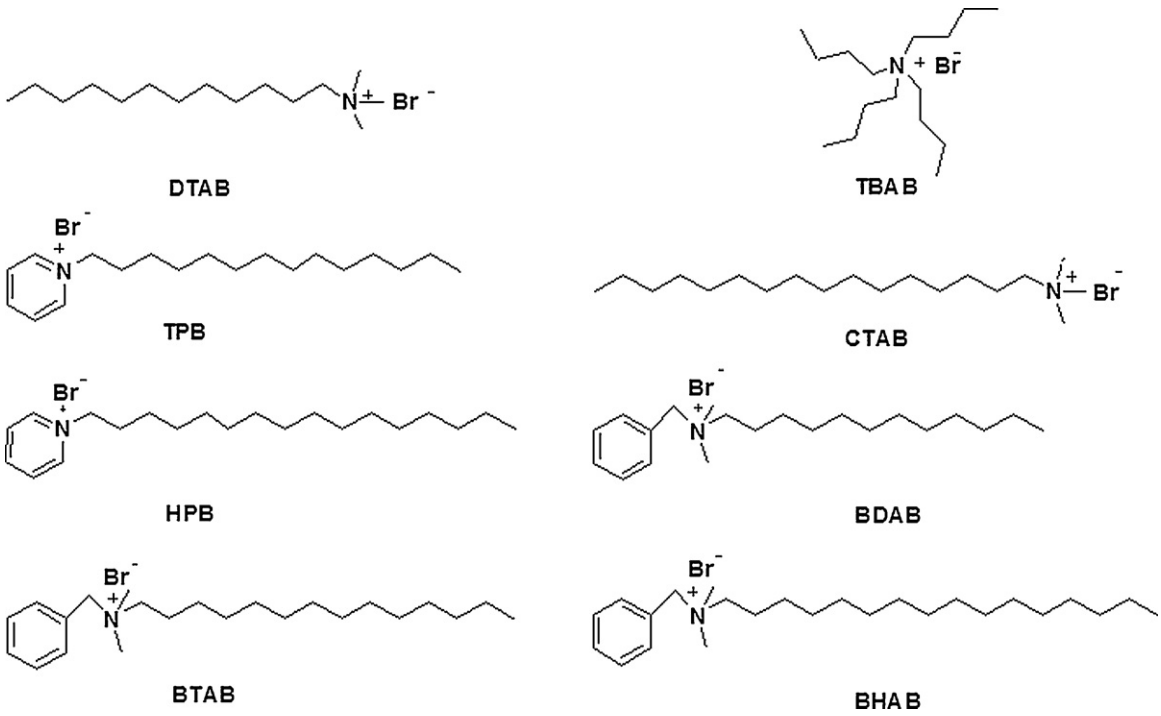

Fig. 1. Molecular structures of the CSs.

have been proposed for the separation of complex CSs mixtures. Among these methods, HPLC is probably the most promising one. Several kinds of HPLC columns packed with cyanopropylsilica [2,7,13,20], aminepropylsilica [3], octadecylsilica (ODS) [6,10–12,21] and hydrophilic polymer [14] have been used to analyze CSs in various sample matrices. However, there are some drawbacks encountered when using these columns. For instance, when separating CSs on a cyanopropylsilica column, the mobile phase always contains noxious organic solvent, such as chloroform, which is not compatible with a MS detector [2,7]; on an octadecylsilica column, peak broadening and tailing were observed because of the ionic interaction between the CSs and the charged sianol groups on the stationary phase [5,11]. Adding ion-pairing reagent may solve this problem to some extent, however, it makes the mobile phase complex and may affect MS-based detection by reducing the ionization yield of target analytes [22].

As shown in Fig. 1, the CSs are ionic compounds containing long alkyl chains, which means that they can be retained on a stationary phase by hydrophobic and ionic interaction. If such a stationary phase is available, it would provide alternative separation selectivity to these analytes compared to the traditional chromatographic modes [2,3,6,7,10–14,20,21]. In addition, probably ion-pairing reagents are not necessary to be added into mobile phase to control the retention and adsorption of these analytes. In such a case, the chromatographic unit can be conveniently coupled with a MS detector, which is beneficial for the detection of the CSs.

