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Short communication

Solid-phase microextraction of organophosphorus pesticides from water

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Abstract

Frequent occurrences of pollution in natural drainage by industrial chemicals, especially pesticides, have triggered interest in the development of fast and unambiguous analytical techniques to verify these pollutants in order to facilitate rapid remedial actions. In this work, we report the development of a solid-phase microextraction (SPME) method to analyse two common industrial pesticides in water, i.e. malathion and parathion. SPME analysis facilitates direct analysis of chemical species in aqueous systems and avoids lengthy sample preparation procedures. In this study, we compare five commercially available fibres: 7 μm polydimethylsiloxane, 30 μm polydimethylsiloxane, 85 μm polyacrylate, 65 μm Carbowax–divinylbenzene and 65 μm polydimethylsiloxane–divinylbenzene fibres. Profiles of uptake by the fibres against adsorption times were established. The results obtained indicated that the polarity of the fibres is not the main factor affecting the uptake. The structures of the fibres also affected the permeation of the analytes onto the fibres. The limits of detection were determined to be in the low ppb level with a flame ionization detector. These methods have great potential for use in rapid on-site analytical work which is highly demanded in environmental studies.

Keywords: Water analysis; Environmental analysis; Extraction methods; Organophosphorus compounds; Pesticides; Malathion; Parathion

1. Introduction

Pollution of natural drainage by industrial chemicals in rapidly developing countries has caused severe environmental pollution problems. Efforts to solve these problems entail fast and accurate analytical methods to verify such pollutants in environmental matrices. Solid-phase microextraction (SPME), which is a solventless method to extract organic compounds from aqueous samples, provides a good solution to establish such methods. SPME works according to the principle of adsorption of analytes from the matrix onto a phase-coated fibre immersed in this matrix. Analysis of the trapped analytes is then facilitated by thermally desorbing the fibre in a gas chromatograph (GC) injection port. This method does not employ the solvents used in conventional liquid–liquid extraction (LLE) and solid-phase extraction (SPE).

The theory of SPME has been discussed [1]. Louch et al. [2] have shown that the number of moles of analyte, n, absorbed on the fibre has a linear relationship with the analyte concentration in the solution, C:

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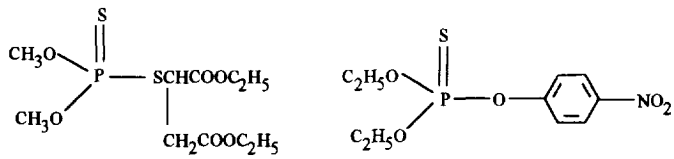

Malathion Parathion

Scheme 1. Structures of malathion and parathion.

$n = \kappa VC = AC$

where κ is the distribution constant, V is the volume of the coating on the fibre and $A = \kappa V$.

Pollution of natural drainage by pesticides malathion and parathion are common in industrializing countries. The interest to analyse them in aqueous system has led to the development of several new analytical methods. Malathion and parathion (see Scheme 1) have been successfully extracted from water using solid-phase extraction (SPE) [3]. Parathion has also been successfully extracted using polydimethylsiloxane [4] and polyacrylate [5] fibres in SPME. However, no comparative study was done on the extraction efficiency of the different commercially available fibres. In this study, a comparison of the performance of different fibres in extracting malathion and parathion from water was performed. The A-values of these two compounds were established for the following fibres: 7 μm polydimethylsiloxane (7PDMS), 30 μm polydimethylsiloxane (30PDMS), 85 μm polyacrylate (PACRY), 65 μm Carbowax–divinylbenzene (CXDVB) and 65 μm polydimethylsiloxane–divinylbenzene (PDDVB) fibres. The equilibration time for uptake by the different fibres was also determined. Earlier studies have indicated equilibration periods for different analytes ranging from 50 min for herbicides [6] to 100 s for benzene [2].

2. Experimental

The SPME device was from Supelco. Fibres coated with 7 μm PDMS, 30 μm PDMS, 85 μm PACRY, 65 μm CXDVB and 65 μm PDDVB were used for these studies. All fibres were conditioned for 3 h at 250°C and the PACRY fibre conditioned overnight.

Analysis was performed on a HP 5890II gas chromatograph equipped with a flame ionization detector. Separation was carried out using a HP-5 column, 25 m×0.25 mm, 0.33 μm film thickness. Splitless injections were performed. The temperature program was: 40°C, hold for 2 min, then to 250°C at 10°C/min and hold for 5 min. The carrier gas was helium at 1 ml/min at 40°C. The split/splitless injector and the detector were maintained at 250°C.

