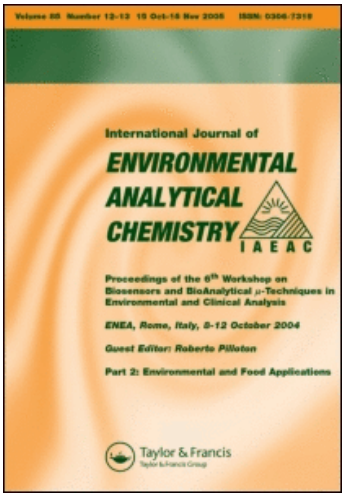

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Comparison of efficiencies between single-drop microextraction and continuous-flow microextraction for the determination of methomyl in natural waters

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Two liquid-phase microextraction (LPME) approaches, static direct-immersed single-drop microextraction (DI-SDME) and continuous-flow microextraction (CFME), were used to extract methomyl in water samples and their respective extraction efficiencies were compared. Several important parameters affecting extraction efficiency such as the type of extraction solvent, solvent drop volume, stirring speed or flow rate, extraction time and salt concentration were optimised. The optimised conditions were as follows: 3.0-μL tetrachloroethane ($C_2H_2Cl_4$) as the extraction solvent, 15% NaCl (w/v), 15 min extraction time and stirring speed at 600 rpm for DI-SDME; 3.5-μL $C_2H_2Cl_4$ as the extraction solvent, 15% NaCl (w/v), 21 min extraction time and flowing rate at 0.8 mL min^{-1} for CFME. Under the previous optimal conditions, the linear range, detection limit (S/N = 3) and precision (RSD, $n = 6$) were 5.0-5000 ng mL^{-1}, 1.5 ng mL^{-1}, 6.9% for DI-SDME, and 4.0–10000 ng mL^{-1}, 2.5 ng mL^{-1}, 4.6% for CFME, respectively. Lake and river water samples were successfully analysed by DI-SDME and CFME. The result demonstrated that both SDME and CFME techniques are simple, low cost and amity to environment. As a result, the two approaches have tremendous potential in trace analysis of methomyl in natural waters.

Keywords: single-drop microextraction (SDME); continuous-flow microextraction (CFME); carbamates; methomyl; water analysis

1. Introduction

In recent years, N-methylcarbamate pesticides (NMCs), represented by methomyl and carbaryl, have been become increasingly important to combat a variety of pests in agriculture. However, since they are acetylcholinesterase inhibitors, NMCs are suspected carcinogens and mutagens [1]. Thus, the increasing use of NMCs poses a risk to aquatic systems and further becomes a potential hazard to the human environment. NMCs have been on the priority blacklist released by the US Environmental Protection Agency (EPA).

Methomyl (S-methl-N[(methylcarbamoyl)oxy]-thioacetimidate), a broad spectrum carbamate insecticide, has been widely used in China and many agricultural countries for crop protection during the past decade [2]. Because of its high solubility in water and

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low affinity for sediment binding it may have potential for groundwater and surface water contamination [3]. Recent investigations have shown that the soluble concentration of methomyl is higher in coastal waters than offshore, and now, the concentration of methomyl in seawater is increasing [4]. In order to do risk assessment on methomyl, a simple and sensitive method should be established to determine methomyl in natural waters.

There are many techniques for the determination of methomyl in environmental matrices. Since methomyl is thermally unstable, it is necessary to analyse it by liquid chromatography [5–7] rather than by gas chromatography. Nowadays, GC-MS [8] and HPLC-MS [9–11] are often used to determine the residue of methomyl besides HPLC. Other chromatographic techniques, such as supercritical fluid chromatography (SFC) [12], thin-layer chromatography (TLC) [13] and micellar electrokinetic capillary chromatography (MEKC) [14,15] are also used for carbamate analysis.