In the present study, an automatic on-line polymer monolith microextraction (PMME) coupled to HPLC–MS (PMME–HPLC–MS) was presented for the rapid and high-throughput determination of CSs in environmental water samples. A poly (MAA-Co-EDMA) monolithic capillary, which had been applied to extract many analytes from various sample matrices in off-line mode [23–26], was installed at the sample loop position of a six-port valve and was used as the online extraction medium. Compared with our previous methods, in which the sample solutions were injected by manual operation, the sample solutions were loaded by an autosampler automatically to achieve the extraction, which greatly increased the operational convenience and the throughput of sample detection, while eliminated the possibility of manually operational uncertainty. For separation of the CSs, a new stationary phase of octyl and sulfonic acid co-bonded silica (OSS) was fabricated, which can provide hydrophobic and strong cationic-exchange interaction towards the analytes. On this column, the mobile phase was composed of acetonitrile/10 mM ammonium formate (80/20, v/v, pH 2.5), which was compatible with MS detectors.

2. Experimental

2.1. Reagents and solution

A set of CSs, including benzyl-hexadecyl-dimethyl-ammonium bromide (BHAB), benzyl-dimethyl-tetradecyl-ammonium bromide (BTAB), benzyl-dodecyl-dimethyl-ammonium bromide (BDAB), hexadecyl-trimethyl-ammonium bromide (CTAB), 1-tetradecyl-pyridinium bromide (TPB), 1-hexadecyl-pyridinium bromide (HPB), tetrabutyl-ammonium bromide (TBAB), dodecyl-trimethyl-ammonium bromide (DTAB), were purchased from Aladdin (Shanghai, China). The molecular structures of them were shown in Fig. 1. Analytical grade ammonium formate ($HCOONH_4$), formic acid (FA) and ammonia were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). HPLC-grade acetonitrile (ACN) and methanol (MeOH) were purchased from Tedia (Ohio, USA). Other chemicals used in the experiment were of analytical grade, and were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Purified water was obtained with a Milli-Q water system (Millipore, Billerica, MA, USA).

Individual stock solutions were prepared by accurately weighing 25 mg CSs into 25 mL volumetric flasks and dissolved in ACN to get a concentration of 1000 μg/mL. The mixture standard solutions of 1 μg/mL or 0.1 μg/mL were prepared by diluting stock solutions with water. Internal standard (I.S.) solution of 1 μg/mL was prepared in the same way. All the solutions were stored at 4 °C.

