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Ultrasound-assisted surfactant-enhanced emulsification microextraction for the determination of carbamate pesticides in water samples by high performance liquid chromatography

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ABSTRACT

A novel ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) coupled with high performance liquid chromatography-diode array detection has been developed for the extraction and determination of six carbamate pesticides (metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb) in water samples. In the UASEME technique, Tween 20 was used as emulsifier, and chlorobenzene and chloroform were used as dual extraction solvent without using any organic dispersive solvent that is normally required in the previously described common dispersive liquid–liquid microextraction method. Parameters that affect the extraction efficiency, such as the kind and volume of the extraction solvent, the type and concentration of the surfactant, ultrasound emulsification time and salt addition, were investigated and optimized for the method. Under the optimum conditions, the enrichment factors were in the range between 170 and 246. The limits of detection of the method were 0.1–0.3 ng mL^{-1} and the limits of quantification were between 0.3 and 0.9 ng mL^{-1}, depending on the compounds. The linearity of the method was obtained in the range of 0.3–200 ng mL^{-1} for metolcarb, carbaryl, pirimicarb, and diethofencarb, 0.6–200 ng mL^{-1} for carbofuran, and 0.9–200 ng mL^{-1} for isoprocarb, with the correlation coefficients (r) ranging from 0.9982 to 0.9998. The relative standard deviations varied from 3.2 to 4.8% (n = 5). The recoveries of the method for the six carbamates from water samples at spiking levels of 1.0, 10.0, 50.0 and 100.0 ng mL^{-1} were ranged from 81.0 to 97.5%. The proposed UASEME technique has demonstrated to be simple, practical and environmentally friendly for the determination of carbamates residues in river, reservoir and well water samples.

1. Introduction

Carbamates are one of the major classes of the pesticides that are widely used in agriculture due to their broad biological activity, low bioaccumulation potentials and relatively low mammalian toxicities. However, carbamates affect the nervous system by disrupting an enzyme that regulates acetylcholine, a neurotransmitter. These compounds are considered hazardous to the environment and human health. They are on the priority list released by the United States Environmental Protection Agency (EPA) [1]. Their acute toxicity is of great concern and therefore, the determination of the carbamates at low concentrations is of particular interest.

Most of the carbamates compounds have high melting points and low vapor pressures. They may persist in the environment after their application, with some even remaining for many years. Their residues may appear in fruits, vegetables and usually distribute in aqueous environments by leaching and runoff from soil into ground and surface water because of their high solubility in water [2–4]. The widespread use of carbamates in agriculture could lead to an increase of their residues in environmental matrices. Therefore, the evaluation and monitoring of trace levels of these compounds are imperative.

Several analytical methods, such as gas chromatography (GC) [3,5], enzyme-linked immunosorbent assays (ELISAs) [6–7], micellar electrokinetic chromatography (MEKC) [2,4], biosensor [8] and high performance liquid chromatography (HPLC) [9–16], have been reported for the separation and quantification of carbamate residues in different matrices. However, the thermal instability of carbamates does not permit their direct determination by gas chromatography unless they are derived into thermally stable derivatives. For this reason, HPLC with different detectors has become the most commonly used techniques for the determination of carbamate residues. Different pretreatment methods, including liquid–liquid extraction (LLE) [10], solid-phase extraction

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(SPE) [11], supercritical fluid extraction (SFE) [12,13], microwave-assisted extraction (MAE) [13,14], solid-phase microextraction (SPME) [15–17] and liquid-phase microextraction (LPME) [3,5], have been used for the preconcentration and cleanup of the carbamate pesticide residues from different samples prior to instrumental analysis.

