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Field analysis of benzene, toluene, ethylbenzene and xylene in water by portable gas chromatography–microflame ionization detector combined with headspace solid-phase microextraction

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Abstract

In this work, portable gas chromatography–microflame ionization detection (portable GC–μFID) coupled to headspace solid-phase microextraction (HS-SPME) was developed for the field analysis of benzene, toluene, ethylbenzene and xylene (BTEX) in water samples. The HS-SPME parameters such as fiber coating, extraction times, stirring rate, the ratio of headspace volume to sample volume, and sodium chloride concentration were studied. A 65 μm poly(dimethylsiloxane)-divinylbenzene (PDMS-DVB) SPME fiber, 900 rpm, 3.0 ml of headspace (1.0 ml water sample in 4.0 ml vial), and 35% sodium chloride concentration (w/v) were respectively chosen for the best extraction response. An extraction time of 1.0 min was enough to extract BTEX in water samples. The relative standard deviation (R.S.D.) for the procedure varied from 5.4% to 8.3%. The method detection limits (MDLs) found were lower than 1.5 μg/l, which was enough sensitive to detect the BTEX in water samples. The optimized method was applied to the field analysis of BTEX in wastewater samples. These experiment results show that portable GC–μFID combined with HS-SPME is a rapid, simple and effective tool for field analysis of BTEX in water samples.

Keywords: Portable gas chromatography–microflame ionization detector; Headspace solid-phase microextraction; Benzene; Toluene; Ethylbenzene; Xylene; Field analysis

1. Introduction

Benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene (BTEX) are important industrial chemicals used worldwide for plastic, as chemical intermediates and solvents. Recently, they have acquired great relevance as ubiquitous pollutants of the outdoor and indoor environment [1,2]. Due to the toxicological properties of benzene [3,4], there is an interest in the development of specific analytical procedures to measure these aromatic hydrocarbons in water samples [5].

Gas chromatography-flame ionization detection (GC–FID) or gas chromatography–mass spectrometry (GC–MS) has been used for analysis of BTEX in wastewater. Prior to analysis, extraction and concentration of BTEX from the aqueous samples are required. Conventional techniques such as solid-phase extraction and liquid–liquid extraction were used for this purpose [6,7]. However, these techniques require large volume of organic solvents, some of which may be toxic and carcinogenic. Moreover, the extraction course is time-consuming. Recently, several novel techniques of purge-and-trap (PT) [8,9], membrane extraction [10], solid-phase microextraction (SPME) [11–14] and single-drop microextraction [15–17] were developed for the analysis of BTEX and other volatile compounds in water samples. Among these techniques, SPME is a solvent-free sample technique with the advantage of extraction and concentration in a single step. SPME technique has widely been used for the analysis of chemical pollutants including BTEX in water [13,18–23].

As mentioned, BTEX in wastewater sample are highly volatile. A careful and strict preservation of wastewater is necessary in order to reduce the loss of BTEX during the process of carrying the wastewater samples to the lab. Therefore, field analysis of BTEX in wastewater samples is very desirable.

To meet with field analysis of environmental samples such as wastewater sample, portable gas chromatography (portable GC) was developed [24–26]. Several papers reporting the use of portable GC for the determination of volatile organic compounds

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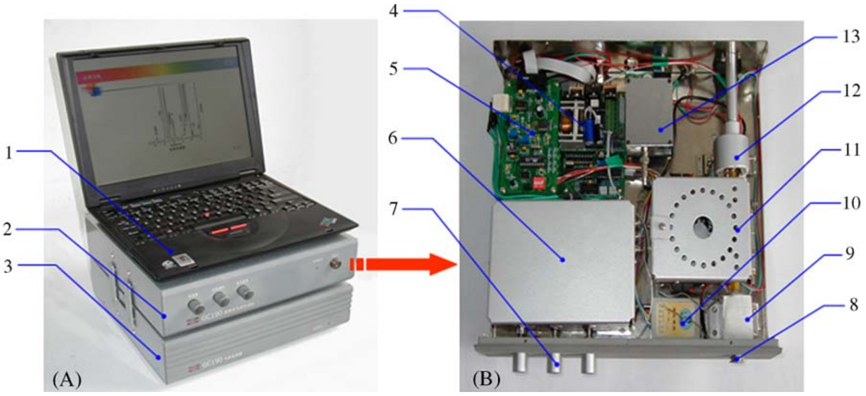