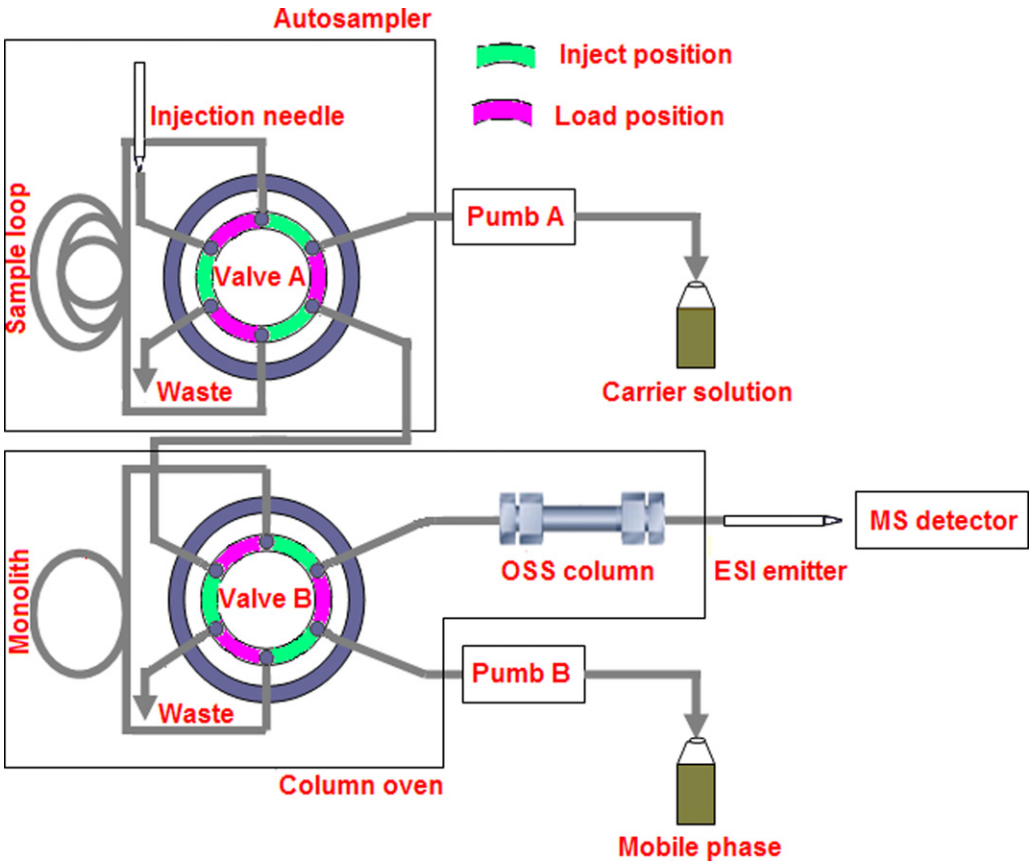

Fig. 2. Scheme of the automated on-line PMME and LC–MS platform.

2.2. Pretreatment of glassware

According to the methods reported by the literatures [2,3], to avoid adsorption of CSs to the walls of glassware, the glassware should be immerged in 5 μg/mL BDAB solution overnight, followed by thoroughly rinsing with hot tap water, distilled water, and then methanol before dry.

2.3. Equipments and separation conditions

An HPLC–ESI–MS system (Shimadzu LC–MS 2010EV, Tokyo, Japan) was used for the determination of the CSs in environmental water samples. A six-port valve was installed into the column oven for automated on-line PMME. The separation column was a homemade OSS column (150 mm × 2.1 mm, 5 μm), which was prepared according to a patent [27]. The mobile phase was consisted of ACN/10 mM ammonium formate (80/20, v/v, pH 2.5). The flow rate of the mobile phase was 0.2 mL/min. The column temperature was controlled at 30 °C. The chromatographic data were acquired and processed by Shimadzu LC Solution software. Selected ion monitoring (SIM) was performed to simultaneously monitor ions at m/z 228, 242, 276, 304, 332, 360 and 284, which corresponded to the cationic ions of DTAB, TBAB, TPB, HPB (BDAB), BTAB, BHAB and CTAB (I.S.), respectively. The capillary voltage was 4.5 kV. Curved desolvation line (CDL) temperature and heat block temperature were set at 250 and 200 °C, respectively. The drying and nebulizer gas of nitrogen were set at 1.5 L/min with a pressure of 0.04 MPa. The detector voltage was set at 1.4 eV.

2.4. Sample preparation

Various environmental water samples, including lake water, plant wastewater, sanitary wastewater, pond water and medical wastewater were collected in Wuhan, China. The pretreated bottles were first rinsed several times with the water, and then completely filled with the same water and tightly closed to minimize any contact with air. The water samples were filtered through a deposable filter (pore size, 0.45 μm). 10 mM $HCOONH_4$ was added to the water samples and the pH was adjusted to 7.0 prior to the PMME.

2.5. PMME procedures

A poly(MAA-co-EDMA) monolithic capillary column (4 cm × 530 μm i.d.) was selected as the extraction medium for the PMME. The PMME was operated on an automated instrumental platform, which was improved on the system described in our previous report [28]. The scheme of the platform is displayed in Fig. 2. The sample was injected to the monolith by the autosampler and the injection volume could be accurately controlled. The extraction temperature was set at 30 °C. The monolith was fixed at the sample loop position on valve B. The carrier solution, which was consisted of ACN/10 mM ammonium formate (80/20, v/v, pH 2.5), was used to drive the sample solution for extraction. After the extraction was completed, the system was momentarily stopped and Valve A was switched back to LOAD position for loading 1 mL pure water into the sample loop by the autosampler. The pure water was driven by carrier solution to wash the monolith. Then the mobile phase was delivered by Pump B to desorb the extracted analytes from the monolith. The chromatographic separation was started and the MS detection began to record. Meanwhile, the carrier solution continued to wash residual analytes on the sample loop and PEEK tube. The above-mentioned procedures can be programmed and automatically controlled by the Shimadzu LC Solution workstation (refer to Table 1).

