The Malaysian Journal of Analytical Sciences, Vol 12, No 2 (2008): 468 - 472

CONE-SHAPED MEMBRANE LIQUID PHASE MICROEXTRACTION

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Abstract

A novel sample pre-treatment technique termed cone-shaped membrane liquid phase microextraction (CSM-LPME) was developed and combined with micro-liquid chromatography (micro-LC) for the determination of selected pesticides in water samples. Several important extraction parameters such as types of extraction solvent, agitation rate, pH value, total exposure time and effect of salt and humic acids were investigated and optimized. Enrichment factors of >50 folds were easily achieved within 20 min of extraction. The new developed method demonstrated an excellent performance in terms of speed, cost effectiveness, reproducibility, as well as exceptional low detection limits. Current work provides a great interest to further investigate on the applicability of the CSM-LPME technique in analytical chemistry and explores the possibility of replacing conventional extraction techniques such as soxhlet, solid phase extraction (SPE) and solid phase microextraction (SPME).

Introduction

One of the emerging techniques in the area of sample preparation is liquid-phase microextraction (LPME), where a membrane impregnated with an organic solvent is used to accommodate or protect micro-volumes of acceptor solution [1]. This novel methodology has been proven to be an extremely simple, low-cost and virtually solvent-free sample-preparation technique, which provides a high degree of selectivity and enrichment by additionally eliminating the possibility of carry-over between runs. The quest for novel sample-preparation techniques has never ceased. Recent works in our laboratory [2,3] have successfully introduced pressurized liquid extraction using low organic solvents for the extraction of carotene and tocol-derivatives in residual oil from palm pressed fiber. High pressure combined with high temperature allows rapid analyte diffusivity and thus higher extraction efficiency.

This work describes a simple and inexpensive extraction technique which involves two-phase liquid phase microextraction combined with micro-liquid chromatography (micro-LC) for the analysis of selected pesticides in water. In this novel procedure, a cone-shaped nylon membrane is used to protect the extracting solvent, thus permitting extraction only on the surface of the solvent immobilized in the membrane pores. This technique provides both preconcentration and sample clean-up because of the selectivity of the membrane, and the extract can be directly injected into GC or HPLC. The results demonstrated that the procedure is inexpensive, simple to operate and provide stable and acceptable extraction efficiency.

Experimental

Round-shaped Nylon 66 membrane filters (200 µm thickness, 0.2 µm pore size) were purchased from Whatman (USA). The filter was cut into halves and each half was folded and sealed with flame into a cone-shaped membrane (CSM) with an open diameter of approximately 13 mm and height of approximately 20 mm to fit the vial I.D. (Fig. 1). Before use, the CSM was ultrasonically cleaned in acetone for several minutes in order to remove any contaminants.

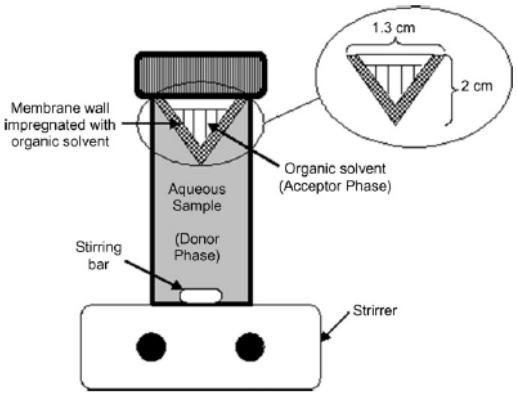

Fig. 1. Schematic of CSM-LPME.

A 15 mL aliquot of sample solution was placed into a 15 mL sample vial. The membrane was immersed into organic solvent for approximately 10s to allow the solvent to impregnate the pores of the membrane wall. After solvent impregnation, the CSM was quickly positioned in the sample vial that already contained the aqueous sample, and a 200 μL aliquot of organic solvent was pipetted into the membrane as shown in Fig. 1. The sample was continuously stirred with a magnetic stirrer at room temperature (25 ^{o}C) to facilitate the mass transfer of the analytes between donor phase and acceptor phase. After 20 min of extraction, the analyte-enriched solvent (100 μL) was withdrawn and transferred into a 1.5 mL cone-shaped vial, the solvent was dried with gentle flow of nitrogen and redissolved with 100 μL of acetonitrile solution containing 1 ppm profenofos (IS). A 0.5 μL of solvent was withdrawn into a syringe and injected into micro-LC system for analysis (Fig. 2).