Fig. 1. The photo of a novel portable GC with micro-FID: (1) laptop; (2) GC190; (3) GC190 power supply and gas supply; (4) control board for microprocessor circuit; (5) board of gas monitoring circuit; (6) pneumatic controls; (7) airflow adjustment knob; (8) injection port; (9) capillary split/splitless inlet; (10) high voltage power; (11) capillary column; (12) μFID detector; (13) FID micro-current amplifier.

(VOCs) have been reported [26,27]. Recently, portable GC combined with SPME technique was developed for the field analysis of VOCs in indoor air [28].

In our lab, a novel portable gas chromatograph with a microflame ionization detector (portable GC–μFID) has been devised and manufactured (Fig. 1). A novel on-column heating system that can make the capillary column temperature rapidly increase up to 10 °C/s is used in the portable GC [29]. The μFID needing only two gases of air and hydrogen is used as the detector of the potable GC [30,31]. It weighs only 4 kg, and with a size of 31 cm × 28 cm × 7.5 cm. Due to its small volume and capacity of rapid analysis, the portable GC is an alternative tool for field analysis. The objective of this work was to develop a portable GC–μFID combined with HS-SPME technique for the field analysis of BTEX in the water samples. The water samples were headspace extracted by SPME technique, and then the extracts were desorbed, and analyzed with the portable GC–μFID. The HS-SPME parameters such as type of fiber, extraction time, stirring rate, the ratio of headspace volume to sample volume, sodium chloride concentration and desorption time were investigated.

2. Experiment

2.1. Reagent and standards

Analytical grade benzene, toluene, ethylbenzene, and xylene (BTEX) were from Guoyao, Shanghai, China. Chromatographic grade methanol was purchased from Merck (Darmstadt, Germany). Distilled water was purified by a Milli-Q system (Milford, MA, USA). A stock BTEX solution was prepared in methanol with a concentration of 500 mg/l for each compound. It was stored in a refrigerator at 4 °C. Standard solutions of BTEX at the concentration level of interest were prepared daily from the stock solution by spiking and mixing them with 1 ml distilled water, and the methanol concentration was restricted to 1% (v/v).

2.2. SPME holder and fibers

SPME holder and fiber assemblies for manual sampling were provided from Supelco (Bellefonte, PA, USA). The fiber coatings used were 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 65 μm carbowax/divinylbenzene (CW/DVB), 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) and 85 μm polyacrylate (PA). Before measurements the PDMS fibers were conditioned in the injector for 3 min at 240 °C, then repeatedly injected into the portable GC until interfering peaks disappeared.

2.3. Portable GC conditions

A portable GC equipped with a 7.5 m × 0.25 mm, 0.25 μm SPB-5 fused silica capillary column (Supelco, Bellefonte, PA, USA) and microflame ionization detection (μFID) system (Fudan University, Shanghai, China) was used for all analyses. The injector and detector temperatures were 200 and 150 °C, respectively. The inlet was operated in split mode with a split ratio of 80:1, and carrier gas was hydrogen with the flow-rate of 1 ml/min. The portable GC column temperature program was: 30 °C for 40 s, 0.5 °C/s to 60 °C, held for 15 s.