Recently much attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques that could greatly reduce the organic solvent consumptions [18,19]. For this purpose, several different types of LPME techniques have emerged for sample preparations. LPMEs have advantages of simplicity, effectiveness, low cost, and minimum use of solvents, and also can overcome some disadvantages often encountered in SPME, such as sample carry-over, the requirement to condition the SPME fiber, and additional instrumental modification [20–25]. More recently, a relatively new mode of LPME, the dispersive liquid–liquid microextraction (DLLME), has been developed [22,26–31]. The advantages of the DLLME method include rapidity, low cost, simplicity of operation and high enrichment factor. However, to enhance the dispersion of the extraction solvent in the aqueous sample phase, the use of a water-miscible organic dispersive solvent is required in DLLME although its use could decrease the partition coefficient of analytes into the extraction solvent. Another disadvantage for DLLME is that the majority of the extraction solvents used in the reported DLLME methods are halogenated hydrocarbons although they are environmentally hazardous.

Very recently, a novel microextraction technique, named ultrasound-assisted emulsification microextraction (USAEME) has been developed by Garcia-Jares and co-workers [23]. In USAEME, a microvolume of water-immiscible extraction solvent is dispersed into sample aqueous solution by ultrasound-assisted emulsification without using any dispersive solvent. The ultrasound-assisted emulsification is usually carried out either at 25 °C for 10 min [23,24] or at 35 °C for 5 min [25].

It is well known that surfactants, or surface-active agents, are amphiphilic molecules. Their heads are polar, or hydrophilic, and their tails hydrophobic. The tail is generally a hydrocarbon chain with different member of carbon atoms, which may be linear or branched, and also contains aromatic rings. Surfactant could serve as an emulsifier to enhance the dispersion of water-immiscible phase into aqueous phase. The application of a surfactant as emulsifier in USAEME would take the advantages of both DLLME and USAEME. Surfactant will accelerate the formation of fine droplets of the extraction solvent in an aqueous sample solution under ultrasound radiations, thus to decrease the extraction time. After extraction, the two phases can be readily separated by centrifugation. Therefore, in this work, an ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME), coupled with HPLC-diode array detection (DAD) was explored and developed for the determination of some carbamates in water samples. The effects of various experimental parameters, such as the kind and volume of the extraction solvent, the type and concentration of the surfactant, ultrasound emulsification time and salt addition, were investigated and optimized. The UASEME technique proved to be simple and efficient. To the best of our knowledge, this is the first report about the application of the UASEME for the determination of pesticides in water samples.

2. Experimental

2.1. Reagents and materials

Metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb were purchased from Agricultural Environmental Protection Institution of Tianjin (Tianjin, China). Chloroform ($CHCl_3$), tetrachloride ethylene (C_2Cl_4), carbon tetrachloride (CCl_4), chlorobenzene, Tween 20, sodium dodecyl sulfate (SDS), Triton X-114 and Triton X-100 were purchased from Beijing Chemical Reagents Company (Beijing, China). Methanol was from Sinopharm Chemcial Reagent Co. (Beijing, China). Sodium chloride (NaCl) was from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China).

Reservoir water was collected from Wangkuai reservoir (Baoding, China); well water from Laiyuan (Baoding, China); river water was collected from Yimu River (Baoding, China), respectively. All the solvents and water samples were filtered through a 0.45-μm membrane to eliminate particulate matters before analysis.

A mixture stock solution containing metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb at 10.0 μg mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with double-distilled water in a 10-mL volumetric flask. All the standard solutions were stored at 4 °C in the dark.

2.2. Instruments

The HPLC system, assembled from modular components (Waters, Milford, MA, USA), consisted of an in-line degasser, a 600E pump, and a DAD detector. A Millennium^{32} workstation (Waters) was utilized to control the system and for the acquisition and analysis of the data. A Centurysil C_{18} column (4.6 mm i.d. × 250 mm, 5.0 μm) from Dalian Jiangshen Separation Science Company (Dalian, China) was used for separations. The mobile phase was a mixture of methanol–water (60:40, v/v) at a flow rate of 1 mL min^{-1}. DAD monitoring wavelengths were chosen at 208, 200, 220, 245, 208 and 207 nm for metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb, respectively.