Table 1
Program for automated on-line PMME and LC–MS procedures.[a]

Program sequence	Time (min)	Module	Parameter	Value	Event
1	0	Autosampler	–	–	Before extraction 1 mL sample solution was injected to sample loop by the autosampler
2	0.01	Valve A	Status	INJECT	Extraction began. The flow rate of pump A and B was kept at 0.1 and 0.2 mL/min, respectively
	0.01	Valve B	Status	LOAD	
	0.01	Pump A	Flow rate	0.1	
	0.01	Pump B	Flow rate	0.2	
3	8.01	System	Status	Stop	After sample loading completed, the system stopped
4	0	Autosampler	–	–	Pure water was injected to the sample loop by the autosampler
5	0.01	Valve A	Status	INJECT	Carrier solution pushed the pure water to washing the sample matrices for 3 min
	0.01	Valve B	Status	LOAD	
	0.01	Pump A	Flow rate	0.1	
	0.01	Pump B	Flow rate	0.2	
6	3.01	Valve B	Status	INJECT	Desorption for 3 min with mobile phase at a flow rate of 0.2 mL/min
7	6.01	Valve B	Status	LOAD	Valve B was switched to LOAD position
8	24	System	Stop	–	Separation finished and the monolith was conditioned by carrier solution until next extraction

[a] The whole process was controlled by the Shimadzu LC Solution workstation.

3. Results and discussion

3.1. Optimization of the separation condition

A homemade OSS column, which can offer ionic exchange and hydrophobic interaction with the CSs, was used for their separation. The HPLC separation conditions were optimized. It is found that, at the same proportion, the ACN/water mixture can elute the analytes easier than the MeOH/water mixture. Therefore, ACN was used as organic modifier in the mobile phase. Different proportions of ACN/water were also investigated. The results demonstrated that 80% ACN was the best suitable for the effective separation of the CSs and good detection sensitivity was obtained. However, when ACN was below 60%, the detection sensitivity decreased significantly. Apparently, the relatively high organic solvent in the mobile phase was beneficial to the spraying and ionization of the analytes in the LC–MS interface, leading to an increase in detection sensitivity. Further investigations were conducted by adjusting pH and salt concentration in mobile phase. As the sulfonic groups on the stationary phase are strong acid and the CSs are strong ionic compounds, the pH ranging from 2.5 to 6.0 had no obvious effect on the retention of them. In this study, the mobile phase also acted as desorption solvent; when the mobile phase was at low pH, it was beneficial to desorb the analytes from the extraction column. Therefore, mobile phase at pH 2.5 was selected for further experiments. The salt concentration was also investigated. As the salt concentration increased, the retention time decreased obviously, which should be due to the decrease in ionic interaction between the cationic CSs and the negative stationary phase. 10 mM salt concentration was found to be optimal for the separation of CSs. Therefore, the mobile phase consisting of ACN/10 mM ammonium formate (80/20, v/v, pH 2.5) was selected as the separation conditions for the analysis of CSs. Under this condition, suitable separation and short analysis time can be achieved.

3.2. Optimization of the on-line PMME

To achieve high extraction efficiency of the on-line PMME, various parameters such as the type and content of organic solvent, the sample loading conditions, the constitute of carrier solution, washing and elution conditions were investigated.

3.2.1. Optimization of the sample loading solution and conditions

It was found that, when loading aqueous samples directly, the extraction efficiency is very low because the sample loop and PEEK tube had strong adsorption for the CSs. Probably addition of organic

