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ORIGINAL PAPER

Application of dispersive liquid–liquid microextraction combined with high-performance liquid chromatography to the determination of carbamate pesticides in water samples

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Abstract A rapid and sensitive method has been established for the determination of four carbamate pesticides (carbofuran, carbaryl, pirimicarb, and diethofencarb) in water samples by using dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography–diode array detection. Parameters that affect the extraction efficiency, such as the kind and volume of the extraction and disperser solvent, extraction time, and salt addition, were investigated and optimized. Under the optimum conditions, the enrichment factors were in the range between 101 and 145. The linearity of the method was obtained in the range of 5–500 ng mL^{-1} with the correlation coefficients (r) ranging from 0.9978 to 0.9997. The method detection limits were 0.4–1.0 ng mL^{-1}. The relative standard deviations varied from 4.7% to 6.5% (n=5). The relative recoveries of the four carbamates from water samples at spiking levels of 5.0 and 20.0 ng mL^{-1} were 84.0–92.0% and 86.5–94.0%, respectively. The proposed method has been successfully applied to the analysis of target carbamate residues in river, rain, well, and tap water samples with satisfactory results.

Keywords Dispersive liquid–liquid microextraction · Carbamate pesticides · High-performance liquid chromatography · Water samples

Introduction

Carbamates are one of the major classes of the pesticides that are widely used worldwide, especially currently in China, as insecticides, acaricides, nematocides, herbicides, and molluscicides for the protection of a large variety of crops, such as rice, cotton, fruit tree, and vegetable. They are increasingly used in agriculture due to their broad biological activity, low bioaccumulation potentials, and relatively low mammalian toxicities. However, since they are acetylcholinesterase inhibitors, these compounds are considered hazardous to the environment and human health. Most of the carbamates have high melting points and low vapor pressures. Their residues may appear in fruits and vegetables and may be usually distributed in aqueous environments by leaching and runoff from soil into ground and surface water because of their high solubility in water. 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 in environmental water samples are imperative.

A few documents have been reported for the determination of carbamate pesticides in different water samples [1–3]. For example, Wu et al. [1] have reported the determination of some carbamate insecticides in paddy water by micellar electrokinetic chromatography (MEKC); Zhang and Lee [2] have developed a gas chromatography–mass spectrometry (GC–MS) method for the determination of five carbamate pesticides in tap and drain water, and Molina et al. [3] have studied the analysis of some carbamates in well, river, and pond water in Spain by MEKC method.

Several analytical methods, such as GC [2, 4], enzyme-linked immunosorbent assays [5, 6], MEKC [1, 3], biosensor [7], and high-performance liquid chromatography (HPLC) [8–15], have been proposed for the separation and quantification of carbamate residues in different matrix samples. However, most carbamates are not conducive to GC analysis without derivatization as they are polar and thermally labile. For this reason, HPLC with different detectors become the

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most commonly used techniques for the determination of carbamate residues.

Sample preparation is one of the most important and crucial steps in the whole analytical process. It is often also the bottleneck for rapidly obtaining the desired results, especially for the determination of trace analytes in samples with complex matrix. For the determination of carbamate pesticide residues, several sample preparation methods have been developed, including liquid–liquid extraction (LLE) [9], solid-phase extraction (SPE) [10], supercritical fluid extraction [11, 12], microwave-assisted extraction [12, 13], solid-phase microextraction (SPME) [14, 15], and liquid-phase microextraction (LPME) [16, 17]. Since conventional extraction techniques, such as LLE and SPE, are laborious and time-consuming and need large volumes of samples and toxic organic solvents, much attention is being paid to the development of more efficient environment-friendly extraction techniques, such as SPME and LPME. SPME, a more recent procedure, is a simple, organic-solvent-free, and efficient extraction technique. However, SPME suffers from some problems such as sample carryover, relatively high cost, and fiber fragility. Recently, LPME has emerged as an attractive alternative for sample preparations because of its simplicity, effectiveness, low cost, minimum use of solvents, and excellent sample cleanup ability. LPME is based on the miniaturization of the traditional LLE method by greatly reducing the use of organic solvent. Different configurations of this technique have recently emerged, including single-drop microextraction (SDME) [16] and hollow-fiber-based liquid-phase microextraction (HF-LPME) [17]. However, several disadvantages, such as the instability of liquid drop in SDME, air bubbles formation in HF-LPME, long analysis time, and relatively low precisions, are often encountered. Efforts to overcome these limitations led to the development of dispersive liquid–liquid microextraction (DLLME) with the advantage of short extraction time, ease of operation, and small amounts of solvents used [18].