Green chemistry is the trend in modern analytical chemistry. The conventional sample preparation techniques such as liquid-liquid extraction (LLE) have the disadvantages of being time-consuming, expensive, and requiring large volumes of toxic organic solvents. Although solid-phase extraction (SPE) requires a lower amount of organic solvent compared to LLE, it can be tedious and easily suffer analyte breakthrough when large sample volumes are analysed. Because of the demerits of conventional extraction approaches, the pretreatment techniques employing less, or no organic solvents are becoming more and more popular. Solid-phase microextraction (SPME), which is a rapid and solvent-free extraction technique developed by Arthur and Pawliszyn [16] in 1990, has been widely used for detecting organic compounds. However, the main drawback of SPME is that the fibre is expensive and has a limited lifetime.

Liquid-phase microextraction (LPME), which was introduced initially by Jeannot and Cantwell [17,18], is a quick, simple, inexpensive and virtually solvent-free sample preparations method. It is based on the distribution of the analytes between an aqueous solution and microdrop of organic solvent at the tip of a microsyringe, and has been widely applied for the determination of organic compounds in various environmental matrices [19–22].

On the basis of the different operating methods, five modes of LPME are devised. They are: static direct-immersed single-drop microextraction (DI-SDME) [21]; dynamic LPME (d-LPME) [23]; hollow-fiber membrane LPME (HFM-LPME) [24]; headspace LPME (HS-LPME) [25]; and continuous-flow microextraction (CFME) [26], respectively. In this research, DI-SDME and CFME were selected to determine methomyl in water samples.

To our knowledge, there is no report concerning methomyl analysis using the different modes of LPME. The purpose of this work was to compare the extraction efficiencies of DI-SDME and CFME for the determination of methomyl in natural waters. The factors affecting the extraction efficiency such as the kind of organic solvent, organic drop volume, stirring speed or flow rate, salt concentration, and extraction time were optimised.

2. Method

2.1 *Standards and reagents*

Methomyl (99.5% purity) was purchased from Research Center of Standard Substances of China (Beijing, China). HPLC-grade methanol was obtained from Tedia (Fair lawn, New Jersey, USA). Deionised water was purified with a Millipore Mill-Q plus System (Bedford, MA, USA). Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), toluene (C_7H_8), carbon tetrachloride (CCl_4), tetrachloroethane ($C_2H_2Cl_4$) and sodium chloride were obtained from the Tianjinbodi Chemical Corporation (Tianjin, China). All were analytical grades.

Stock solution (400 μg mL^{-1} in methanol) of methomyl was prepared freshly every two weeks and stored at 4°C in. Working standard solutions of methomyl were prepared by appropriate dilution of the stock solution using deionised water.

Natural water samples were collected from East Lake and the Yangtse River in the city of Wuhan, China and filtered through a 0.45-μm polypropylene membrane (Membrana GmbH, Wuppertal, Germany) to remove particulate matter before analysis and stored at 4°C.

2.2 *Apparatus*

Chromatographic analysis was performed with an Agilent 1100 HPLC system equipped with a manual injector and variable wavelength detector (VWD). An Eclipse XDB-C_8 column (4.6 mm × 150 mm, 5-μm particle size) was used and thermostated at 25 ± 1°C. The mobile phase used was a 20:80 (v/v) mixture of methanol/water at a flow rate of 0.8 mL min^{-1}. The wavelength of the detector was set at 235 nm, and all injections were performed manually with 5.0-μL sample loop.

Water samples were stirred with A S32-2 Digital magnetic stirrer (Shanghai Sile Instrument Co., Shanghai, China). CFME was performed in a home-made glass chamber (0.5 mL). A HL-2 model peristaltic pump (Hu Xi Analysis Instrument Corporation, Shanghai, China) was used for sample solution delivery, and 10-μL LC microsyringe (Gaoge, Shanghai) was used for extraction solvent introduction. A minimum length of PTFE tube (i.d. 0.5 mm) was used for all connections. All glass tubes were first soaked with potassium dichromate solution for 24 h, then rinsed with deionised water, and finally dried overnight before use.