2.3. UASEME procedure

For the UASEME, a 5.00 mL aliquot of water sample was placed in a 10 mL screw cap glass tube with conical bottom. 150 μL of $CHCl_3$–C_6H_5Cl (1:1, v/v) as extraction solvent and 30 μL 1.0×10^{-2} mol L^{-1} Tween 20 as emulsifier (the concentration of Tween 20 in sample solution was 6.0×10^{-5} mol L^{-1}) were added into the sample solution. The resulting mixture was then immersed into an ultrasonic bath at 25 ± 2 °C for 3 min of sonication. The emulsion was disrupted by centrifugation at 3500 rpm for 5 min and the organic phase was sedimented at the bottom of the centrifuge tube. The sedimented phase was completely transferred to another test tube with conical bottom using 100-μL HPLC syringe and then evaporated to dryness under a mild nitrogen stream. The residue was dissolved in 20.0 μL methanol and 15.0 μL was injected into the HPLC system for analysis.

3. Results and discussion

The objective of the optimization procedure was to obtain maximum extraction recovery. The effects of various experimental parameters, such as the kind and volume of the extraction solvent, the type and concentration of the surfactant, ultrasound emulsification time and salt addition, were investigated.

In this experiment, 5.0 mL of double-distilled water spiked with 50.0 ng mL^{-1} each of the six carbamate pesticides was used to study the extraction performance under different experimental conditions. All the experiments were performed in triplicate and the means of the results were used for optimization.

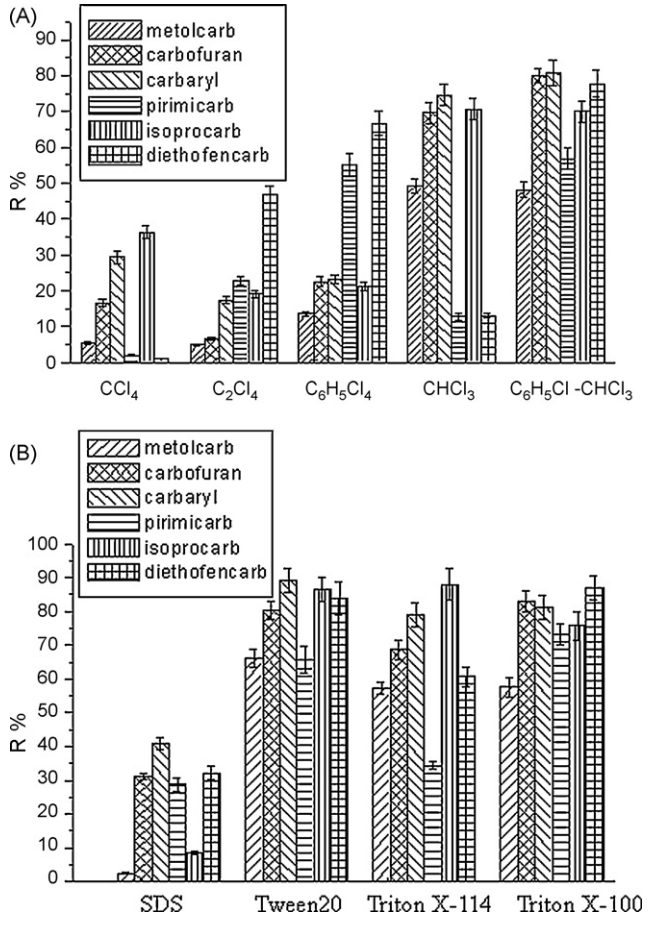

Fig. 1. Effect of different extraction solvents (A) and surfactants (B) on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; ultrasound radiation time, 2 min. (A) Extraction solvent volume, 100 μL; Triton X-100 concentration, 1.0×10^{-4} mol L^{-1}; (B) extraction solvent, 100 μL C_6H_5Cl–$CHCl_3$; surfactant concentration, 1.0×10^{-4} mol L^{-1}.