In DLLME, water-immiscible extraction solvent dissolved in a water-miscible dispersive solvent is rapidly injected into an aqueous sample solution by syringe. A cloudy solution containing fine droplets of extraction solvent dispersed entirely in the aqueous phase is formed, which is attributed to the dispersive role of the dispersive solvent. The analytes in the sample are extracted into the fine droplets, which are further separated by centrifugation, and the enriched analytes in the sedimented phase are determined by GC or HPLC. DLLME has been applied for the analysis of various organic pollutants in environmental samples [18–27].

The main objective of this paper is to explore the applicability of DLLME coupled with HPLC–diode array detection (DAD) to develop a new method for the determination of carbofuran, carbaryl, pirimicarb, and diethofencarb in real water samples. To the best of our knowledge, this may be the first report about the application of the DLLME method for the determination of these pesticides. The effects of various experimental parameters, such as the kind and volume of the extraction and disperser solvent, extraction time, and salt effect, were studied.

Experimental

Reagents and materials

Carbofuran, carbaryl, pirimicarb, and diethofencarb were purchased from Agricultural Environmental Protection Institution in Tianjin, China. Chloroform ($CHCl_3$), dichloroethane ($C_2H_4Cl_2$), dichloromethane (CH_2Cl_2), tetrachloride ethylene (C_2Cl_4), carbon tetrachloride (CCl_4), and chlorobenzene were purchased from Beijing Chemical Reagents Company. Acetone, 1,4-dioxane, acetonitrile, tetrahydrofuran (THF), ethanol, and methanol were from Sinopharm Chemical Reagent Co. Ltd. Sodium chloride was from Tianjin Fuchen Chemical Reagent Factory. Double-distilled water was used for the preparation of aqueous solutions.

River water was collected from Juma River, which passes through local agricultural areas, in autumn, tap water samples from our laboratory, rain water from Baoding in summer, and well water from Wumazhang (Baoding, China), respectively. All the solvents and water samples were filtered through a 0.45-μm membrane to eliminate particulate matter before analysis.

A mixture stock solution containing carbofuran, carbaryl, pirimicarb, 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.

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 Baseline C_{18} column (4.6 id×250 mm, 5.0 μm) from Shijiazhuang Aomek Pharmaceutical Technology Company (Shijiazhuang, China) was used for separations. The mobile phase was a mixture of methanol–water (60:40 *v*/*v*) and the flow rate was 1 mL min^{-1}. DAD monitoring wavelengths were chosen at 200, 220, 245, and 207 nm for carbofuran, carbaryl, pirimicarb, and diethofencarb, respectively.

Dispersive liquid–liquid microextraction procedure

For the DLLME, a 5.00-mL aliquot of water sample was placed in a 10-mL screw-cap glass tube with conical bottom. One milliliter of acetone (as disperser solvent) containing 70 μL $CHCl_3$ (as extraction solvent) was injected rapidly into the sample solution by 1.00-mL syringe and then the solution was vortexed for 5 s. A cloudy solution that consisted of very fine droplets of $CHCl_3$ dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets. After centrifugation at 3,500 rpm for 5 min, the $CHCl_3$ 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 with a mild nitrogen stream. The residue was dissolved in 15.0 μL methanol and 10.0 μL was injected into the HPLC system for analysis.

Calculation of enrichment factor and extraction recovery

In order to evaluate the effect of different experimental parameters such as the type and volume of the extraction and disperser solvents, salt addition, and the extraction time on the performance of DLLME, the terms of the enrichment factor (EF) and the extraction recovery (R) were introduced and used according to Eqs. 1 and 2 as follows [18–20]:

$$\mathrm{EF} = \frac{C_{\mathrm{sed}}}{C_0} \tag{1}$$

where EF, C_{sed}, and C_0 are the enrichment factor, the analyte concentration in the sediment, and the initial analyte concentration in the aqueous samples, respectively.

$$R\% = \frac{C_{\mathrm{sed}} V_{\mathrm{sed}}}{C_0 V_{\mathrm{aq}}} \times 100 \tag{2}$$

where R%, V_{sed}, and V_{aq} are the extraction recovery, the volume of the sediment phase, and the volume of the aqueous sample, respectively.

Results and discussion

In this experiment, 5.0 mL of double-distilled water spiked with 100.0 ng mL^{-1} each of the four 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.