2.3 *Extraction procedures*

2.3.1 *Static direct-immersed single-drop microextraction (DI-SDME)*

An aqueous sample (5.0 mL) was placed into a 7-mL glass vial equipped with a 10 mm × 3 mm PTFE-coated magnetic stir bar and screw capped with a PTFE-faced silicone septum. A specified volume of organic solvent was drawn into a microsyringe, and then the needle of the microsyringe was inserted through the septum and directly immersed into the aqueous sample.The microsyringe plunger was depressed to expose the microdrop to the stirred sample for a period of time. When the extraction was accomplished, the microdrop was retracted from the sample vial and injected immediately into the HPLC for analysis. The setup of DI-SDME is shown in Figure 1. The microsyringe was washed at least five times with solvent in order to eliminate the bubbles in the barrel and the needle.

It must be noted that in this procedure the distance between the tip and stirring should be kept consist (ca.1 cm) for all experiments for accuracy.

2.3.2 *Continuous-flow microextraction (CFME)*

The setup for CFME is also shown in Figure 1, and the operating procedure is summarised as follows [26]: First, switch on the pump, then the aqueous sample is pumped continuously, vertically upward, at a constant flow rate into an extraction chamber (0.5 mL) via the connecting PTFE tubing. Second, a required specified volume of organic solvent was introduced into the chamber by means of the microsyringe after the chamber

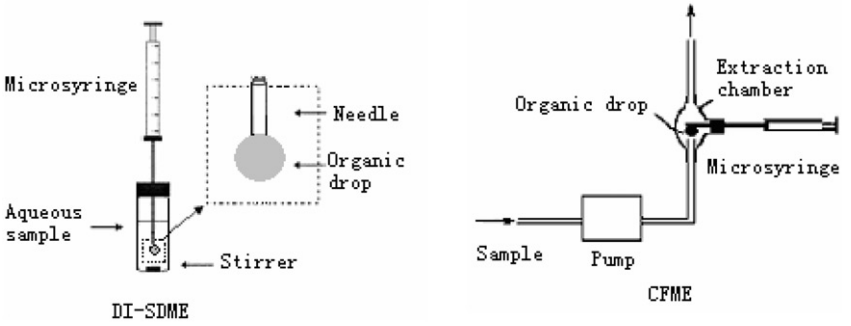

Figure 1. Setups of DI-SDME and CFME.

has been filled with the sample solution, to form a microdrop which remained at the needle tip of the microsyringe above the PTFE tube outlet in the chamber. Third, after extraction for a prescribed period of time, the solvent microdrop was retracted into the microsyringe and injected directly for HPLC analysis.

3. Results and discussion

3.1 *Optimisation of DI-SDME and CFME*

To study the optimal extraction conditions, the enrichment factor of methomyl in HPLC chromatograms was used to evaluate extraction efficiency under different conditions. Experiments were performed in triplicate by spiking the aqueous sample solution with $0.10\,\mu g\,mL^{-1}$ of methomyl for both DI-SDME and CFME.

3.1.1 *Selection of organic solvent*

The selection of a proper extraction solvent should consider two factors, one is that the solvent must be immiscible with water and the other is that it should possess excellent chromatographic behaviour. On the basis of these two considerations, Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), toluene (C_7H_8) and tetrachloroethane ($C_2H_2Cl_4$) were tested in this research. CH_2Cl_2, most commonly used in pesticide extraction in LLE, could be used to extract the analyte, but the solvent peak was high enough to interfere with the methomyl peak. Non-polar CCl_4 could hardly extract methomyl. Nunes *et al.* [27] reported that C_7H_8 could be used to extract methomyl. However, in this research, C_7H_8 had a lower extraction efficiency than that of $CHCl_3$ and $C_2H_2Cl_4$. Although $CHCl_3$ and $C_2H_2Cl_4$ could be used for effective extraction of the analyte, extraction efficiency with $C_2H_2Cl_4$ was 1.5 times higher than with $CHCl_3$. Moreover, less solvent loss of $C_2H_2Cl_4$ was observed in the extraction procedure as compared to that of other solvents. The effect of the kind of solvent on volume loss is shown in Figure 2. As a result, $C_2H_2Cl_4$ was selected as extraction solvent in both DI-SDME and CFME.