3.1. Selection of extraction solvent

The selection of an appropriate extraction solvent is critical to the UASEME process since its physicochemical properties not only affect the emulsification phenomenon but also the extraction efficiency. The extraction solvent should meet the following requirements: it should have a higher density than water, a low solubility in water, high extraction capability for the target analytes, and form a stable emulsion system in the presence of an emulsifier after ultrasound radiation. Based on these considerations, CCl_4, $CHCl_3$, C_2Cl_4 and C_6H_5Cl were selected as potential extraction solvents for the study. Fig. 1A shows the effect of the extraction solvents (CCl_4, $CHCl_3$, C_2Cl_4 and C_6H_5Cl) on the extraction recovery by using Triton X-100 as emulsifier. In the case of CCl_4 and C_2Cl_4 as extraction solvents, the extraction recoveries were low for most of the analytes. For C_6H_5Cl and $CHCl_3$, the former gave a relatively high extraction recoveries for pirimicarb and diethofencarb but a low recovery for metolcarb, carbofuran, carbaryl and isoprocarb while the latter gave a reverse result. This could be because the polarity of C_6H_5Cl is similar to that of pirimicarb and diethofencarb, and the polarity of $CHCl_3$ is similar to metolcarb, carbofuran, carbaryl and isoprocarb. To get a more even and better extraction recovery, a binary extraction solvent system of $CHCl_3$–C_6H_5Cl was investigated. The binary solvent system can take advantages of the different extraction abilities of both $CHCl_3$ and C_6H_5Cl for different analytes. The mixture of the two extraction solvents might alter their individual properties and the result showed a synergic effect of the binary extraction solvent system on the extraction of the analytes. After optimization, a relatively high extraction recovery could be obtained for all the six carbamates when $CHCl_3$–C_6H_5Cl (1:1, v/v) was used as the extraction solvent. Therefore, a binary extraction solvent system of $CHCl_3$–C_6H_5Cl (1:1, v/v) was selected.

3.2. Effect of extraction solvent volume

In order to study the effect of the volume of the extraction solvent on the performance of the presented UASEME procedure, the volume of $CHCl_3$–C_6H_5Cl (1:1, v/v) was varied in the range from 50 to 300 μL. When the volume of the extraction solvent was increased, the extraction recoveries were increased until 150 μL. At higher volumes than 150 μL, the recoveries almost remained constant or slightly decreased. From the obtained results, 150 μL of $CHCl_3$–C_6H_5Cl (1:1, v/v) was chosen for further studies.

3.3. Effect of the type and concentration of surfactant

A choice of a surfactant is of great importance for obtaining a satisfactory preconcentration and extraction effect for analytes. Surfactant, which serves as an emulsifier, could accelerate the emulsification of the water-immiscible extraction solvent into the aqueous solution under ultrasound radiation. After emulsification, the extraction solvent is dispersed as fine droplets in the sample solution, which are favorable for the mass transfer of the analytes from aqueous phase to the organic phase. The effect of different surfactants (SDS, Triton X-100, Triton X-114 and Tween 20) on the extraction recovery is given in Fig. 1B. As a result, among the surfactants investigated, SDS gives a lowest extraction recovery for the analytes. Tween 20 and Triton X-100 give a comparable result for the extraction of the analytes. For metolcarb, carbaryl and isoprocarb, the extraction recovery with Tween 20 is a little higher than that with Triton X-100. But for carbofuran, pirimicarb and diethofencarb, the extraction recovery with Tween 20 is a little lower than that with Triton X-100. SDS is an anionic surfactant with higher hydrophilicity. Tween 20 and Triton are a polyoxyethylene-type nonionic surfactant. The higher hydrophile–lipophile balance (HLB) value means higher hydrophilicity. When the HLB value of a surfactant is between 8 and 18, the surfactant can be used as an emulsifier. The HLBs of Tween 20, Triton X-100, Triton X-114 and SDS are 16.7, 13.4, 12.4 and 40, respectively. So, SDS is not suitable for the use as an emulsifier. Based on the experimental result, selection of either Tween 20 or Triton X-100 as the surfactant is reasonable. Considering that Tween 20 is more commonly used and cheaper than Triton X-100 in China, Tween 20 was selected as the surfactant for subsequent studies.