Selection of extraction and dispersive solvent

The selection of an appropriate extraction solvent is of great importance to the DLLME process. The extraction solvent should meet the following requirements: it should have a higher density than water, have a low solubility in water, have high extraction capability for the target analytes, form a stable two-phase system in the presence of a dispersive solvent when injected to an aqueous solution, and have no interferences with the analyte peaks when directly injected for chromatographic analysis. Based on these criteria, CCl_4, $CHCl_3$, $C_2H_4Cl_2$, CH_2Cl_2, C_2Cl_4, and C_6H_5Cl were selected for the study. On the other hand, the selection of a dispersive solvent is limited to solvents such as acetone, methanol, ethanol, acetonitrile, and 1,4-dioxane, which are miscible with both water and the extraction solvents and could form a cloudy state when injected with the organic extractant into water. Due to a limited number of organic extractants, all combinations using CCl_4, $CHCl_3$, $C_2H_4Cl_2$, CH_2Cl_2, C_2Cl_4, or C_6H_5Cl (50 μL) as extractant with acetone, acetonitrile, methanol, THF, or ethanol (1.0 mL) as dispersive solvent were tried. In the case of $C_2H_4Cl_2$ and CH_2Cl_2 as extraction solvents, a two-phase system was not observed with any dispersive solvents studied. For $CHCl_3$, a two-phase system was not observed either with methanol or ethanol as dispersive solvent. For C_6H_5Cl, its chromatographic peak cannot be separated from the peak of diethofencarb. Based on the above results, CCl_4, $CHCl_3$, and C_2Cl_4 were selected as potential extraction solvents for further study. Figure 1 shows the effect of the extraction solvents (CCl_4, $CHCl_3$, and C_2Cl_4) on the recoveries with the use of acetone as disperser solvent. As can be seen in Fig. 1, $CHCl_3$ gives the highest overall extraction efficiency for the target analytes among the three solvents investigated. Therefore, $CHCl_3$ was selected as the extraction solvent.

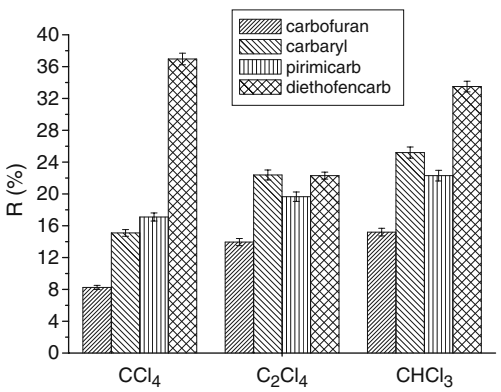

Fig. 1 Effect of different extraction solvents on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; dispersive solvent, 1.0 mL acetone; extraction solvent volume, 50 μL

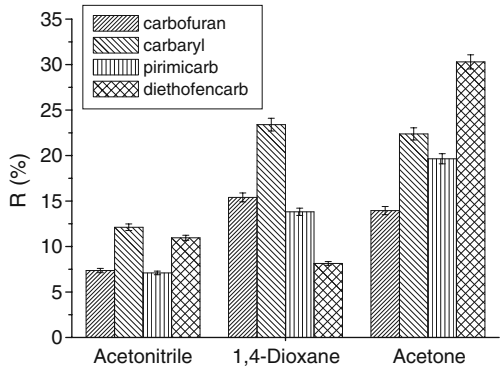

Fig. 2 Effect of different dispersive solvents on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; dispersive solvent volume, 1.0 mL; extraction solvent, 50 μL $CHCl_3$

With $CHCl_3$ as extraction solvent, the use of acetonitrile, acetone, or 1,4-dioxane as dispersive solvent could produce a two-phase system. The effect of different dispersive solvents (acetonitrile, acetone, and 1,4-dioxane) on extraction recovery is given in Fig. 2. As a result, acetone gives the best extraction efficiency for pirimicarb and diethofencarb but a little bit lower extraction efficiency for carbofuran and carbaryl than 1,4-dioxane. Giving an overall consideration, acetone was selected as the dispersive solvent for subsequent studies.