3.1.2 *Effect of microdrop volume*

Different volumes of $C_2H_2Cl_4$ were exposed to the spiked aqueous sample to value the effects on DI-SDME and CFME efficiencies. $C_2H_2Cl_4$ microdrop volumes ranged from

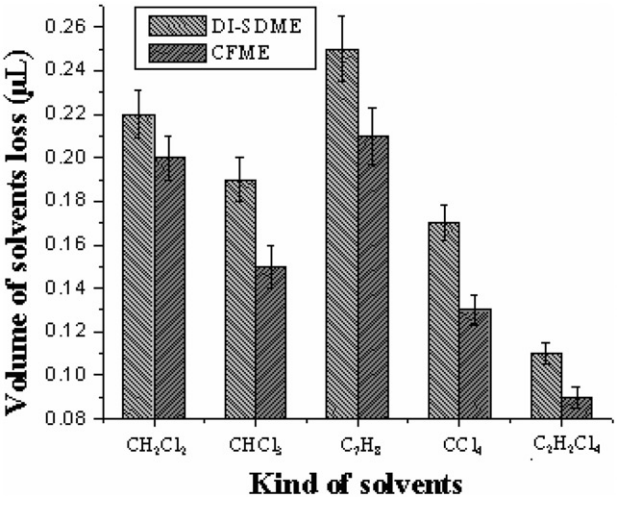

Figure 2. Effect of the kind of solvents on the volume loss by DI-SDME and CFME (stirring speed 500 rpm for DI-SDME, flow rate 0.7 mL min^{-1} for CFME, extraction time 15 min and microdrop volume 3.0 μL).

1.5 to 3.5-μL and the analyte peak area, shown in Figure 3, increased with increasing microdrop volume of $C_2H_2Cl_4$ after the DI-SDME and CFME procedure. However, in the DI-SDME mode, when the microdrop volume exceeded 3.0-μL, such microdrops are difficult to manipulate and unstable at the needle tip. As a result, 3.0-μL was considered to be the optimal microdrop volume for DI-SDME. In comparison with DI-SDME, the optimal microdrop volume was observed at 3.5-μL for CFME. Hence, microdrop volumes of 3.0-μL for DI-SDME and 3.5-μL for CFME were selected for subsequent experiments.

3.1.3 *Effect of stirring speed for DI-SDME and flow rate for CFME of sample solution*

In terms of DI-SDME, the effect of stirring speed on extraction efficiency is shown in Figure 4a. Apparently, the extraction efficiency increased with the increase of the stirring speed. According to the film theory of convective diffusive mass transfer [28], at stable state, the diffusion rate in the aqueous phase increases with increasing stirring speed because faster agitation can decrease the thickness of the diffusion film in the aqueous phase. The observations in this research are consistent with the former theory. Whereas, when the stirring speed exceeded 800 rpm, the organic microdrop was easily detached from the needle tip. On the basis of these observations, the optimum stirring speed for DI-SDME was fixed at 600 rpm.

For CFME, the effects of different flow rates (0.2–1.0 mL min^{-1}) on extraction efficiencies were investigated. The results shown in Figure 4b reveal that the increase of sample flow rate could lead to the increase of analyte peak area when the flow rate was below 0.8 mL min^{-1}. However, when the flow rate exceeded 0.8 mL min^{-1}, the analyte peak area decreased with the increase of flow rate (0.8–1.0 mL min^{-1}). Maybe, the extraction equation between two phases was difficult to establish especially at high flow rate. In addition, the high sample flow rate resulted in the flow stream bypassing the organic drop without significant interaction with it. Therefore, 0.8 mL min^{-1} was chosen as the optimal flow rate in CFME.

