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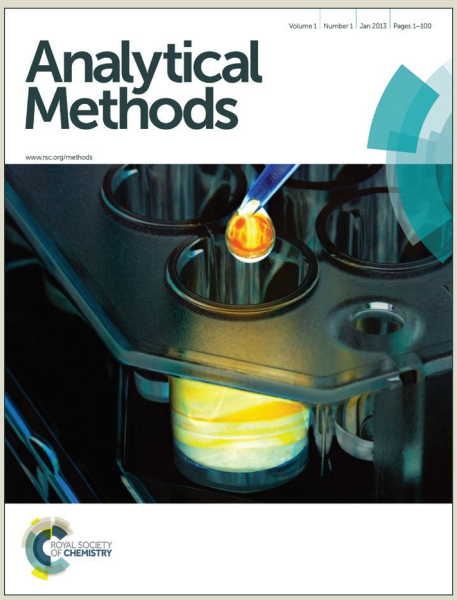

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Simultaneous Determination of Tetrabutyl Ammonium and Tetrabutyl Phosphonium in Environmental Water Sample by Solid Phase Extraction and Ion Chromatography

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Abstract Ion Chromatography method by solid-phase extraction which was used for simultaneous determination of tetrabutyl ammonium ($[TBA]^+$) and tetrabutyl phosphonium ($[TBP]^+$) in environmental water sample was developed. The samples were first concentrated and purified through a SCX solid-phase extraction column, and eluted with 0.02 mol L^{-1} hydrochloric acid - 98% methanol (v/v), then analyzed by a carboxylic acid base cation exchange column. The optimized chromatographic conditions were 3 mmol L^{-1} methanesulfonic acid-20% acetonitrile as mobile phase, flow rate of 1.2 mL min^{-1} and column temperature of room temperature. Under these conditions, $[TBA]^+$ and $[TBP]^+$ achieved baseline separation. The retention times of the two cations were 11 min and 14 min, the resolution between peaks was 2.059. The recovery of solid-phase extraction reached 97.1%, the linear regression equations were $y = 0.0142\ x - 0.0132$ and $y = 0.0195\ x - 0.0265$, the correlation coefficients were $r = 0.9996$ and $r = 0.9997$, the detection limits (S/N = 3) were 0.502 mg/L and 0.448 mg/L, the relative standard deviations ($n = 5$) of retention times of $[TBA]^+$ and $[TBP]^+$ were 1.22%, 1.23% and of peak areas were 0.24%, 0.25%,

respectively. Recoveries were 94.8% to 103.2%. The method is accurate, rapid, sensitive and efficient to meet the requirements for quantitative analysis.

Keywords tetrabutyl ammonium, tetrabutyl phosphonium, solid-phase extraction, ion chromatography, conductivity detection

1. Introduction

Quaternary ammonium salt disinfectant and quaternary phosphonium salt disinfectant are all used as cationic surfactant. [1-4] Nitrogen and phosphorus atoms linked to the alkyl formation of the cation is an effective part of sterilization and disinfection effects. [5-8] Based on many researches of the quaternary ammonium salt and quaternary phosphonium salt physical and chemical properties, their bactericidal mechanism, influence factor, advantages of the low side effects, have been widely acknowledged, thus quaternary ammonium salt disinfectant and quaternary phosphonium salt disinfectant have been widely used in daily routine, healthcare, food and many other fields. [9-12] Additionally, it was found that with long chain alkyl quaternary ammonium salt and quaternary phosphonium salt groups, the antimicrobial properties of them were enhanced. There were reports of quaternary ammonium salts detection by ion chromatography method, [13-16] mass spectrometry method [17-20]. Analysis methods of quaternary phosphonium salt are rarely reported, only the infrared spectrum and nuclear magnetic resonance (NMR) were studied, it might be due to the structure and chemical properties of the quaternary phosphonium salt is similar to quaternary ammonium salt. However, the report of long chain quaternary

ammonium salt and quaternary phosphonium salt analysis was scarce. Refer to the detection method of quaternary ammonium salt, quaternary phosphonium salt was studied simultaneously.