Parathion and malathion were purchased from Supelco. Water was obtained from a Labconco WaterPro system. Stock solutions of 2000 ppm were prepared separately by dissolving 2 μl of the compound in 1 ml of ethyl acetate (resi-analysed grade, J.T. Baker). All concentrations were calculated based on v/v. The calibration standards were prepared by dilution of the 2000 ppm stocks and range from 2 to 1000 ppm. The spiked water stock of parathion was prepared in a 100-ml volumetric flask by adding 50 μl of the 2000 ppm stock solutions and making up to 1 ml with methanol (HPLC grade, Lab-Scan) before topping up to the mark with deionized water. For malathion the spiked stock was of a concentration of 10 ppm. Subsequent concentrations of the spiked water was prepared by dilution of this stock. Duplicate analyses were carried out for all studies.

A 20-ml volume of the spiked water sample was placed into a 22-ml vial with a stirrer bar. The vial was sealed with a screw-cap with PTFE septum and a 1-mm O.D. hole. Stirring was carried out on a Stuart Scientific SM1 magnetic stirrer. The fibre was first drawn into the needle and then lowered into the solution. The plunger was then depressed and the fibre immersed completely into the solution. The sampling time was kept constant at 30 min when determining A-values. For determining the optimum sampling period, the time was varied from 10 to 120 min. After sampling the fibre was again drawn into

Table 1
A-values of malathion and parathion on the fibres

Types of fibres	A-values	
	Malathion	Parathion
7PDMS	2.09	23.13
30PDMS	10.20	67.37
85PACRY	156.32	466.8
65CXDVB	80.92	25.25
65PDDVB	Non-linear	1070.7

the needle. The SPME device was then injected into the GC injector and held there for 2 min. The oven program was started once the fibre was exposed.

3. Results and discussion

The A-value for malathion was determined from 0.5 to 10 ppm on all fibres, whereas for parathion the concentration range was from 0.001 to 1 ppm. The A-values for malathion and parathion on the different fibres are shown in Table 1. The graphs of the uptake by the fibres vs. the spiked concentrations are shown in Fig. 1 and Fig. 2 for malathion and parathion, respectively.

As can be seen from the A-values, the uptake for parathion is much higher than for malathion on all fibres except for the CXDVB fibre. The solubility of malathion in water is 145 ppm whereas the solubility for parathion is 20 ppm, hence malathion is 7 times more soluble than parathion. Its recovery is therefore expected to be poorer. The performance of the CXDVB fibre for parathion is almost equivalent to that of the 7PDMS fibre. From the A-values, the uptake on the 7PDMS fibre is the least efficient whereas the uptake on the 65 μm PDDVB is the most efficient and is twice that of the 85 μm PACRY fibre for both compounds. The non-linearity of the curve of the PDDVB fibre for malathion indicates a saturation of the fibre. The A-value was then determined at a lower concentration range of 0.001 to 1 ppm. The curve is shown in Fig. 3.

The uptake curve of malathion at the lower concentration range of 0.001 to 1 ppm is linear. As the uptake of malathion on the various fibres varied considerably, the equilibration studies were performed at concentrations of 0.1, 1 and 2 ppm. At 120 min of equilibration, all the fibres were found to be approaching equilibrium (Fig. 4).

The concentration of the spiked solution used for the equilibration study was 0.1 ppm for parathion. As shown in Fig. 5, increasing the equilibration period increases the response area of the peaks on all fibres.