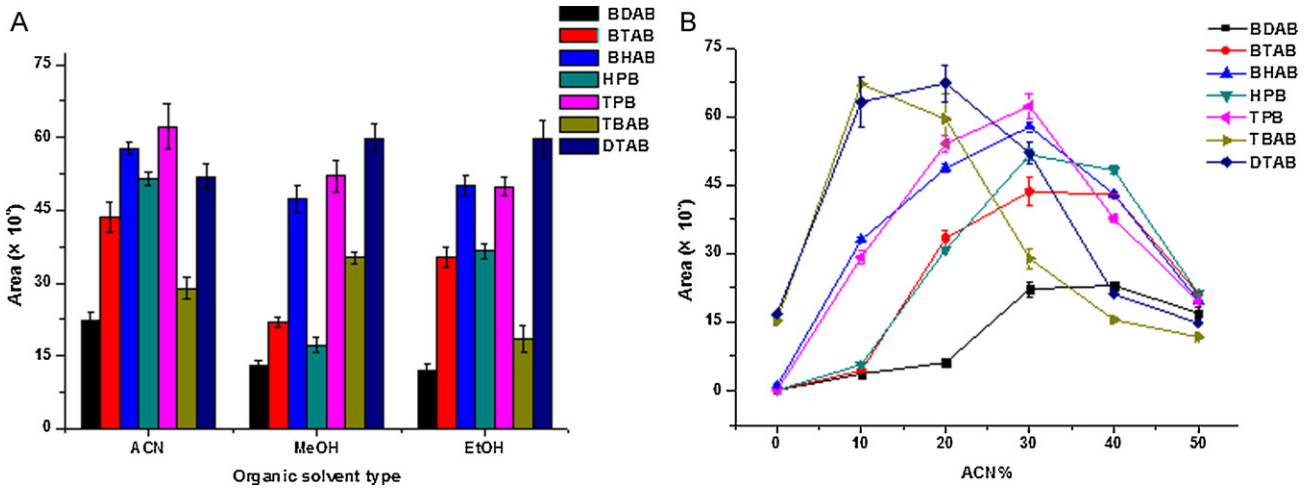

Fig. 3. Effect of the type of organic solvent and the ACN content on the extraction efficiency. (A) The targets were spiked at 25 ng/mL in a mixture of the organic solvent/10 mM ammonium formate (30/70, v/v, pH 7.0); (B) the targets were spiked at 25 ng/mL in 10 mM, pH 7.0 $HCOONH_4$ with ACN content ranging from 0 to 50%. The HPLC–MS and microextraction experiments were performed under their optimal conditions (as shown in Sections 2.3 and 2.5, respectively).

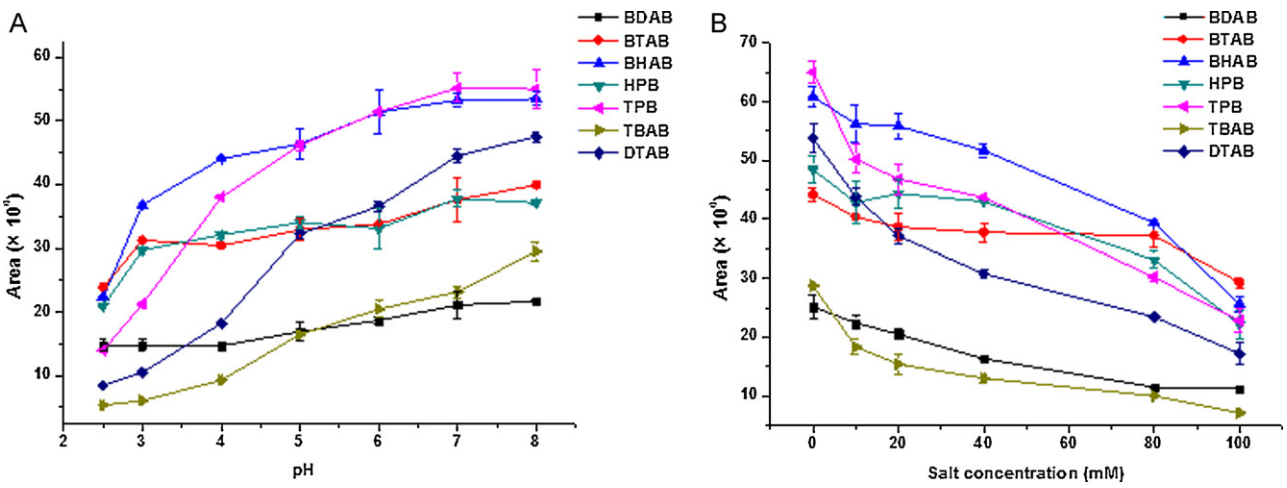

Fig. 4. Effect of pH and salt concentration in sample solution on extraction efficiency. (A) The targets were spiked at 25 ng/mL in ACN/10 mM ammonium formate (30/70, v/v) with pH ranging from 2.5 to 8.0; (B) the targets were spiked at 25 ng/mL in ACN/10 mM ammonium formate (30/70, v/v, pH 7.0) with NaCl concentration ranging from 0 to 100 mM. The HPLC–MS and microextraction experiments were performed under their optimal conditions (as shown in Sections 2.3 and 2.5, respectively).