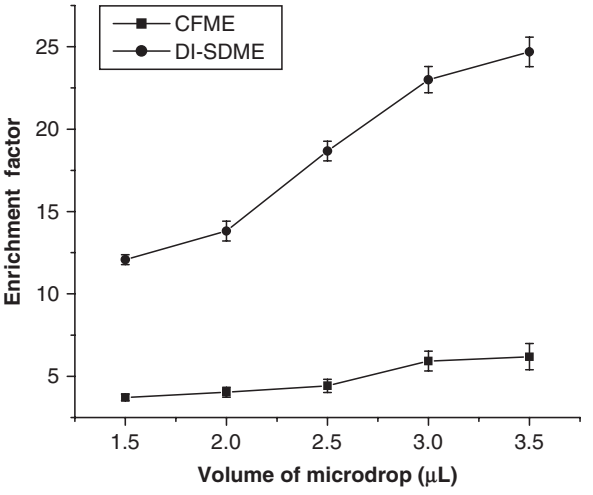

Figure 3. Effect of the organic solvent volume on the extraction of methomyl by DI-SDME and CFME (for DI-SDME: extraction time 15 min and stirring speed 400 rpm; for CFME: extraction time 10 min and flow rate 0.5 mL min^{-1}).

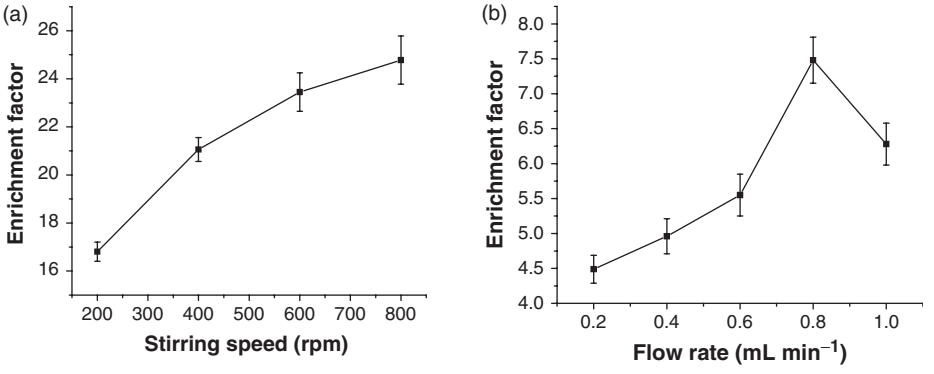

Figure 4. (a) Effect of stirring speed on the extraction of methomyl by DI-SDME (microdrop volume 3.0 μL and extraction time 15 min). (b) Effect of flow rate on the extraction of methomyl by CFME (microdrop volume 3.5 μL and extraction time 10 min).

3.1.4 *Effect of extraction time*

Mass transfer is a time-dependent process and equilibrium is attained only after a certain period of time. For DI-SDME, the extraction time ranged from 3 to 21 min at a stirring speed of 600 rpm. As can be seen from Figure 5, the long extraction time could lead to high extraction efficiency of methomyl in the range of 3–15 min, whereas with a further prolongation of extraction time (15–21 min), no increasing in the peak area was observed. Therefore, 15 min was selected as the optimal extraction time for DI-SDME. For CFME, a longer extraction time (3–21 min) also resulted in higher extraction efficiency with a flow rate of 0.8 mL min^{-1}. Additionally, the extraction equilibrium was not reached even by 21 min. However, a longer extraction time always results in more loss of solvent microdrop, which reduces the