Effect of extraction solvent volume

In order to study the effect of the volume of the extraction solvent on the performance of the presented DLLME procedure, the volume of $CHCl_3$ was varied in the range 50–100 μL in 10-μL intervals. With less than 50 μL of $CHCl_3$, no two-phase system was observed. Figure 3 shows the variation of extraction recovery versus volume of the

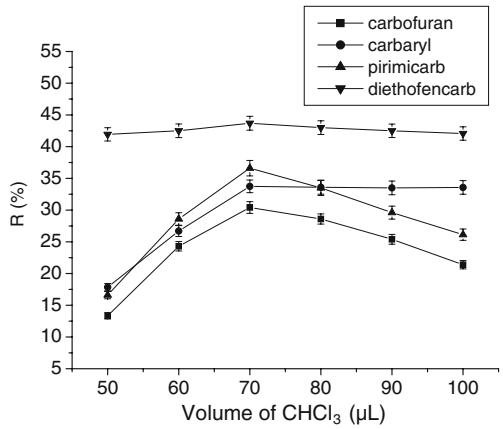

Fig. 3 Effect of the volume of the extraction solvent ($CHCl_3$) on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; dispersive solvent, 1.0 mL acetone; extraction solvent, $CHCl_3$

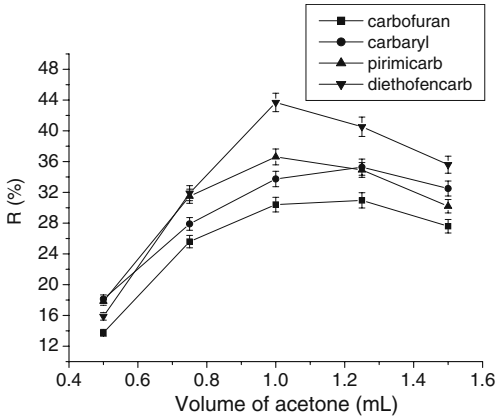

Fig. 4 Effect of the volume of the dispersive solvent (acetone) on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 70 μL $CHCl_3$

extraction solvent. By increasing the volume of $CHCl_3$, the extraction recovery increased until 70 μL. At higher volumes than 70 μL, the recovery remained almost constant for carbaryl and diethofencarb whereas it decreased for carbofuran and pirimicarb. Based on the above results, 70 μL of $CHCl_3$ was chosen as the optimal volume for the extraction solvent.

Effect of the disperser solvent volume

The influence of the volume of the disperser solvent acetone was investigated by changing its volume to 0.5, 0.75, 1.0, 1.25, and 1.5 mL, respectively. The results are shown in Fig. 4. According to Fig. 4, the extraction efficiency increases first and then decreases by increasing the volume of acetone for all the carbamates. The reason could be that, at a low volume of acetone, a cloudy state could not be well formed, therefore, resulting in a low recovery. At a higher volume of acetone, the solubility of

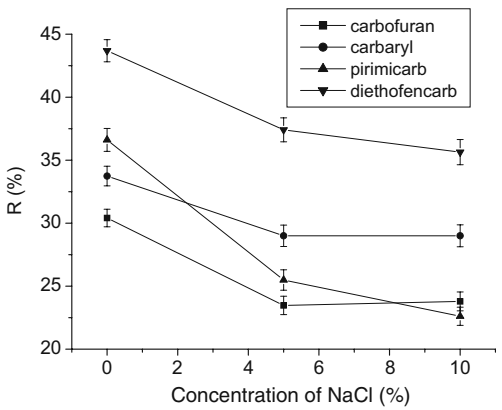

Fig. 5 Effect of salt addition on the extraction recovery of the carbamates. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 70 μL $CHCl_3$; dispersive solvent, 1.0 mL acetone

Table 1 Analytical performance data for the carbamates by the DLLME method

Carbamate	LR (ng mL^{-1})	r	RSD (%; n=5)	EF	LOQ (ng mL^{-1})	MDL (ng mL^{-1})	
						This method	EPA method
Carbofuran	5–500	0.9998	4.7	101	3.3	1	1.5
Carbaryl	5–500	0.9997	5.1	112	1.3	0.4	2.0
Pirimicarb	5–500	0.9997	4.8	122	2.0	0.6	–
Diethofencarb	5–500	0.9978	6.5	145	2.0	0.6	–

LR linear range

the pesticides in water was increased, leading to a decreased extraction efficiency because of a decrease in distribution coefficient. Based on the experimental results, 1.0 mL of acetone was chosen.

Effect of extraction time

Extraction time is one of the most important factors in DLLME as in most extraction procedures. The extraction time is defined as the time interval between the addition of the mixture of dispersive solvent (acetone) and extraction solvent ($CHCl_3$) to the sample and the start of centrifugation. After the addition of the mixture of acetone and $CHCl_3$, the solution was vortexed for 5 s and then gently shaken in a shaker for an appropriate time before centrifugation. The effect of extraction time was studied over the time range between 1 and 10 min. The results indicated that the extraction time has no impact on the extraction recoveries. Because equilibrium state can be achieved quickly, the extraction time required can be very short. The short extraction time is one of the remarkable advantages of the DLLME technique.