Surfactant concentration is another important parameter for effective extraction. The influence of the Tween 20 concentration was investigated by changing its concentration to 1.0, 2.0, 4.0, 6.0 and 10.0×10^{-5} mol L^{-1}, respectively. The surfactant molecules can be associated in an aqueous solution to form molecular aggregates called micelle. The minimum concentration of the surfactant required for this phenomenon to occur is called critical micellar concentration (CMC). The results indicated that when the concentration of Tween 20 in the sample solution was higher than its CMC (6.5×10^{-5} mol L^{-1}) [32], the extraction efficiency began to decrease. The reason for this could be that a fraction of the analytes could incorporate into the micelles when the surfactant concentration was higher than the CMC, thus resulting in an increased solubility of the analytes in the sample solution. Based on the experimental results, the concentration of Tween 20 was chosen at 6.0×10^{-5} mol L^{-1}.

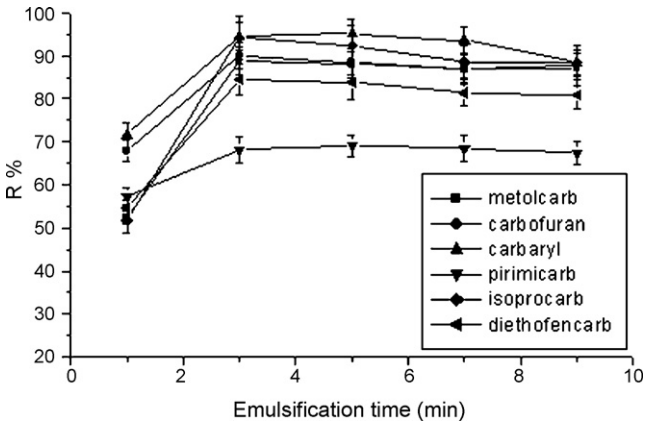

Fig. 2. Effect of emulsification time on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 100 μL C_6H_5Cl–$CHCl_3$; concentration of Tween 20: 6.0×10^{-5} mol L^{-1}.

3.4. Effect of extraction temperature

Temperature could affect both mass transfer and emulsification process, thus influencing the extraction efficiency. The effect of extraction temperature was studied over different temperatures ranging from 25 to 45 °C. In the whole temperature range from 25 to 45 °C, the emulsification was all easily achieved and remained during the whole extraction time. The results indicated that the sample solution temperature had no significant effect on the extraction recoveries of the carbamates. This may be due to that the contact surface between the organic solvent and the aqueous phase is very large and mass transfer is not a limiting factor for the extraction. For the convenience of the experiment, the extractions were carried out at room temperature (25 ± 2 °C).

3.5. Effect of ultrasound extraction time

Ultrasound extraction time is one of the main factors in SAUSEME as in most extraction procedures. It affects both emulsification and mass transfer process, and thus influences the extraction recovery of the analytes. The ultrasound extraction time was defined as the time interval between the addition of the extraction solvent ($CHCl_3$–C_6H_5Cl) to the sample (the start of the sonication) and the end of the sonication. The effect of the ultrasound extraction time was studied over the time range between 1 and 10 min. The results (Fig. 2) indicated that the extraction recoveries are increased by increasing the extraction time before 3 min, and after that, remained almost constant. Therefore, 3 min of sonication time was chosen for the experiments.

3.6. Effect of salt addition

To evaluate the possibility of salting out effect, the extraction recoveries were studied over the NaCl concentration range from 0 to 15% (w/v) while the other parameters were kept constant. The obtained results showed that the salt addition had no significant effect on the extraction recoveries for all the target analytes. Hence, NaCl was not added in all the subsequent experiments.