2.4. Optimization of the headspace SPME conditions

At first, five types of SPME fiber coatings were tested to select the most efficient one for the extraction of BTEX. The fiber coating, which had the best extraction efficiency, would give the largest peak area under the same chromatographic conditions. Next, extraction time, stirring rate, the ratio of sample volume to headspace volume, and sodium chloride concentration were tested in the work, in order to get the optimum conditions that would have the best extraction efficiency. For the field analysis, the temperature of determination is usually the temperature of environment. So the influence of temperature on the extraction was not considered, as its control in field analysis in not necessary and would make the process more difficult.

2.5. Linear range, detection limit, and precision

The optimized conditions were used for validating the method (linear range, detection limit, and precision). Linear range for BTEX was studied by replicate analysis of the standard stock solutions (10–2000 μg/l). The linear regression values were calculated with the average peak areas of three replicate injections for each analyte. Relative standard deviation (R.S.D.) was the average value of different concentrations of BTEX in the linear range. The peak height of each compound of the lowest concentration was used to calculate the detection limit (S/N = 3) of this work. Finally, real sample spiked with standard solutions of BTEX were determined, and matrix effect was examined with the recoveries of the four analytes.

2.6. Determination of BTEX in wastewater

Two wastewater sample collected from chemical plants in Shanghai, China, were put into a 4 ml glass vials (Chromacol, Herts, UK) with a PTFE-silicon septa. Water sample was saturated with NaCl, and agitated with a Teflon-coated stir bar. The solution volume of each sample was 1 ml. Sampling extraction was performed in the headspace mode by exposing the SPME fiber over stirred samples. The fiber was withdrawn into the needle of the holder after extraction, and immediately injected into the portable GC inlet.

To quantify BTEX in the wastewater samples, aqueous standard solutions ranged from 10 to 1000 μg/l were analyzed at the same SPME and GC analysis procedure described above.

3. Results and discussion

3.1. Selection of SPME fiber

The choice of an appropriate coating is necessary for the SPME method. The extraction efficiency of each fiber is different depending on the molecular mass and the polarity of the analytes. Five commercially available SPME fiber coatings, with different polarity and inner structure, as mentioned above were tested for efficiency of headspace SPME extraction of BTEX. A concentration of 500 μg/l was used for each analyte in the study. As shown in Fig. 2, extraction efficiency of PDMS–DVB fiber with weak polarity was the best. The PA fiber showed very poor efficiency for the extraction of BTEX, for it prefers relatively polar analytes. The other three kinds of fiber had efficiencies between that of PDMS–DVB and PA, and tailing peaks were observed for CAR/PDMS and PDMS, which were kinds of non-polar coating. Similar results were found in several literatures [32–34]. Therefore, the PDMS–DVB fiber was selected for the further study.

3.2. Parameters influencing the HS-SPME process

HS-SPME is an equilibrium process that involves the portioning of analytes from aqueous phase to gas phase and gas phase into the polymeric phase according to their partition coefficients K_d [35]. Thus, the optimization of parameters is extremely important. Temperature, stirring rate, ionic strength, the ratio of headspace volume to sample volume, and time for the extraction are the main parameters that should be taken into account. But in the field analysis, temperature was not considered as the reason discussed already.

3.2.1. Effect of stirring rate

The intensity of stirring is one of the most important parameters, especially when the extraction time is very short. Stirring