Effect of salt addition

To evaluate the possibility of salting out effect, the extraction efficiency was studied with the NaCl concentration in the range from 0% to 15% (*w*/*v*). Figure 5 depicts the extraction recovery versus concentration of NaCl, respectively. It can be seen that the best extraction efficiencies for each target analyte were obtained without the addition of NaCl. Hence, NaCl was not added in all subsequent experiments.

Under the above optimized experimental conditions, the enrichment factors of this method for carbofuran, carbaryl, pirimicarb, and diethofencarb were 101, 112, 122, and 145, respectively.

Calibration curve, repeatability, method detection limits, and limits of quantification

A series of working solutions containing each of carbofuran, carbaryl, pirimicarb, and diethofencarb at six concentration levels of 5.0, 20.0, 100.0, 200.0, 300, and 500.0 ng mL^{-1} were obtained for the establishment of the calibration curve.

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

Fungicides	Spiked (ng mL^{-1})	River water (n=5)			Tap water (n=5)			Rain water (n=5)			Well water (n=5)		
		Measured (ng mL^{-1})	RR (%)	RSD (%)	Measured (ng mL^{-1})	RR (%)	RSD (%)	Measured (ng mL^{-1})	RR (%)	RSD (%)	Measured (ng mL^{-1})	RR (%)	RSD (%)
Carbofuran	0	3.8			nd			nd			nd		
	5	7.9	82.0	6.5	4.3	86.0	6.3	4.4	88.0	5.5	4.5	90.0	5.8
	20	21.0	86.0	6.2	17.7	88.5	7.2	18.1	90.5	5.1	18.7	93.5	4.3
Carbaryl	0	nd			nd			nd			nd		
	5	4.1	82.0	7.6	4.4	88.0	6.6	4.5	90.0	6.3	4.2	84.0	4.6
	20	16.5	82.5	6.5	17.3	86.5	5.8	18.6	93.0	5.7	18.3	91.5	4.1
Pirimicarb	0	nd			nd			nd			nd		
	5	4.0	80.0	6.8	4.4	88.0	6.7	4.6	92.0	5.6	4.3	86.0	6.2
	20	16.6	83.0	6.1	17.9	89.5	5.6	18.5	92.5	4.9	18.8	94.0	5.6
Diethofencarb	0	nd			nd			nd			nd		
	5	3.8	76.0	6.7	4.2	84.0	7.9	4.3	86.0	5.9	4.6	92.0	5.6
	20	16.8	84.0	6.3	18.1	90.5	5.9	18.3	91.5	5.5	18.5	92.5	4.9

nd not detected, *RR* relative recovery

For each level, five replicate extractions were performed. The characteristic calibration data listed in Table 1 were obtained under optimized conditions. Linearity was observed in the range 5–500 ng mL^{-1} with the correlation coefficient (r) ranging from 0.9978 to 0.9997. Method detection limits (MDLs, S/N=3) ranged between 0.4 and 1.0 ng mL^{-1} for the target carbamates, which are lower than that given by the US Environmental Protection Agency (EPA) method (EPA method 531.1). The limits of quantification (LOQs, S/N= 10) for the target analytes were 1.3 to 3.3 ng mL^{-1}. The repeatability study was carried out by five parallel experiments at the concentration of 10 ng mL^{-1} for each of the carbamates under the optimal conditions. The resultant repeatabilities expressed as relative standard deviations (RSDs) varied from 4.7% to 6.5%. These results show that the proposed method has a high sensitivity and repeatability.

Evaluation of method performance

To evaluate the accuracy and applicability of the proposed method, the extraction and determination of the four carbamates in different water samples, i.e., river, tap, rain, and well water, were performed. To check the presence of interferences due to the matrix, these water samples were spiked with the standards of the target analytes at the concentration of 5 and 20 ng mL^{-1}, respectively. For each concentration level, five replicate experiments were made and the results are given in Table 2. The relative recoveries for the carbamates in river, tap, rain, and well water samples were in the range 76.0–94%. Figure 6a, b shows the typical chromatograms of the extracted carbamates from tap water sample before and after spiking with 10 ng mL^{-1} each of the four carbamates. Figure 6c shows the chromatogram of the river water sample.