Solid phase extraction is a kind of sample pretreatment technology developed in recent years. It is mainly used for sample separation, purification and concentration, it allows the separation of interfering component, thus provides the more effective analysis and reduces the sample pretreatment process. It was widely used in medicine, food, environment, commodity inspection, chemical and other fields. [21-25] For example, quaternary ammonium herbicides (e.g. paraquat) and its structural modifications used solid phase extraction to extract and enrich the sample.[26]

This study aims to develop an ion chromatography method by solid-phase extraction which was used for the simultaneous determination of tetrabutyl ammonium and tetrabutyl phosphonium. This method could be applied to determine quaternary ammonium salt and quaternary phosphonium salt in antiseptic and disinfectant agent to provide the corresponding reference.

2. Experimental

2.1. Instrumentation and Reagents

2.1.1. Instrumentation

Sample preparation was carried out on an ASE-24 solid-phase extraction apparatus,

which was equipped with a Model AP-9950 oil-free vacuum pump (Tianjin Automatic Science Instrument Co. Ltd). The whole experimentation was carried out on a 886 Basic plus ion chromatograph, which was equipped with a Model 863 Compact Autosampler. The chromatographic system control and data acquisition were performed using the MagIC.net 3.1 workstation (Metrohm, Switzerland). Model BSA124S electronic analytical balance (Sartorius Scientific Instrument Corporation, China) was used. Model Milli-Q Reference water purification system (Millipore, USA) was used. To check the experiment pH, a Model PHSF-3F pH meter (Shanghai Precision Scientific Instrument Corporation, China) was used. Model EMS-9A Heating Magnetic Stirrer (Tianjin Honour lnstrument Co. Ltd) was used to homogenize solutions. The SPE procedure used the UF-SCX solid phase extraction column（200 mg/ 3 mL，Dalian Zhongpu Technology Co. Ltd）. A Model DHG-9070A Electro-thermostatic blast oven (Shanghai Yiheng lnstrument Co. Ltd) was used. Other instruments are conformed to the requirements of the chromatographic analysis.

2.1.2. Reagents

Tetrabutyl ammonium bromide, tetrabutyl phosphonium bromide and tetraethyl ammonium bromide (purity 99%) were purchased from Shanghai Cheng Jie Chemical Co. Ltd (Shanghai, China). Methanol and acetonitrile (chromatographically pure) were obtained from Sigma-Aldrich Co. (USA). Methanesulfonic acid, quinolinic acid and orthoboric acid (analytically pure) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), Tartaric acid, hydrochloric acid,

phosphoric acid and sodium dihydrogen phosphate (analytically pure) were purchased from Beijing Bailingwei Technology Co. Ltd (Beijing, China).

2.2. Preparation of solutions

All the solutions in experiment were prepared with 18.2 MΩ cm deionized water. Stock standard solutions of concentration 1 g L^{-1} were prepared. The solutions were diluted to the required concentration of this experiment, and then filtered using a 0.22 μm membrane filter before injection. Buffer solutions of 10 mmol L^{-1} phosphoric acid-sodium dihydrogen phosphate were prepared with 18.2 MΩ cm deionized water in 250 mL volumetric flask. The mobile phases were filtered through a 0.22 μm filter, and then degassed for 15 min prior to use.

2.3. Environmental water sample

The water sample was taken from river in Harbin for optimization and quantitative analysis. The pH of environmental water sample was 7.39-7.42. The water sample was taken from the upstream, which is the end of chemical plant and households sewage, therefore the freshwater sample contains many contaminants. The freshwater was passed through a quantitative filter paper of 9 cm diameter, and finally stored in the dark at ambient temperature.