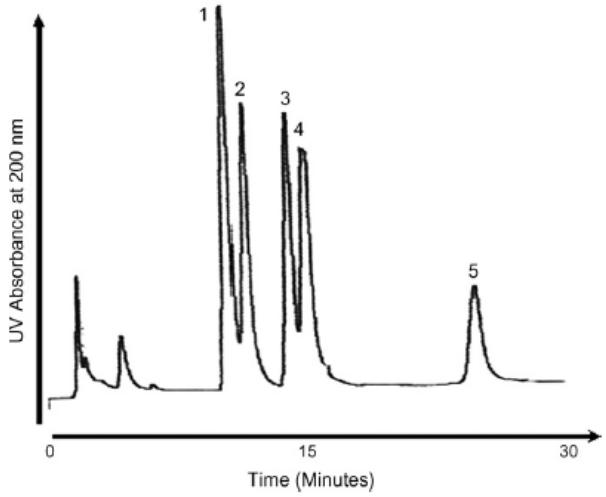

Fig. 2. Micro-LC separation of four pesticides on C-18 microcolumn (150 mm × 1 mm I.D.). Chromatographic conditions: mobile phase, acetonitrile–water 55:45 (v/v); flow rate, 30 μL/min; temperature, 40 °C; detection, UV absorbance at 200 nm; injection volume, 0.5 μL; solute concentration, 1 μg/mL. Peaks (1) hexaconazole; (2) procymidone; (3) vinclozolin; (4) quinalphos; (5) profenofos (internal standard).

Results and Discussion

Optimization of CSM-LPME

Extraction solvent

The type of organic solvent used to immobilize the pores of the CSM is a critical factor in CSM-LPME since extraction occurs on the surface of the immobilized solvent. The final choice of the organic solvent should have a low solubility in water so as to prevent dissolution into the aqueous phase, and a low volatility, which will restrict solvent evaporation during extraction [4]. In this work, 15 mL of double-distilled deionized water samples were spiked with all pesticides at 20 μg/L, and the optimization was performed on hexane and nonane as extraction solvent with a stirring rate of 400 rpm, exposure time 10 min, and pH value of 6. Fig. 3 shows the effect of extraction solvent on the enrichment factor in the CSM-LPME of the pesticides. It can be observed that under experimental conditions mentioned previously, enrichment factor was higher for *n*-hexane as extraction solvent for all pesticides except hexaconazole.

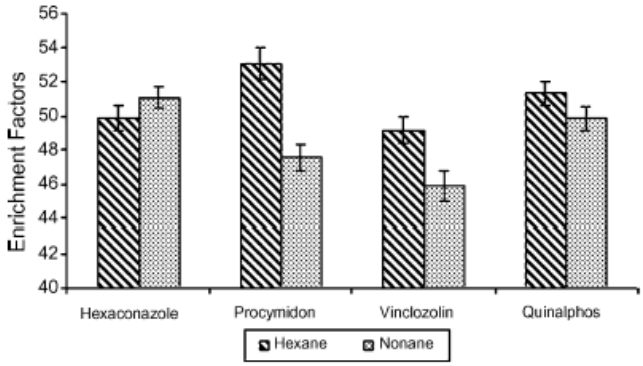

Fig. 3. Effect of extraction solvent on enrichment factor of pesticides in CSM-LPME.

Agitation

In CSM-LPME, agitation of the sample is routinely applied to accelerate the extraction kinetics. Increasing the agitation rate of the donor solution enhances extraction, as the diffusion of analytes through the interfacial layer of the membrane is facilitated, and improves the repeatability of the extraction method [5]. At agitation rates of 200 and 400 rpm, the extraction generally resulted in poor enrichment factor (Fig. 4). An increase of agitation to 600 rpm dramatically increased the enrichment factor to the highest values for all pesticides except hexaconazole. When the agitation rate was increased to 800 rpm, no further increase of enrichment factor was observed and slightly decreased recoveries were noted. This could be due to the back extraction of analyte from the acceptor phase to the donor phase in terms of the phase equilibrium theory.

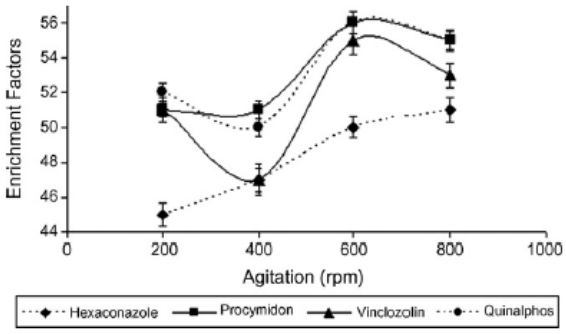

Fig. 4. Variation of total enrichment factor of pesticides with agitation rate in CSM-LPME.

Exposure time

Mass-transfer is a time-dependent process and equilibrium is attained only after certain period of time. For method optimization, it is therefore important to establish the extraction-time profiles of target compounds so as to configure the time after which equilibrium is attained in practice. It can be observed that the enrichment factors increased radically on going from 10 min to 20 min (Fig. 5). This is probably due to the longer exposure time that allowed better mass transfer between the analytes from the donor phase to the acceptor phase to reach equilibrium state. However, the enrichment factors gradually decreased when longer exposure times (30 and 40 mins) were applied onto the extraction.