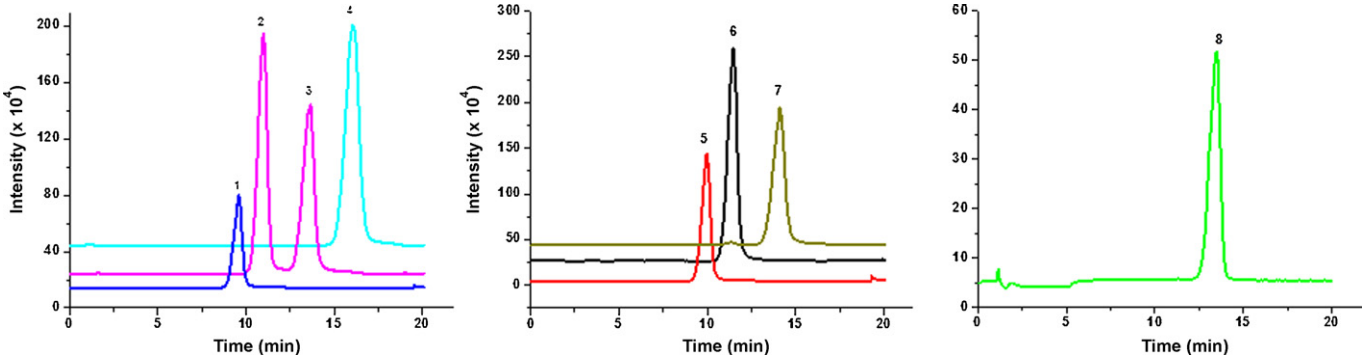

Fig. 5. Chromatograms of the CSs obtained after extraction under the optimized conditions. Peaks: 1, BHAB; 2, BDAB; 3, HPB; 4, DTAB; 5, BTAB; 6, TBAB; 7,TPB; 8, CTAB (I.S.). The HPLC–MS and microextraction experiments were performed under their optimal conditions (as shown in Sections 2.3 and 2.5, respectively).

solvent into the sample solutions would solve the problem. In this study, several kinds of organic solvent, including ACN, methanol and ethanol, were investigated. They were added to sample solutions respectively before sample loading. It was found that most analytes had best extraction efficiencies when ACN was used as the organic additive, as shown in Fig. 3A. Further studies demonstrated that the ACN content also played an important role for the extraction. As shown in Fig. 3B, it indicated that 30% (v/v) ACN in sample solution would be suitable for most of the analytes. Therefore, ACN in this ratio was added into the aqueous samples prior to PMME.

The pH of the sample solution plays an important role in the preconcentration of CSs from aqueous solution. The effect of pH on extraction efficiency was investigated by changing the pH of sample solution from 2.5 to 8.0. The results are shown in Fig. 4A. It can be found that the extraction performance generally increased with increasing pH in sample solution. The phenomenon should be ascribed to the fact that, at low pH, the carboxylic groups on the monolithic column protonated, which decreased the ionic interaction between the CSs and the extraction column, leading to low extraction efficiency. When the pH of the sample solution was high, the carboxylic groups deprotonated, which is beneficial for ionic interaction. Therefore, at high pH values, good extraction efficiency was obtained. Compared with other CSs, the chromatographic signals of DATB and TBAB showed more remarkable change in the range of pH 2.5–7.0. The reason might be that the hydrophobicity of DTAB and TBAB was poorer than that of the other CSs. As a result, the extraction of DTAB and TBAB may be mainly controlled by ionic exchange while the other five analytes by hydrophobic interaction. According to the investigation, the sample solution with a pH value of 7.0 would be suitable for extraction.

The ionic strength of sample solution has influence on the extraction of CSs. NaCl was added to the sample solution in the range of 0–100 mM to study the influence of ionic strength on the extraction of CSs. The results are shown in Fig. 4B. As the ionic strength increased from 0 to 100 mM, the extraction efficiency decreased gradually. It should be ascribed to the decrease in ion exchange interaction between the monolithic column and the CSs as the ionic strength increased. Therefore, no NaCl was added in sample solution for extraction.