2.4. Sample pretreatment

Prior using, the SCX solid-phase extraction column were conditioned with 5 mL

of methanol followed by 5 mL of deionized water. After decompression, the loading was controlled in drain velocity of 1 mL/min, then 10 mL of 20% acetonitrile (prepared with deionized water) was added to buffering. After the buffering process was done, dry vacuum was applied for 10 min to remove the residual moisture. Sample was loaded into column, and the 5 mL of 0.24 mol L^{-1} hydrochloric acid - 98% methanol (v/v) was used to elute all the neutral and acidic impurities from sample. The chromatographic analysis was conducted on 5 mL of collected sample. The final eluent composition is discussed in the ‘‘Results and discussion’’ section. The solid-phase extraction protocol applied is shown in Fig. 1.

2.5. Chromatographic conditions

The separations were performed on a carboxylic acid base cation exchange column (Shodex IC YK-421, 4.6 mm I.D. × 125 mm, Showa Denko, Japan). The mobile phase was 3 mmol L^{-1} methanesulfonic acid-20% acetonitrile (v/v，pH=2.51). The flow rate was 1.2 mL min^{-1}. Column temperature was room temperature. The injection volume was 20 μL. The detection mode was direct conductivity detection. The chromatographic system control and data acquisition were performed using the MagIC.net 3.1 workstation (Metrohm, Switzerland).

3. Results and discussion

3.1. Selection of solid-phase extraction conditions

3.1.1. Selection of eluent

The elution capacity of eluent on solid-phase extraction was investigated using acetonitrile, 3 mmol L^{-1} methanesulfonic acid - 20% acetonitrile (v/v), 10 mmol L^{-1} phosphoric acid - sodium dihydrogen phosphate and 0.24 mol L^{-1} hydrochloric acid - 98% methanol (v/v), respectively. Using 10 mmol L^{-1} phosphoric acid-sodium dihydrogen phosphate and 0.24 mol L^{-1} hydrochloric acid - 98% methanol (v/v) as eluents, the existence of analytes were able to be detected. The SCX solid-phase extraction has a strong acid property, it was because of the column consists of a polymerically bonded benzene sulfonic acid functional group with a proton counterion on a silica support. The solid phase, thus, be able to absorb or exchange the cations in solution, under all pH range, as long as the pH of solution also be able to guarantee that the analytes are in charged state. The SCX can be used to separate compounds of strong cation and weak cation. For the analysis of cationic compounds, pH of solution should be two units less than the pK_a of analytes. This is to ensure that the analytes are in electric charge, because when the elution was conducted in a pH two units larger than the target objects, the analytes could be joined with another cation instead. Hydrochloric acid - methanol was chosen as eluent and the concentration of HCl was further studied. This optimization study was conducted by varying HCl concentrations of 0.36, 0.24, 0.12, 0.09, 0.07, 0.05 and 0.02 mol L^{-1}. The result showed that 0.02 mol L^{-1} hydrochloric acid - 98% methanol (v/v) as eluent recovery is the highest. The results of the study are shown in Table. 1.

3.1.2. Selection of buffer solutions

The sample washing capacity of buffer on solid-phase extraction was investigated using acetonitrile - water, 10 mmol L^{-1} phosphoric acid - sodium dihydrogen phosphate and hydrochloric acid - methanol, respectively. The collected buffer solution was investigated by chromatographic analysis. It was found that the buffer consists of 10 mmol L^{-1} of phosphoric acid - sodium dihydrogen phosphate and hydrochloric acid – methanol have washing effect. They destroyed the retention of sample, thus the retained samples were washed off. The acetonitrile – water had shown desirable effect and was capable of maintaining the equilibrium of samples to the stationary phase. To optimize the washing eluent, the variations of acetonitrile concentrations studied were 100, 80, 60, 40, 20%, together with water were studied. By considering that the enrichments of the environmental water sample are maintained on the solid phase extraction column, 20% acetonitrile - water as rinsing environmental water sample eluent was selected.

3.1.3. Breakthrough volume

In order to obtain a perfect balance between the maximum recoveries of the target compound and the minimum consumption of loading eluent, various volumes of loading eluent in the range of 5.0–35.0 mL were investigated. When the volume was greater than 10 mL, the environmental water sample was detected in the loading eluent. This indicated that the volume was beyond the solid phase extraction capacity, which is in line with the standard calculation of adsorbent capacity. In the process of enrichment and samples purification experiments, the weight of the sample was controlled to be less than 5 mg, to reduce the effect of exceeding weight to recovery.