3.7. Extraction recovery and enrichment factor for UASEME

The enrichment factor (*EF*) and the extraction recovery (*R*) for this UASEME were calculated according to the same equations as in Ref. [31]. As a result, under the optimum conditions, the enrichment factors were in the range between 170 and 246, and the recoveries were 67–93%. They are higher than those obtained previously by us with the common DLLME [31] (see Table 1). The reason for this could be that in UASEME, there is no need to use dispersive solvent, which could reduce the partition coefficients of the analytes between the extraction solvent and aqueous samples.

3.8. Application of UASEME in water samples

3.8.1. Linearity, repeatability and limits of detection (LODs)

A series of working solutions containing each of metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb at seven concentration levels of 0.3, 1.0, 10.0, 20.0, 50.0, 100 and 200.0 ng mL^{-1} were prepared for the establishment of the calibration curve. For each level, five replicate extractions and determinations were performed under the optimized experimental conditions as described in Sections 2.2 and 2.3. The characteristic calibration data obtained are listed in Table 1. The limits of detection (LOD, $S/N = 3$) ranged between 0.1 and 0.3 ng mL^{-1} for the target carbamates, which are lower than that given by the United States Environmental Protection Agency (USEPA) method (EPA method 531.1). The limits of quantification (LOQ, $S/N = 9$) ranged between 0.3 and 0.9 ng mL^{-1}. The linear signal was observed in the range from their corresponding LOQs to 200.0 ng mL^{-1} for all the six carbamate pesticides with the correlation coefficients (*r*) ranging from 0.9981 to 0.9998. The repeatability study was carried out by five parallel experiments at the concentration of 2.0 ng mL^{-1} for each of the carbamates under the optimal conditions. The resultant repeatabilities expressed as relative standard deviations (RSDs) varied from 3.4 to 4.8%. These results show that the proposed method has a high sensitivity and good repeatability.

3.8.2. Water samples analysis and recoveries of the method

To evaluate the applicability of the proposed method, the extraction and determination of the six carbamates in different water samples, i.e., river, well and reservoir water, were performed according to the procedures described in Sections 2.2 and 2.3. As a result, no residues of the target carbamates were found in either well or reservoir water samples. For river water, metolcarb was found at 0.8 ng mL^{-1}.

To test the accuracy of the method, these water samples were spiked with the standards of the target analytes at the concentrations of 1.0, 10.0, 50.0 and 100.0 ng mL^{-1}, respectively. For each

Table 1
Analytical performance data for the carbamates by the UASEME technique.

Carbamate	LR[a] (ng mL^{-1})	*r*	RSD (%) ($n = 5$)	EF		LOD (ng mL^{-1})	
				This method	DLLME [31]	This method	EPA method
Metolcarb	0.3–200	0.9995	3.4	223	–	0.1	
Carbofuran	0.6–200	0.9997	3.6	227	101	0.2	1.5
Carbaryl	0.3–200	0.9993	4.6	246	112	0.1	2.0
Pirimicarb	0.3–200	0.9998	3.8	170	122	0.1	–
Isoprocarb	0.9–200	0.9981	4.0	235	–	0.3	
Diethofencarb	0.3–200	0.9996	4.8	216	145	0.1	–

[a] LR: linear range.

Table 2
Recoveries obtained in the determination of carbamates in spiked river, reservoir and well water samples.