The loading flow rate of the sample solution was optimized in the range of 0.05–0.2 mL/min. No obvious change of the extraction performance was found in the investigated range. Therefore,

Table 2
Enrichment factors and extraction yield of the CSs by the poly (MAA-co-EDMA) monolith.

Compound	Enrichment factors	Extraction yield (%)
BDAB	21.7	54.2
BTAB	24.0	60
BHAB	23.6	59
HPB	30.2	75.5
TPB	26.7	66.8
TBAB	28.0	70
DATB	24.8	62
CTAB	20.3	50.8

Table 3
Linear regression, LOD and LOQ of the seven CSs by the PMME and LC–MS from environmental water samples.

Compound	Linear range (ng/mL)	R^2	LOD (ng/mL)	LOQ (ng/mL)
BDAB	0.08–80	0.99819	0.024	0.08
BTAB	0.06–80	0.99461	0.018	0.06
BHAB	0.05–80	0.98954	0.015	0.05
HPB	0.08–80	0.99789	0.024	0.08
TPB	0.07–80	0.99764	0.021	0.07
TBAB	0.07–80	0.99474	0.021	0.07
DATB	0.08–80	0.99683	0.024	0.08

Table 4
The method precisions and recoveries of the seven CSs by the PMME and LC–MS from environmental water samples spiked at three concentration levels.

Compound	Intra-day precision RSD (%, $n=4$)			Inter-day precision RSD (%, $n=4$)			Method recoveries (%)		
	1.0[a]	10.0[a]	50.0[a]	1.0[a]	10.0[a]	50.0[a]	1.0[a]	10.0[a]	50.0[a]
BDAB	9.9	8.3	7.9	12.1	9.2	11.0	115.1	100.1	99.2
BTAB	9.4	3.2	2.2	10.4	10.1	3.3	80.5	109.3	106.2
BHAB	3.9	4.6	2.0	9.9	11.5	6.0	92.9	104.9	111.6
HPB	9.3	2.3	7.7	12.4	8.3	10.9	110.6	102.7	105.4
TPB	6.7	4.6	2.1	7.3	7.2	4.3	96.3	99	106.7
TBAB	7.9	7.3	2.4	11.6	5.1	4.3	88.9	114	108.5
DATB	2.6	7.2	2.7	10.4	9.9	6.8	84.7	108	107.8

[a] Spiked level: ng/mL.

0.1 mL/min was chosen to shorten extraction time as well as to ensure better column stability.

One milliliter of sample solution was injected into the sample loop by the autosampler. Then the sample loading time from 2 min to 9 min was investigated to assay the extraction performance of the poly (MAA-co-EDMA) monolith for the CSs. The results demonstrated that the extraction amount of target compounds increased as the sample loading time increased. Since 8 min are enough to achieve sufficient sensitivity, it was selected as the suitable loading time for the extraction.

3.2.2. Optimization of the carrier solution, washing solution and elution solution

It was found that, when solution with low proportion of organic solvent served as carrier solution, the CSs serious adsorbed to the sample loop and PEEK tube after sample loading, which posed serious memory effect for next analysis. Therefore, the mobile phase, ACN/10 mM ammonium formate (80/20, v/v, pH 2.5), which can desorb the analytes efficiently, was used as the carrier solution.

During the extraction, in addition to the target analytes, some components in the sample matrices may also adsorb onto the extraction column. To prevent them from disturbing chromatographic separation and MS detection, a washing step is necessary. However, carrier solution was not suitable for washing sample matrices due to its strong eluting capacity for the CSs. In our experiments, we found that the interferences mainly resulted from the inorganic salts in sample solutions, which had bad effect on the chromatographic separation and ionization of the CSs. Therefore, pure water was used to wash the extraction column after sample loading. Pure water (1 mL) was injected into the sample loop on Valve A by the autosampler and then was pushed by the carrier solution to pass through the extraction column to remove the possible sample matrices for 3 min. It was found that, after the washing step, the MS signal is much better than that without washing.

Elution of CSs from the extraction column was achieved by the HPLC mobile phase. It was found that the analytes could be desorbed completely within 3 min by the mobile phase at a flow rate of 0.2 mL/min.