3.2. Selection of chromatographic conditions

3.2.1. Selection of eluent

Using 5 mmol L^{-1} tartaric acid - 50% acetonitrile (v/v) as mobile phase, the determination and separation of $[TBA]^+$ and $[TBP]^+$ were investigated. The results were peak shape was excellent and peaks appeared in 6 min, however it cannot achieve the baseline separation. This result indicated that tartaric acid's elution ability to these two kinds of cations was equal, as shown in Fig. 2. Another investigation was conducted by using 3 mmol L^{-1} methane sulfonic acid - 30% acetonitrile (v/v) as eluent, the result showed that $[TBA]^+$ and $[TBP]^+$ were overlapping, the resolution factor was less than 1. Thus, it was needed to further choose the different ratio of methanesulfonic acid – acetonitrile, as shown in Fig. 2.

3.2.2. Selection of methanesulfonic acid concentration

Using methanesulfonic acid-30% acetonitrile as eluent, the effect of methanesulfonic acid concentrations of 1, 2, 3, 4 and 5 mmol L^{-1} were investigated. The chromatographic analysis found that with the increase of methanesulfonic acid concentration, the retention times were shortened. This complied with the principle of ion exchange chromatography, however the resolution of two peaks was not obvious improved. The value greater than 4 mmol L^{-1} methanesulfonic acid (pH < 2.1) is approaching the limit of the pH that column allows, affecting the system conductivity and baseline instability. While if the concentration of methanesulfonic acid is less

than 2 mmol L^{-1}, the retention time was at about 16 min as shown in Fig. 3. Thus, the 3 mmol L^{-1} methanesulfonic acid - 30% acetonitrile eluent was chosen for further investigation.

3.2.3. Selection of acetonitrile concentration

Using 3 mmol L^{-1} methanesulfonic acid and acetonitrile as the eluent, the effect of acetonitrile concentrations of 10, 20, 30, 40 and 50% were investigated. The chromatographic analysis found that as the concentration of acetonitrile was reduced, the retention time of both ions was increased. The reason is the increasing of organic modifier acetonitrile had enhanced the interaction between hydrophobic ions and the surface of the stationary phase. Result showed that there is an improved in separating degree by the decreasing the concentration of organic modifier, as shown in Fig. 4. However, when the concentration of acetonitrile was 10%, the tailing phenomenon was obvious. The concentration of 20% acetonitrile was chosen because the degree of separation reached 2.059 and the peak shape was excellent. The optimum compositions of the final eluent are for 3 mmol L^{-1} methanesulfonic acid - 20% acetonitrile.

3.2.4. Selection of flow rate

Using 3 mmol L^{-1} methanesulfonic acid - 20% acetonitrile as eluent, at room temperature, the effects of flow rate of 0.4, 0.6, 0.8, 1.0, and 1.2 mL/min were investigated. The influence of flow rates to the degree of separation, column pressure and column efficiency were studied. The experimental results showed that with the increase of flow rate, both ions' retention times were shortened, without impacting

the degree separation, as shown in Fig. 5. The flow rate of 1.2 mL/min was chosen as the optimum flow rate used in the entire experiment, because it permitted the relatively short retention time and the stable baseline.

3.3. Quantitative parameter

Through the above discussions, the optimal chromatographic conditions for determination of $[TBA]^+$ and $[TBP]^+$ were as follow: the samples were first enriched and purified through a SCX solid-phase extraction column, and eluted with 0.02 mol L^{-1} hydrochloric acid - 98% methanol (v/v), then analyzed by a carboxylic acid base cation exchange column, 3 mmol L^{-1} methanesulfonic acid-20% acetonitrile(v/v，pH=2.51) as mobile phase, flow rate of 1.2 mL min^{-1} and column temperature of room temperature was applied. Under these conditions, the chromatogram of two cations is shown in Fig. 6.