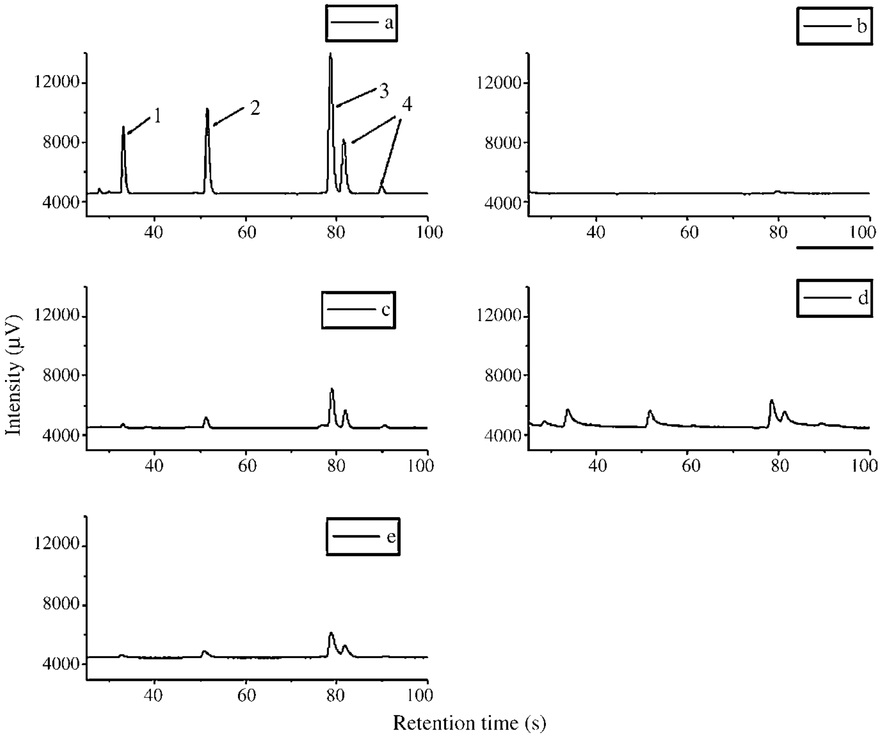

Fig. 2. Comparison between the different fibers in the extraction of BTEX at the concentration level of 500 μg/l. Fibers: PDMS/DVB (a), PA (b), CW/DVB (c), CAR/PDMS (d), PDMS (e). Peaks: benzene (1), toluene (2), ethylbenzene (3), and xylene (4). Stirring speed 900 rpm, extraction time 60 s, desorption time of 30 s.

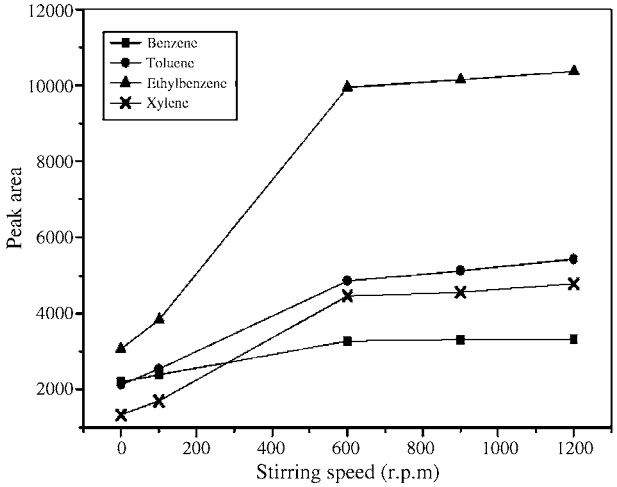

Fig. 3. Effect of stirring speed on detector response area by using 65 μm PDMS/DVB fiber, BTEX concentration 500 μg/l, and other extraction conditions were the same as Fig. 2.

should be vigorous and has to be maintained constant in all experiments to ensure the reproducibility [3–6]. The optimum stirring rate was determined by analyzing samples containing 500 μg/l of BTEX at different stirring rates between 0 and 1200 rpm (Fig. 3). From the obtained results it can be stated that the extraction level was poor without stirring, and the extraction efficiency was obviously enhanced when the stirring rate increased from 0 to 600 rpm. But increase of extraction efficiency for benzene was not observed after the stirring rate reached 600 rpm for its highest volatility, when the extraction efficiencies for toluene, ethylbenzene and xylene also increased slowly at the same time. Another reason for this phenomenon was that the volume of the glass vial used in this study was only 4 ml, in which the headspace was also small. Speeding up the transfer of compounds from water to headspace is pointless when the speed becomes faster than that of the mass transfer from headspace to fiber coating. So after 600 rpm, the high volatility of BTEX and the comparatively small volume of headspace make the mass transfer becomes the rate-determining step and thus, a stirring speed increase does not improve the HS-SPME kinetics. The stirring speed at 900 rpm was used in the subsequent experiments to ensure the extraction efficiency for the four compounds.