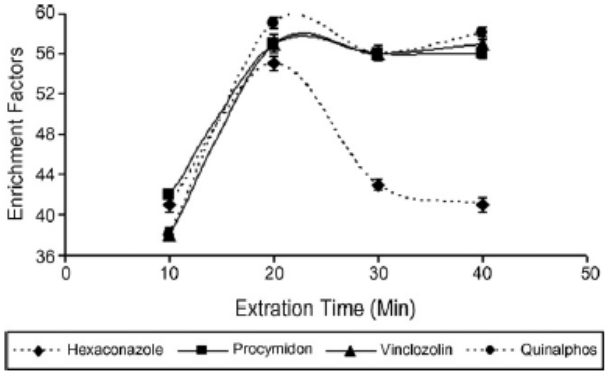

Fig. 5. Variation of total enrichment factor of pesticides with exposure time in CSM-LPME.

Salting out effect

Depending on the nature of the target analytes, addition of salt to the sample solution can decrease their solubility and therefore enhance extraction because of the salting-out effect. In this study, the effect of salt on extraction efficiency was determined by adding sodium chloride to 15 mL of water samples at concentrations of 0, 2.5, 5, and 10 % (w/v). Based on the results obtained, the extraction enrichment factors obtained highest values when no salt was added to the water samples. Therefore, the consecutive experiments were carried out without adding any salt to enhance the extraction efficiency.

Effect of pH

Adjustment of the pH can enhance extraction, as dissociation equilibrium is affected together with the solubility of the acidic/basic target analytes. In the present study, the extractions were performed under different pH conditions ranging from pH 3 to 8. It can be noted that, best extraction efficiency for all the pesticides was observed at pH 6 and the EFs decreased dramatically when the pH increase to 7 and 8 (Fig. 6).

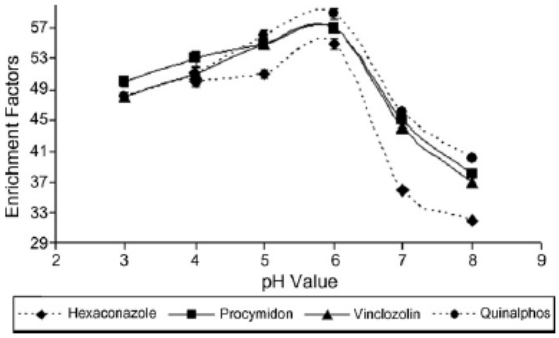

Fig. 6. Effect of pH of sample solution of total enrichment factor of pesticides in CSM-LPME.

Effect of Humic Acids

The effect of humic acid was also investigated on CSM-LPME. The concentration of humic acids was varied in the range of 0 to 200 μg/L. It was observed that the addition of humic acids did not significantly decrease the overall extraction efficiency (results not shown). The EFs remained unchanged as the concentration of humic acids increased. The pores of the CSM wall only allow the low molecular weight analytes to diffuse through while excluding high molecular interfering compounds.

Linearity, limits of detection, and repeatability

To validate the applicability of the proposed CSM-LPME procedure, the linearity, limits of detection, and repeatability were investigated using the optimum extraction condition. The linearity of the extraction technique was studied by spiking the water samples with pesticides to give final concentrations of 1.5, 3.0, 5.0, 10, 50, 100 μg/L and followed by extraction of the analytes. The calibration plots were linear over the range of 0 to 100 μg/L with correlation (*r*) ranging from 0.9995 to 0.9998 (Table 1). The LODs of the developed method ranged from 1.1 to 1.9 μg/L and the overall proposed method showed excellent repeatability with RSDs of less than 10 %.

Table 1
Analytical performance of CSM-LPME in spiked water samples

Analyte	Relative recovery (%)	Enrichment factors	Linearity range (μg/L)	Correlation (*r*)	LODs (μg/L)	RSD (%)
Hexaconazole	83	55	2.0–100	0.9998	1.1	6.5
Procymidone	91	57	2.0–100	0.9997	1.4	7.5
Vinclozolin	98	57	2.0–100	0.9995	1.7	6.3
Quinalphos	108	59	2.0–100	0.9998	1.9	8.5

Relative recovery = (spiked analytes concentration/concentration of analytes detected) × 100%. RSD (%) represents method repeatability ($n = 6$).

Conclusion

A novel and simple method for the determination of pesticides in water has been developed using CSM-LPME prior to micro-LC. The CSM-LPME technique is advantageous in terms of total extraction time, total solvent usage, cost, linearity, LODs as well as the method repeatability. Current work provides a great interest to further investigate on the applicability of the CSM-LPME method to the analysis of ionizable compounds and also the study of other commercially available polymeric membrane.

References

1. J. A. Jonsson, L. Mathiasson, J. Sep. Sci. 24 (2001) 495.
2. M. M. Sanagi, H.H. See, W. A. W. Ibrahim, A. A. Naim, Anal. Chim. Acta 538 (2005) 71-76.
3. M. M. Sanagi, H. H. See, W. A. W. Ibrahim, A. A. Naim, Chromatographia (11/12) (2005) 567-571
4. G. Shen, H. K. Lee, Anal. Chem. 74 (2002) 648.
5. L. Zhao, H. K. Lee, Anal. Chem. 74 (2002) 2486.