The calibration curve, detection limits and precision of the method were determined by analyzing a series of standard solutions of $[TBA]^+$ and $[TBP]^+$ under the selected chromatographic conditions. Linear regression equations were obtained from the relationship between peak area (integral value) and ionic concentration (mg L^{-1}). Detection limits were calculated by a triple signal-to-noise ratio (S/N = 3), and noise value of experiment was 0.0029μS/cm. Relative standard deviations (RSD) were obtained by five repeated measurement of a standard mixture solution of $[TBA]^+$ and $[TBP]^+$ under the optimal chromatographic conditions. The results are shown in **Table 2**. It showed that the reproducibility and linearity of the method meet the requirements of quantitative analysis.

3.4. Analysis of sample

This method was applied to the simultaneous determination of quaternary ammonium salts and quaternary phosphonium salts in environmental water samples. The samples were left standing overnight, and then filtered through filter paper. The 5 mL sample solutions were first enriched and purified through a SCX solid-phase extraction column, and filtered through a 0.22 μm membrane filter. The final solutions were used for the determination of $[TBA]^+$ and $[TBP]^+$ under optimized conditions. Recoveries were determined by the standard addition method. Analytical results and recoveries of $[TBA]^+$ and $[TBP]^+$ in the environmental water samples are listed in **Table 3**. The data in Table 3 were the average values (n = 5), and the RSD were less than 3%. Data from Table 3 proved that the method are accurate and reproducible, and it meets the requirements of quantitative analysis of $[TBA]^+$ and $[TBP]^+$.

4. Conclusion

This paper reported a novel approach using solid phase extraction to concentrate and purify tetrabutyl ammonium and tetrabutyl phosphonium in environmental water. The method was using methanesulfonic acid and acetonitrile as the eluent and direct conductivity for determination of tetrabutyl ammonium and tetrabutyl phosphonium in environmental water. The study showed that in solid phase extraction, the change of hydrochloric acid concentration could greatly affect the sample recovery. In ion chromatography detection, reducing the content of acetonitrile in mobile phase had significantly improved the tetrabutyl ammonium and tetrabutyl phosphonium

separation. The appropriate adjustment of methanesulfonic acid and acetonitrile concentration was able to improve the retention time. This method has been successfully applied to determine the tetrabutyl ammonium and tetrabutyl phosphonium in environmental water. By using laboratory generally-available ion chromatography and conductivity detection, which has high practical value, the method was accurate, reliable, and relatively simple to be applied.