3.2.2. *Effect of extraction time*

The time required for the extraction process was an important parameter to be investigated. The most adequate time for the HS-SPME extraction was considered to be the time reaching the equilibrium of the analytes between the vapor phase and fiber coating. Extraction time between 5 and 120 s were tested for the samples of 100 μg/l (Fig. 4). An increasing efficiency was observed for all the four compounds when the longer extraction time was used. But the increasing was not so evident from 60 to 120 s especially for benzene. A short extraction time is preferred in rapid detection, and desorption of the analytes from the fiber was supposed to compete with the absorption process for excessively long extraction time. So the extraction time of 60 s was considered to be adequate for the subsequent experiments.

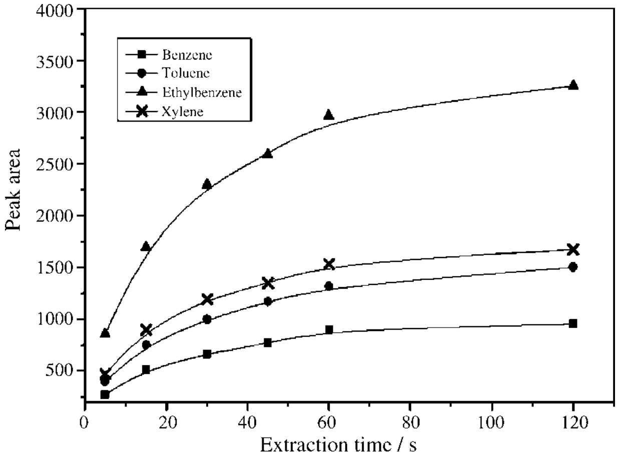

Fig. 4. Effect of extraction time on detector response area by using 65 μm PDMS/DVB fiber, BTEX concentration 100 μg/l, and other extraction conditions were the same as Fig. 2.

3.2.3. *Effect of salt additives*

The influence of salt additives to HS-SPME procedure was investigated by comparing the extraction efficiency of samples with different concentration of sodium chloride (NaCl) added (Fig. 5). A slight increase in extraction yield was observed with the increasing of NaCl concentration according to Fig. 5, and it reached the peak yield when NaCl 35% (w/v) was used to saturate the samples. The reason was considered to be the increase of ionic strength in aqueous samples by adding salt, therefore the solubility of analytes was decreased and more analyte was released into the headspace. Thus, saturation with salt additives was an effective method to lower the detection limits of determination, and it could also normalize the influence of a random salt concentration in sample matrix to improve reproducibility.

3.2.4. *Effect of the ratio of sample volume to headspace volume*

The ratio of sample volume to headspace volume is an important parameter that affects the extraction efficiency of SPME. In the work, 1.0, 2.0 and 3.0 ml of standard solutions with the concentration of 500 μg/l for each analyte was introduced into three

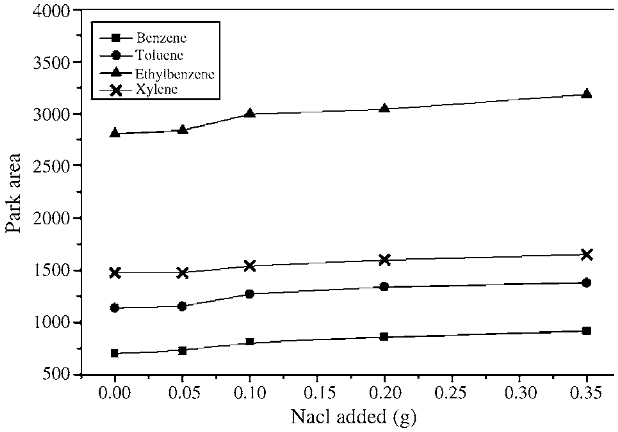

Fig. 5. Effect of NaCl additives on detector response area by using 65 μm PDMS/DVB fiber, BTEX concentration 100 μg/l, and other extraction conditions were the same as Fig. 2.