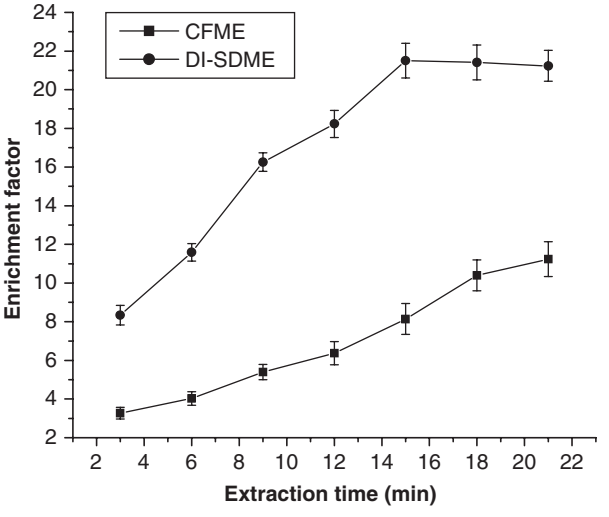

Figure 5. Effect of extraction time on the extraction of methomyl by DI-SDME and CFME (for DI-SDME: microdrop volume 3.5 μL and stirring speed 600 rpm; for CFME: microdrop volume 3.0 μL and flow rate 0.8 mL min^{-1}).

experimental sensitivity and precision. Therefore, for the CFME mode, 21 min rather than equilibrium time was chosen as a reasonable extraction time for further experiments.

3.1.5 *Effect of salt concentration*

The presence of salt can increase the ionic strength of the solution and affect the solubility of organic analyte due to a salting out effect. In LPME, some researchers reported that addition of NaCl to an aqueous sample may have various effects on extraction: it may enhance [29,30], not influence [31,32], or limit extraction [11,33]. The possible explanation may be that the NaCl dissolved in the aqueous solution may have changed the physical properties of the Nernst diffusion film and reduced the rate of diffusion of the target analyte into the microdrop [34], thus affecting the extraction efficiency exception for the salting out effect.

In this study, experiments were conducted to evaluate the effect of salt concentration on the extraction of methomyl by adding different amounts of NaCl from 0 to 30% (w/v). The results (Figure 6) show an initial increase in extraction efficiency with an increase of salt concentration, with a maximum being reached at 15% (w/v), followed by a decrease in the extraction efficiency with the further increase of salt concentration (15–20%) in both DI-SDME and CFME. Similar results were also obtained by other reports [35,36]. As a result, 15% NaCl (w/v) was chosen as the optimal salt concentration for two microextraction approaches.

3.2 *Performance of the DI-SDME and CFME*

After analysing all experimental results, the following conditions have been selected to evaluate the performance of the methods: 3.0-μL $C_2H_2Cl_4$ as the extraction solvent,

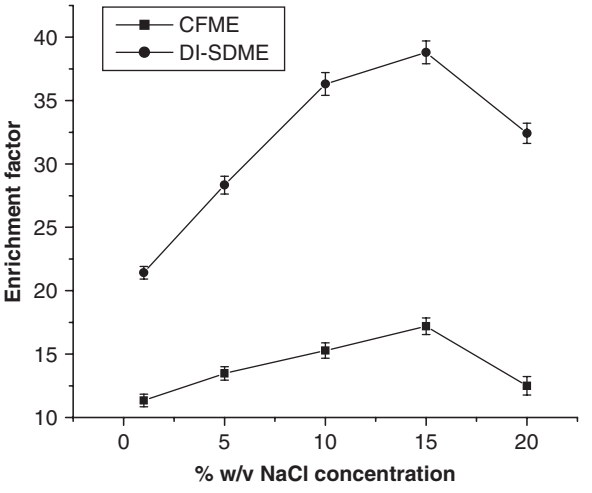

Figure 6. Effect of salt concentration on the extraction of methomyl by DI-SDME and CFME (extraction time for DI-SDME 15 min and for CFME 21 min, other extraction conditions were as Figure 5).