Acknowledgments

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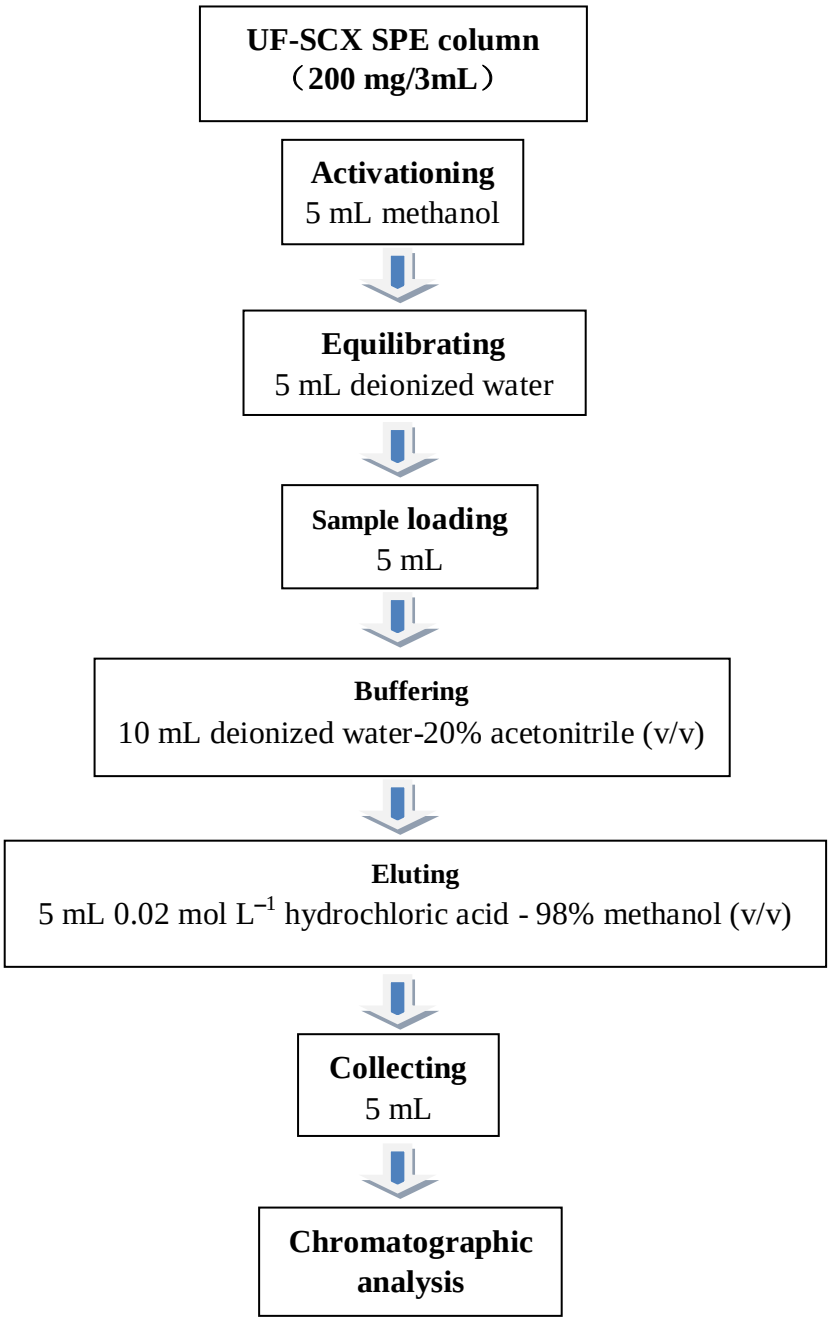

Fig. 1 Solid-phase extraction protocol of tetrabutyl ammonium cation and tetrabutyl phosphonium cation

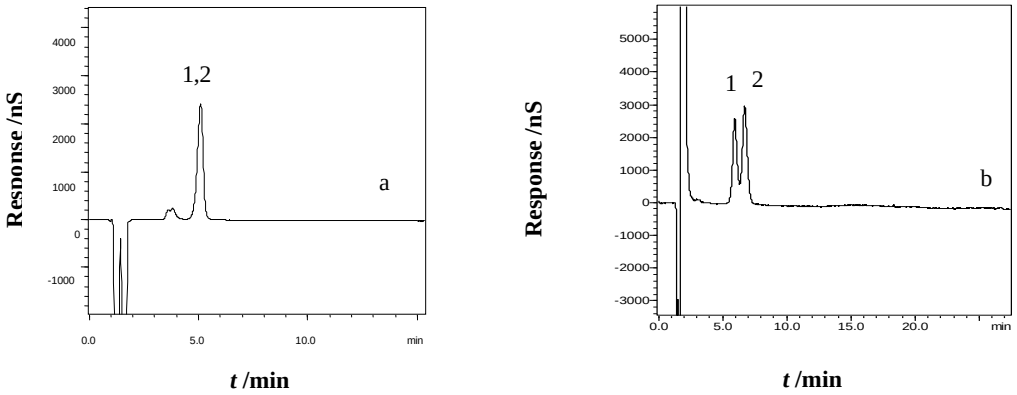

Fig. 2 Chromatograms obtained with mobile phases containing different acids

Mobile phase, (a) 5 mmol L^{-1} tartaric acid - 50% acetonitrile (v/v); (b) 3 mmol L^{-1} methane sulfonic acid - 30% acetonitrile (v/v). Peaks（50 mg L^{-1}）: 1, tetrabutyl ammonium ($[TBA]^+$) ; 2, tetrabutyl phosphonium ($[TBP]^+$)