Fungicides	Spiked (ng mL^{-1})	River water (n = 5)			Reservoir water (n = 5)			Well water (n = 5)		
		Found (ng mL^{-1})	R[a] (%)	RSD (%)	Found (ng mL^{-1})	R[a] (%)	RSD (%)	Found (ng mL^{-1})	R[a] (%)	RSD (%)
Metolcarb	0	0.8			nd[b]			nd[b]		
	1.0	0.87	87.0	4.4	0.85	85.0	4.2	0.90	90.0	3.8
	10	9.16	91.6	5.1	9.36	93.6	5.0	9.6	96.0	3.5
	50	43.6	87.2	4.5	42.6	85.2	3.5	46.5	93.0	3.7
	100	88.5	88.5	4.6	89.4	89.4	4.7	95.5	95.5	4.2
Carbofuran	0	nd[b]			nd[b]			nd[b]		
	1.0	0.83	83.0	4.1	0.82	82.0	3.8	0.81	81.0	4.8
	10	8.50	85.0	4.3	8.60	86.0	3.7	9.57	95.7	5.8
	50	42.5	85.0	5.1	42.1	84.2	5.3	41.4	82.8	4.6
	100	88.1	88.1	4.5	87.3	87.3	3.6	89.5	89.5	4.8
Carbaryl	0	nd[b]			nd[b]			nd[b]		
	1.0	0.85	85.0	4.6	0.86	86.0	4.3	0.89	89.0	4.7
	10	8.72	87.2	4.5	8.69	86.9	4.2	9.20	92.0	5.4
	50	43.2	86.4	4.3	42.2	84.4	4.6	46.2	92.4	3.6
	100	91.1	91.1	4.1	90.2	90.2	4.6	93.1	93.1	3.8
Pirimicarb	0	nd[b]			nd[b]			nd[b]		
	1.0	0.84	84.0	4.9	0.85	85.0	4.8	0.86	86.0	4.0
	10	9.40	94.0	5.2	9.37	93.7	4.7	8.98	89.8	3.7
	50	43.2	86.4	5.3	42.4	84.8	3.8	47.5	95.0	5.3
	100	93.5	93.5	4.8	97.5	97.5	4.6	94.2	94.2	4.5
Isoprocarb	0	nd[b]			nd[b]			nd[b]		
	1.0	0.84	84.0	5.4	0.86	86.0	5.2	0.88	88.0	4.1
	10	8.60	86.0	5.2	8.77	87.7	5.1	9.46	94.6	3.3
	50	44.2	88.4	5.5	43.2	86.4	5.6	43.9	87.8	4.6
	100	90.5	90.5	5.3	91.6	91.6	5.0	96.9	96.9	4.5
Diethofencarb	0	nd[b]			nd[b]			nd[b]		
	1.0	0.84	84.0	5.0	0.83	83.0	5.2	0.85	85.0	5.0
	10	9.02	90.2	5.5	9.11	91.1	5.8	8.46	84.6	4.7
	50	43.5	87.0	5.0	42.6	85.2	4.7	43.9	87.8	4.9
	100	92.7	92.7	5.2	94.8	94.8	5.0	95.7	95.7	4.4

[a] R: recovery of the method.
[b] nd: not detected.

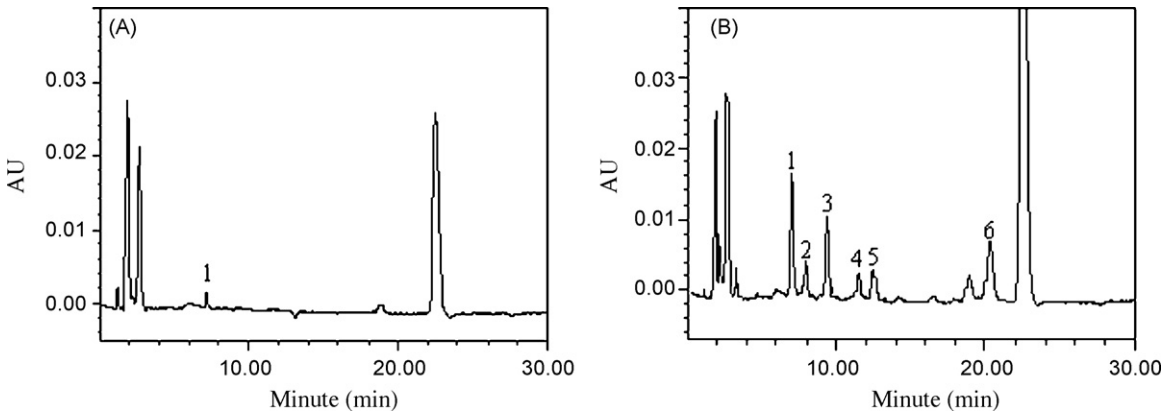

Fig. 3. The typical chromatograms of (A) river water sample and (B) river water sample spiked with carbamate pesticides at each concentration of 10 ng mL^{-1} (210 nm). Peak identification: (1) metolcarb, (2) carbofuran, (3) carbaryl, (4) pirimicarb, (5) isoprocarb, (6) diethofencarb.