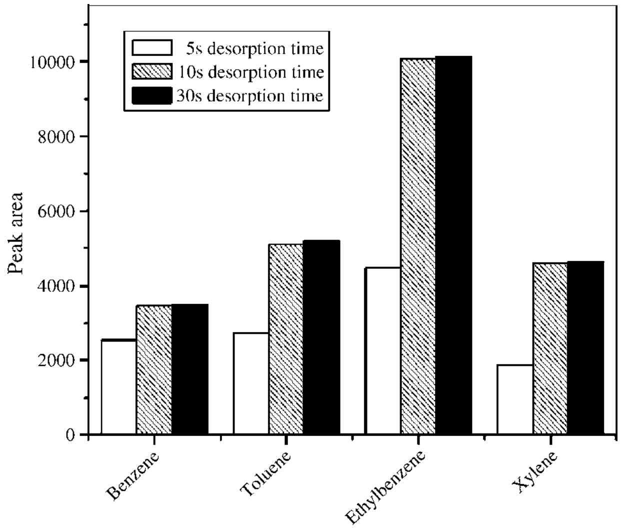

Fig. 6. Effect of desorption time on detector response area by using 65 μm PDMS/DVB fiber, BTEX concentration 500 μg/l, and other extraction conditions were the same as Fig. 2.

headspace vials (4 ml), respectively. Headspace extraction and GC analysis were performed. Little effect of the ratio of sample volume to headspace volume on the extraction efficiency was observed. In the work, sample volume of 1.0 ml (in 4.0 ml vial) was used.

3.3. Desorption time

Desorption procedure was not the parameter influencing extraction efficiency, because it did not directly participate in the extraction process. But the time taken by the desorption procedure would impact on the overall determination time; for a short desorption time would help to reduce the total determination time. As shown in Fig. 6, desorption time for 10 s would release nearly all the BTEX from the PDMS–DVB fiber coating. So, 10 s was selected as the optimal desorption time.

3.4. Method validation

Series of several levels were obtained by spiking distilled water with BTEX in a concentration range from 10 to 2000 μg/l. Each solution was submitted to the HS-SPME analysis three times. Fig. 7 shows a typical chromatogram obtained after HS-SPME of BTEX with the optimum conditions obtained above. The linear regression values and relative standard deviation (R.S.D.) for benzene, toluene, ethylbenzene and xylene were also tested (Table 1).

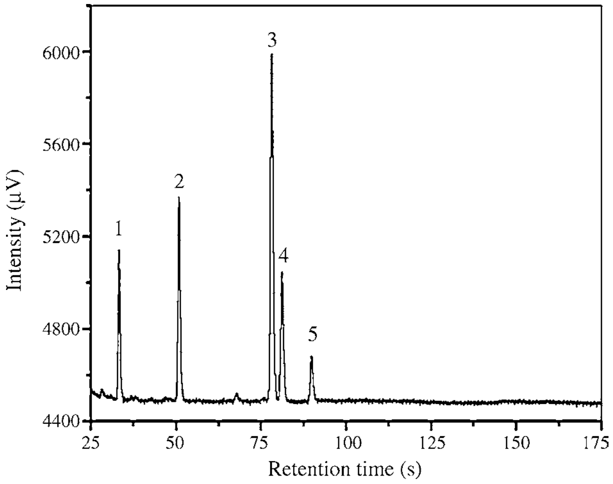

Fig. 7. portable GC–FID chromatogram obtained by 65 μm PDMS/DVB fiber for 50 μg/l of BTEX. Peaks: benzene (1), toluene (2), ethylbenzene (3), *m*- and *p*-xylene (4), and *o*-xylene (5). Chromatographic conditions were the same as Fig. 2.