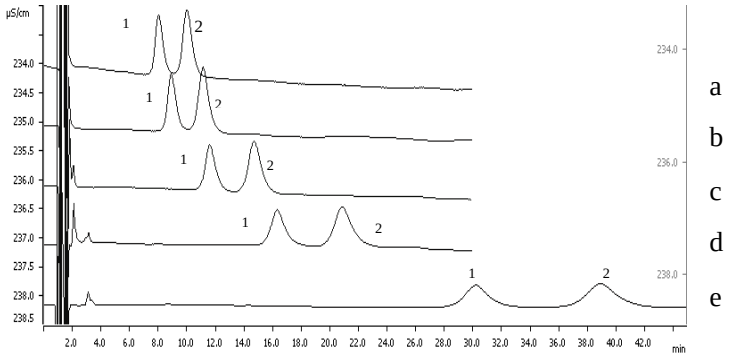

Fig. 3 Chromatograms obtained with mobile phases containing different concentrations of methanesulfonic acid

(a) 5 mmol L^{-1}; (b) 4 mmol L^{-1}; (c) 3 mmol L^{-1}; (d) 2 mmol L^{-1}; (e) 1 mmol L^{-1}. Mobile phase: different concentrations of methanesulfonic acid - 30% acetonitrile (v/v). Peaks（50 mg L^{-1}）: 1, $[TBA]^+$; 2, $[TBP]^+$

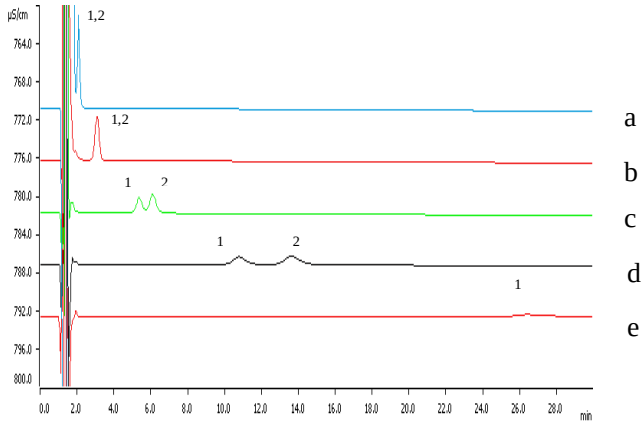

Fig. 4 Chromatograms obtained with mobile phases containing different volume fractions of acetonitrile

(a) 50%; (b) 40%; (c) 30%; (d) 20%; (e) 10%. Mobile phase: 3 mmol L^{-1} methanesulfonic acid - different volume fractions of acetonitrile (v/v). Peaks（50 mg L^{-1}）: 1, $[TBA]^+$; 2, $[TBP]^+$

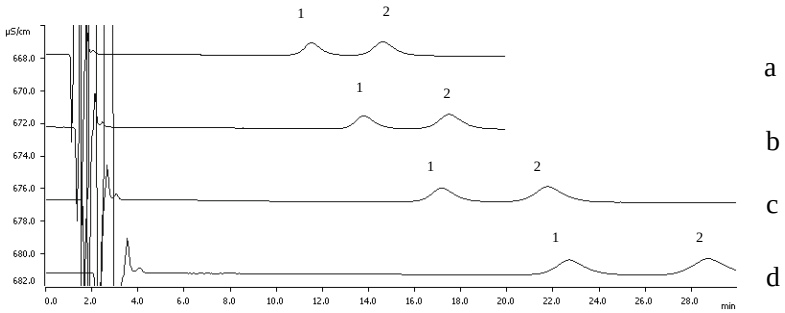

Fig. 5 Chromatograms of different flow rates

(a) 1.2 mL/min; (b) 1.0 mL/min; (c) 0.8 mL/min; (d) 0.6 mL/min. Peaks（50 mg L^{-1}）: 1, $[TBA]^+$; 2, $[TBP]^+$