Table 3
Comparison of UASEME with other sample preparation techniques for the determination of the carbamates.

Methods	Linearity (ng mL^{-1})	LOD (ng mL^{-1})	RSD (%)	Extraction time (min)	References
HF-LPME-HPLC-UV	1–1000	0.024–0.42	1.90–9.53	30	33
HF-LPME-GC–MS	1–400	0.2–0.8	4.86–7.81	20	3
SPME-GC–MS	–	1.2–4.6	13–17	120	34
SPME-HPLC–MS	50–5000	1–10	1–6	90	16
DLLME-HPLC-UV	5–500	0.4–1.0	4.7–6.5	1	31
UASEME-HPLC-UV	1–200	0.1–0.3	3.2–4.5	3	This method

concentration level, five replicate experiments for a whole analysis process as described in Sections 2.2 and 2.3 were made. The recoveries of the method were expressed as the mean percentage between the amounts found and the ones added. The results are given in Table 2. The recoveries for the carbamates in river, reservoir and well waters were in the range from 81.0 to 97.5%. Fig. 3A and B show the typical chromatograms of the extracted carbamates from river water sample before and after being spiked at 10 ng mL^{-1} each of the six carbamates. It can be seen from Fig. 3 that there is a peak at retention time of about 22 min in the chromatogram for the analysis. It came from the extraction solvent that were not evaporated completely in the sample preparation procedure before reconstitution of the sample residue by methanol. However, it does not interfere with the determination of any of the pesticides studied.

In this work, the commonly used HPLC-DAD detection was used. The identification of the analytes was confirmed by both the retention time and the ultraviolet absorption spectra of each carbamate. However, for real sample analysis, if LC–MS, a more selective analysis method, could be used, it could further improve the sensitivity and selectivity of the method and would be better for the identification and confirmation of the identity of the analytes.

3.9. Comparison of UASEME with other sample preparation techniques

The extraction efficiency of the presented UASEME method was compared with other reported methods such as LPME [3,33], SPME [16,34] and DLLME [31] from the viewpoint of LOD, RSD and extraction time. As listed in Table 3, the UASEME method has comparable LODs and RSDs with other extraction methods, but requires much shorter extraction time. SPME and HF-LPME required a longer time for equilibrium to be established. The time to reach equilibrium determines the maximum amounts of the analytes that can be extracted, and therefore affect the sensitivity of the method. Generally, the extraction time for SPME and HF-LPME required about 20–90 min. Compared with conventional DLLME [31], higher extraction efficiency could be obtained with the current UASEME technique and there is no need of the addition of an organic dispersive solvent. Under the above optimized experimental conditions, the enrichment factors of the current UASEME method for metolcarb, carbofuran, carbaryl, pirimicarb, isoprocarb and diethofencarb were 223, 227, 246, 170, 235 and 216, respectively, which are much higher than those obtained by DLLME (the EFs for DLLME were between 101 and 145) [31]. Compared with USAEME [23–25], UASEME required shorter extraction time.

4. Conclusions

In this paper, a novel ultrasound-assisted surfactant-enhanced emulsification microextraction technique coupled with HPLC-DAD detection has been developed for the determination of carbamates in water samples. The results indicated that it can be used as a simple and efficient extraction and preconcentration technique especially for some organic compounds in aqueous samples. The method can provide a good repeatability, high enrichment factor and good recovery with a short analysis time.

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