Fig. 5 shows the typical chromatograms of the CSs obtained after extraction under the optimized conditions. The enrichment factors were calculated by comparing the peak area obtained by PMME and direct injection. The extraction efficiencies were based on the peak ratios of the extracted CSs from the spiked water sample to the total amounts loaded. The enrichment factors and extraction yields were found to be 20.3–30.2 and 50.8–75.5% for the CSs, respectively (as shown in Table 2).

3.3. Validation of the automated on-line PMME and HPLC–MS method

3.3.1. Calibration curves, detection limits, accuracy and precision

CTAB was used as an internal standard during analysis. The calibration curve was established by plotting the ratio of the absolute abundance of the analytes to the internal standard versus the CSs' concentrations.

Limits of detection (LODs) and limits of quantification (LOQs) were calculated as the concentrations corresponding to a signal of 3 and 10 times the standard deviation of the baseline noise, respectively. As listed in Table 3, all analytes show good linearity with satisfactory squared regression coefficients (R^2) greater than 0.9895. The LODs and LOQs for these analytes were found to be in the range of 15 and 24 ng/L, and 50 and 80 ng/L, respectively.

To assay the accuracy of the method, recoveries were investigated on spiked water samples at three different concentrations of 1.0, 10.0 and 50.0 ng/mL. The recoveries were determined by comparing the calculated amounts of CSs in the samples (using calibration curve) with the spiking amounts. The precision of the method was assessed by determining the intra- and inter-day relative standard deviations (RSDs) at three concentration levels. As listed in Table 4, the method recoveries were in the range of 80.5 to 115.1% and the intra-day and inter-day RSDs were below 9.9% and 12.4%, respectively, indicating the proposed method was suitable for routine analysis.

3.3.2. Application of the proposed method for the determination of the CSs in water samples

The proposed automated on-line PMME–HPLC–MS method was successfully applied to trace analysis of the CSs in five environmental water samples from different sources in Wuhan. As shown in Table 5, the CSs were detectable in three water samples. The

Table 5
Application of the proposed method for the determination of the CSs in five environmental water samples.

Compound	Sanitary wastewater concentration[a] (RSD)	Lake water concentration (RSD)	Medical wastewater concentration (RSD)	Plant wastewater concentration (RSD)	Pond water concentration (RSD)
BHAB	1.2 (5.3%)	ND	ND	0.9 (5.6%)	ND
BTAB	3.4 (9.2%)	ND	ND	ND	ND
BDAB	2.8 (6.8%)	ND	1.3 (10.2%)	2.1 (7.3%)	ND
HPB	2.0 (8.8%)	ND	ND	ND	ND
TPB	ND[b]	ND	ND	ND	ND
TBAB	ND	ND	ND	ND	ND
DATB	ND	ND	3.7 (4.8%)	1.9 (3.7%)	ND

[a] Concentrations: ng/mL.
[b] Not detected.

concentrations ranged from 0.9 to 3.7 ng/mL, with RSDs less than 10.2%.

3.3.3. Method comparison

In this study, by integrating the extraction, chromatographic separation and MS detection into one automatic platform, about 30 min would be needed to complete the whole analysis of the CSs in environmental water samples. It can be estimated that about 40–45 samples could be analyzed in one day (24 h) due to its automated process. Compared with other analytical methods, which took much more time in sample pretreatment step [2,6,7,11], the proposed method used less or equivalent time for analysis of CSs in environmental water samples. Furthermore, on-line automatic method minimizes laborious repetitive work and ensures high reproducibility for the analysis.

4. Conclusion

An on-line PMME–HPLC–MS method was constructed for automated determination of the CSs in environmental water samples. A poly (MAA-co-EDMA) monolith was used for the on-line extraction and a new octyl and sulfonic co-bonded silica was fabricated and packed in a column for separation of the CSs. Comparing with other off-line sample preparation methods, this automated method allows the development of a fast, sensitive, laborsaving and high-throughput method. The LODs obtained were from 15 to 24 ng/L for the CSs, which is suitable for trace determination of them in environmental water samples. Moreover, high recoveries were obtained with the RSDs less than 12.4%, indicating the high reliability and good stability of the proposed method.

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