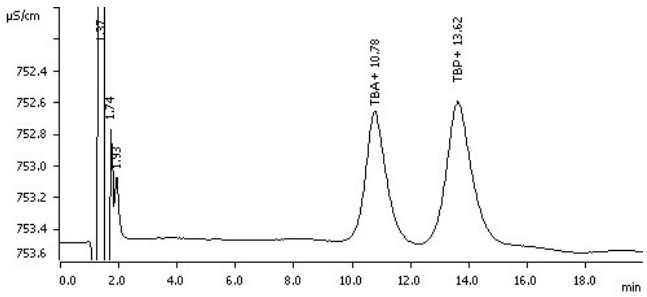

Fig. 6 Chromatogram of standard mixture solution

Sample pretreatment: solid-phase extraction column, UF-SCX（200mg/3mL）; eluent, 0.02 mol L^{-1} hydrochloric acid - 98% methanol (v/v). Chromatographic conditions: column, Shodex IC YK-421; mobile phase, 3 mmol L^{-1} methanesulfonic acid - 20% acetonitrile; flow rate, 1.2 mL min^{-1}; column temperature, room temperature; direct conductivity detection; inject volumn, 20 μL. Peaks（50 mg L^{-1}） : 1, $[TBA]^+$; 2, $[TBP]^+$

Table 1 Recoveries of solid-phase extraction

Eluent (mol L^{-1})	Recovery（%）	
Hydrochloric acid-methanol	$[TBA]^+$	$[TBP]^+$
0.02	90.5	97.1
0.05	74.7	5.0
0.07	58.6	8.0
0.09	69.4	17.8
0.12	52.8	19.9
0.24	46.0	20.1
0.36	30.5	21.0

Table 2 Linear regression equations, limits of detection (LOD) and relative standard deviations of retention time (RSD_t) and peak area (RSD_s)

Ion	Linear regression equation y = area x = concentration, mg L^{-1}	Correlation coefficient (r, n = 5)	LOD (S/N=3, mg L^{-1})	Linear range (mg L^{-1})	RSD_t/RSD_s (%, n = 5)
$[TBA]^+$	y = 0.0142x-0.0132	0.9996	0.502	1.67–100	1.22/0.24
$[TBP]^+$	y = 0.0195x-0.0265	0.9997	0.448	1.49–100	1.23/0.25

Table 3 Contents and spiked recoveries of tetrabutyl ammonium cation and tetrabutyl phosphonium cation in environmental water sample

Sample	Ion	Original (mg/L)	Added (mg/L)	Total found (mg/L)	Recovery (%)
Environmental water	$[TBA]^+$	0.0	40.0	41.3	103.2
	$[TBA]^+$	0.0	50.0	48.5	97.0
	$[TBA]^+$	0.0	60.0	58.3	97.2
	$[TBP]^+$	0.0	40.0	40.4	100.9
	$[TBP]^+$	0.0	50.0	47.5	95.0
	$[TBP]^+$	0.0	60.0	56.9	94.8

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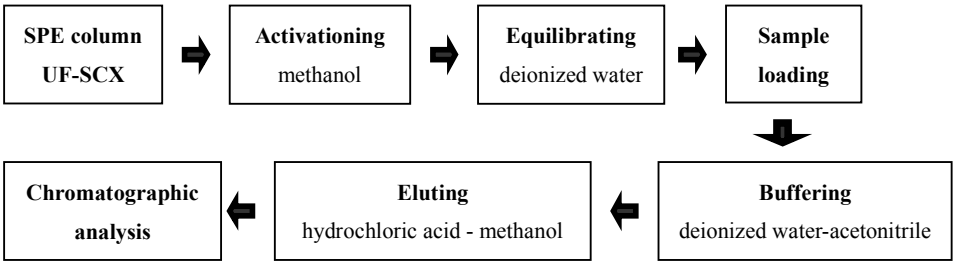

Solid phase extraction and ion chromatography for simultaneous determination of tetrabutyl ammonium and tetrabutyl phosphonium in environmental water sample