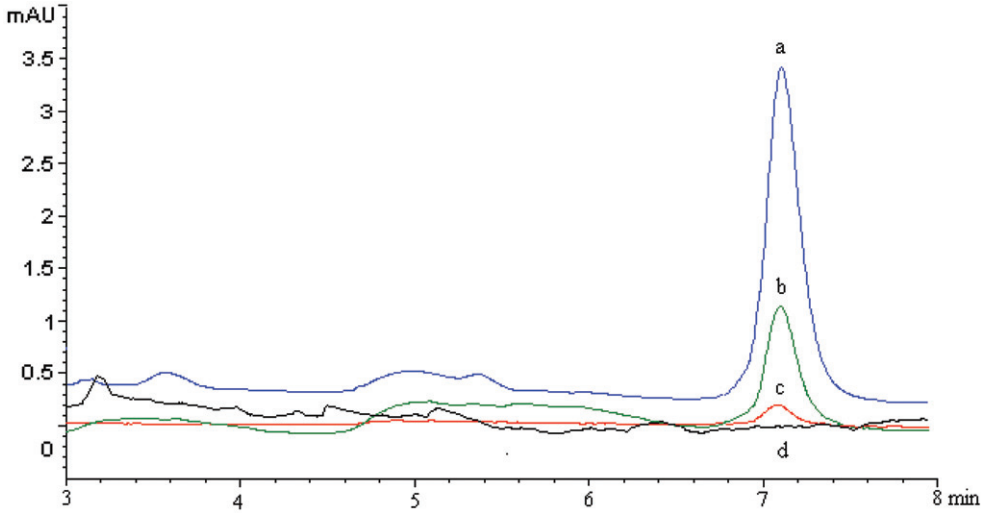

Figure 7. Chromatograms obtained from aqueous samples by spiking at 0.10 μg mL^{-1} for methomyl before extraction (c), after CFME (b) and DI-SDME (a), and from East lake waters (d) by DI-SDME under the optimum conditions.

15% (w/v) NaCl concentration, 15 min extraction time and stirring speed at 600 rpm for DI-SDME; 3.5-μL $C_2H_2Cl_4$ as the extraction solvent, 15% (w/v) NaCl concentration, 21 min extraction time and flowing rate at 0.8 mL min^{-1} for CFME. Chromatograms obtained from an aqueous sample by spiking at 0.10 μg mL^{-1} for methomyl before and after microextraction under the optimum conditions are shown in Figure 7. It was obvious that the peak area of methomyl was much increased when the sample was subjected to DI-SDME or CFME.

Table 1. Analytical data for DI-SDME and CFME.

	EF (-fold)		RSD (%, n = 6)		Linearity range ($ng\,mL^{-1}$)		r		LOD ($ng\,mL^{-1}$, S/N = 3)	
Analyte	DI-SDME	CFME	DI-SDME	CFME	DI-SDME	CFME	DI-SDME	CFME	DI-SDME	CFME
Methomyl	38.8	17.2	6.9	4.6	5.0–5000	4.0–10000	0.9971	0.9996	1.5	2.5

For the purpose of quantitative analysis, a calibration plot for concentrations ranging over five orders of magnitude was constructed by spiking deionised water directly with methomyl standards and extracting under the optimum conditions. The results are given in Table 1. The linear range, detection limit (S/N = 3) correlation coefficients (r) were 5.0–5000.0 $ng\,mL^{-1}$, 1.5 $ng\,mL^{-1}$, 0.9971 for DI-SDME, and 4.0–10000.0 $ng\,mL^{-1}$, 2.5 $ng\,mL^{-1}$, 0.9996 for CFME, respectively. The precision of DI-SDME and CFME were determined by successive six-time analysis of a 0.10 $\mu g\,mL^{-1}$ standard solution of methomyl; the relative standard deviation (RSD) was 6.9% and 4.6%, respectively.

3.3 *Comparison of DI-SDME and CFME*

In DI-SDME and CFME, the analyte distributes between the organic and aqueous phase. Equations of the extraction efficiency (E) and enrichment factor (EF) are:

$$E = \frac{n}{n_s} \tag{1}$$

$$EF = \frac{C_o}{C_s} \tag{2}$$

Where n is the amount of analyte extracted in the organic solvent, n_s is the total analyte amount contained in the original sample. C_o and C_s are the final concentrations of the analyte in the extraction solvent and the initial concentration of the analyte in the sample, respectively. In microextraction, the absolute amount of analyte extracted into the organic solvent is usually negligible compared with its total amount in solution [37–39], in other words, the value of E is very small, and therefore EF is a good indication of extraction efficiency in LPME. As a result, the extraction efficiency was presented as EF in this research.