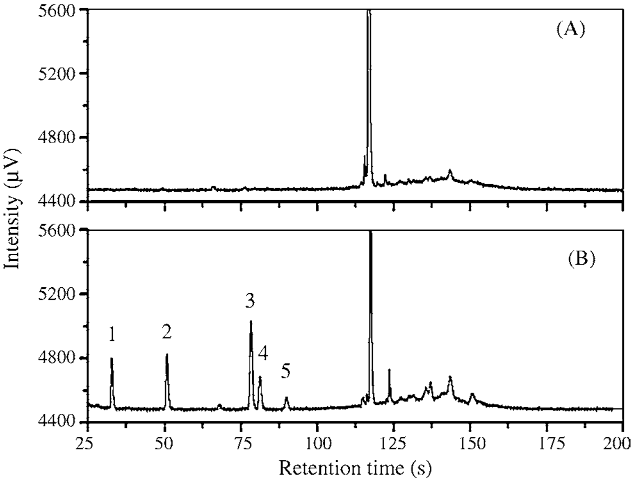

Fig. 8. portable GC–FID chromatogram obtained by 65 μm PDMS/DVB fiber for (A) real samples and (B) 25 μg/l of BTEX in spiked real samples. Peaks: benzene (1), toluene (2), ethylbenzene (3), *m*- and *p*-xylene (4), and *o*-xylene (5). Chromatographic conditions were the same as Fig. 2.

Table 1 shows the linear regression for toluene, ethylbenzene and xylene with correlation coefficients greater than 0.990, and 0.984 for benzene. And the linear range was 10–1000 μg/l for benzene and 10–2000 μg/l for toluene, ethylbenzene and xylene. The R.S.D. values for the four analytes were between 5% and 9%. In further study, real aqueous samples were tested (collected from several Chemical Plants in Shanghai, China) with 25 μg/l standard BTEX solution spiked (Fig. 8) and no evident

Table 1
Analytical performance characteristics of combined HS-SPME–portable GC–FID for BTEX determinations in aqueous samples

Compound	t_R (s)	R^2	Precision (% R.S.D.)	LOD (μg/l)	Linear range (μg/l)
Benzene	32	0.984	6.1	1.0	10–1000
Toluene	51	0.991	8.3	0.75	10–2000
Ethylbenze	79	0.998	7.0	0.44	10–2000
Xylene	82, 90	0.996	5.8	1.4	10–2000

matrix effects were observed. Apparent recoveries for benzene, toluene, ethylbenzene and xylene were 111.4%, 98.4%, 98.6% and 108.5%, respectively.

3.5. Quantification of BTEX concentration in real water sample

Two wastewater samples (samples A and B) collected from Chemical Plants in Shanghai, China, were field analyzed by portable GC–μFID combined with HS-SPME at the optimal experimental conditions described above. BTEX concentrations were calculated on basis of external standard method. The concentrations of benzene, toluene, ethylbenzene and xylene in the wastewater samples are 21, 14, 18 and 26 μg/l (sample A), and 32, 37, 14 and 12 μg/l (sample B), respectively. It was shown that by using the proposed method, quantification of BTEX in real wastewater sample can complete in a short time of 3 min.

4. Conclusions

In the study, portable GC–μFID combined with HS-SPME has successfully been developed for filed analysis of BTEX in water samples. Extraction and concentration of BTEX in water samples needed only 1 min by using SPME technique. The analysis time of BTEX by portable GC was less than 2 min. Therefore, the total analysis time was about 3 min. This indicates that portable GC–μFID combined with HS-SPME is an alternative method for rapid analysis of BTEX in water samples and is a potential and powerful tool for environment field monitoring.

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