Comparison of DLLME with other sample preparation techniques

The extraction efficiency of the presented DLLME method was compared with other reported methods such as SPME and LPME from the viewpoint of MDL, RSD, and extraction time. As listed in Table 3, the DLLME method has comparable MDLs and RSD 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 affects the sensitivity of the method. Generally,

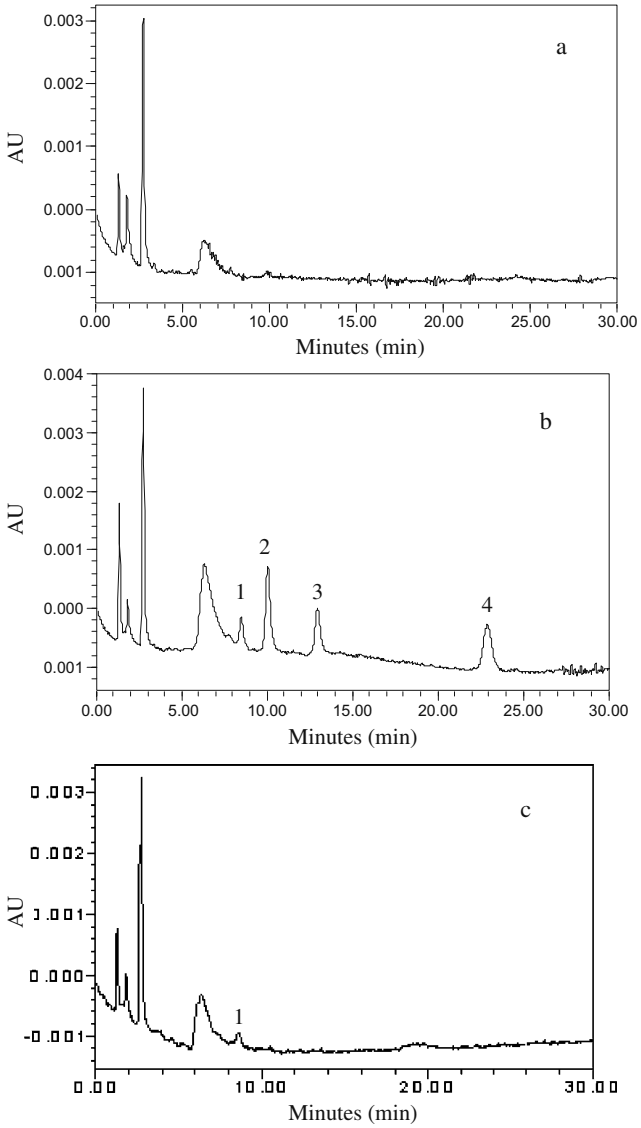

Fig. 6 The typical chromatogram of (**a**) tap water sample, (**b**) tap water sample spiked with carbamate pesticides at each concentration of 10 ng mL^{-1}, and (**c**) river water sample (230 nm). Peak identification: (1) carbofuran, (2) carbaryl, (3) pirimicarb, and (4) diethofencarb

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

Methods	Linearity (ng mL^{-1})	MDL (ng mL^{-1})	RSD (%)	Extraction time (min)	References
HF-LPME–HPLC-UV	1–1,000	0.024–0.42	1.90–9.53	30	[28]
HF-LPME–GC–MS	1–400	0.2–0.8	4.86–7.81	20	[17]
SPME–GC–MS	–	1.2–4.6	13–17	120	[29]
SPME–HPLC–MS	50–5,000	1–10	1–6	90	[15]
DLLME–HPLC-UV	5–500	0.4–1.0	4.7–6.5	1	This method

the extraction time for SPME and HF-LPME required about 20–90 min. However, the DLLME method can reach the equilibrium extremely quickly due to the large surface area between the extraction solvent and the aqueous solution. This is the most important advantage of DLLME. Furthermore, DLLME process does not require special instrumentation. Therefore, DLLME is indeed simple, rapid, easy to use, and environment friendly.

Conclusions

In this paper, a simple, rapid, and sensitive DLLME concentration technique coupled with HPLC–DAD has been developed for the determination of carbofuran, carbaryl, pirimicarb, and diethofencarb in water samples. The method can provide a good repeatability, high enrichment factor, and good recovery with a short analysis time. The comparison of the proposed DLLME method with other extraction methods such as SPME, LPME, and SPE indicates that DLLME can offer advantages of speed, simplicity, ease of operation, and a low consumption of organic solvent.

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