As shown in Table 1, the EF values of DI-SDME and CFME are 38.8 and 17.2, respectively, which suggested that DI-SDME provides a high extraction efficiency in comparison with CFME. Additionally, LOD (1.5 $ng\,mL^{-1}$) for DI-SDME was lower than that for CFME (2.5 $ng\,mL^{-1}$), suggesting that DI-SDME possesses a high sensitivity. The observations can be explained by the following equations of surface renewal theory [40,41]:

$$k_R \propto \sqrt{DS} \tag{3}$$

where k_R is individual mass transfer coefficient, D diffusivity of species, and S is surface renewal rate which can be expressed as:

$$S \propto \left(\frac{\rho g u_T}{\mu \Phi}\right)^{1/2} \tag{4}$$

Table 2. Summary of results of analysis of methomyl in spiked natural water samples after DI-SDME and CFME.

	Lake water				River water			
	Relative recovery (%)		RSD (%, $n=6$)		Relative recovery (%)		RSD (%, $n=6$)	
Analyte	DI-SDME	CFME	DI-SDME	CFME	DI-SDME	CFME	DI-SDME	CFME
Methomyl	84.0	91.1	7.6	5.1	85.5	98.2	7.0	5.3

where ρ is the density, μ the viscosity of the organic phase, u_T the stirring speed or flow rate of sample solution, and Φ is the size of organic droplet.

According to the surface renewal theory, we can see that u_T of DI-SDME is much larger than that of CFME. In addition, the droplet size of DI-SDME and CFME are 3.0-μL and 3.5-μL, respectively. Thus, the value of u_T/Φ, in other words, k_R, is larger for DI-SDME. As a result, the extraction efficiency of DI-SDME is higher than that of CFME.

Other aspects, for example, precision, expressed as RSD, linearity range, and correlation coefficients, were found to be somewhat better for CFME than for DI-SDME, showing that CFME is the more accurate method. This observation may be explained by insignificant fluctuations in the volume of microdrop because the flow rate was very stable.

3.4 *Application to real water samples*

In order to investigate the applicability of the proposed microextraction methods, two natural water samples, from East Lake and the Yangtse River, were studied. It was free from methomyl both in lake and the Yangtse River waters under the optimal conditions (Figure 7). The water samples were spiked with concentration of 10 ng mL^{-1} methomyl by DI-SDME and CFME to assess matrix effect and the results are shown in Table 2. It can be seen that the relative recoveries ranged from 84.0% to 98.2%, which demonstrated that the matrix had little effect on DI-SDME and CFME.

3.5 *Comparison of DI-SDME and CFME with SPE and SPME method*

For extraction and determination of NMCs from water samples, comparison of the methods under examination with other methods, such as SPE [42,43] and SPME [44], was made and found that the experimental methods have some advantages. For example, the whole extraction process only needs a 5 mL water sample and extraction time is very short. Both SDME and CFME have a wide linear range and they do not require special instruments. Therefore, it is very simple, rapid, easy to use, inexpensive and benign to the environment.

4. Conclusions

Both DI-SDME and CFME coupled with HPLC, have been comparatively studied and used to determine methomyl in water samples at low ng mL^{-1} levels in this work.

Some important experimental parameters affecting extraction efficiency were also optimised. DI-SDME possesses a higher enrichment factor, higher extraction efficiency, lower detection limit than CFME. In addition, comparison with SPE and SPME method was made and found that both modes of LPME in conjunction with HPLC share the advantages of being fast, simple and sensitive analytical procedure for determination of methomyl in the surface water samples. Therefore, the resulting procedure was shown to be a good alternative methodology for the determination of selected carbamates residues in environmental water samples.

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