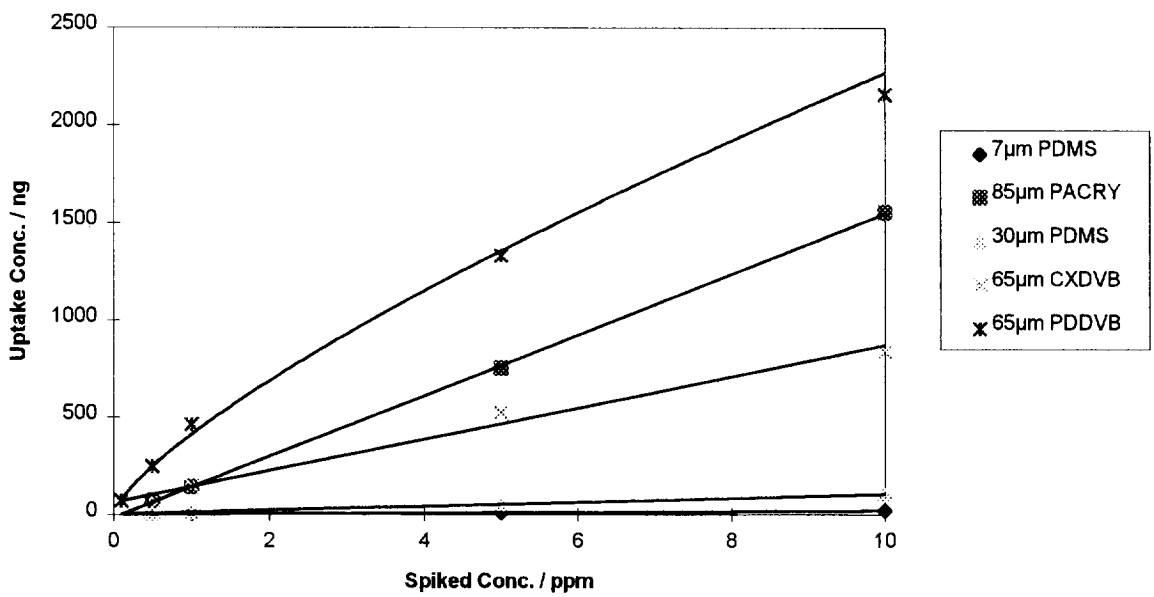

Fig. 1. Uptake of malathion by the various fibres.

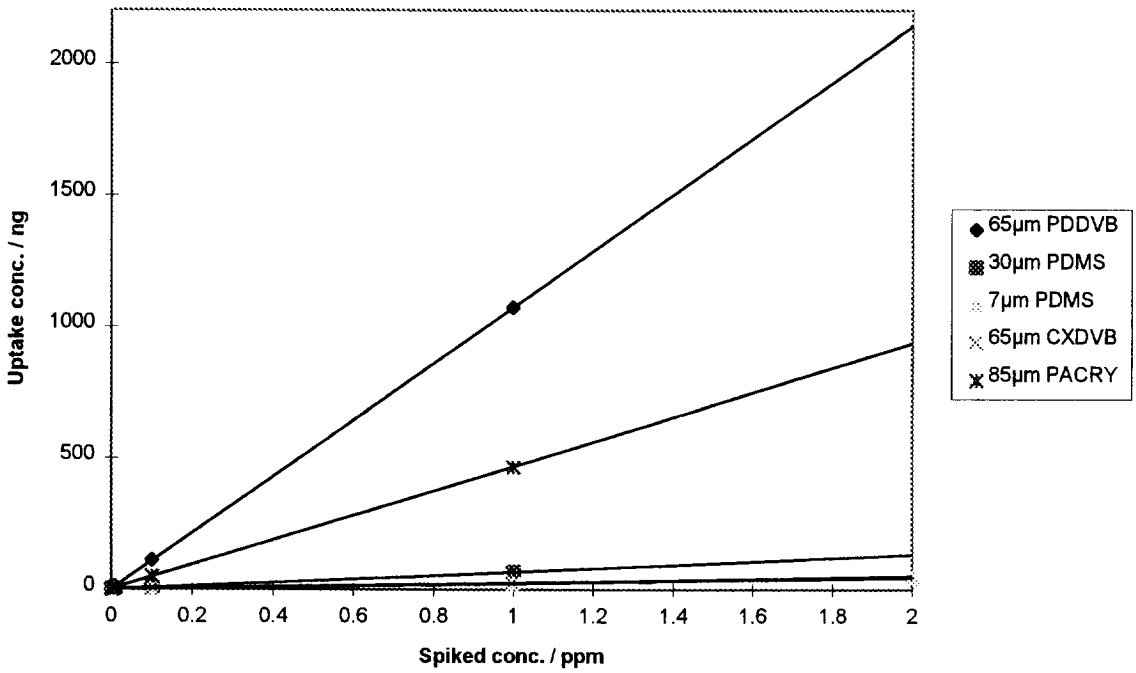

Fig. 2. Uptake of parathion by the various fibres.

However the values are approaching equilibrium towards 120 min of equilibration on three of the fibres: 7PDMS, 30PDMS and CBXDVB. The uptake on the PACRY and PDDVB fibres does not seem to be reaching equilibrium even after 120 min of equilibration. As discussed elsewhere [2], SPME is a non-exhaustive extraction process and hence the results will be reproducible as long as the equilibration period is kept constant.

The detection limits of malathion and parathion extraction from water using the PDDVB fibre were determined to be 0.5 ppb.

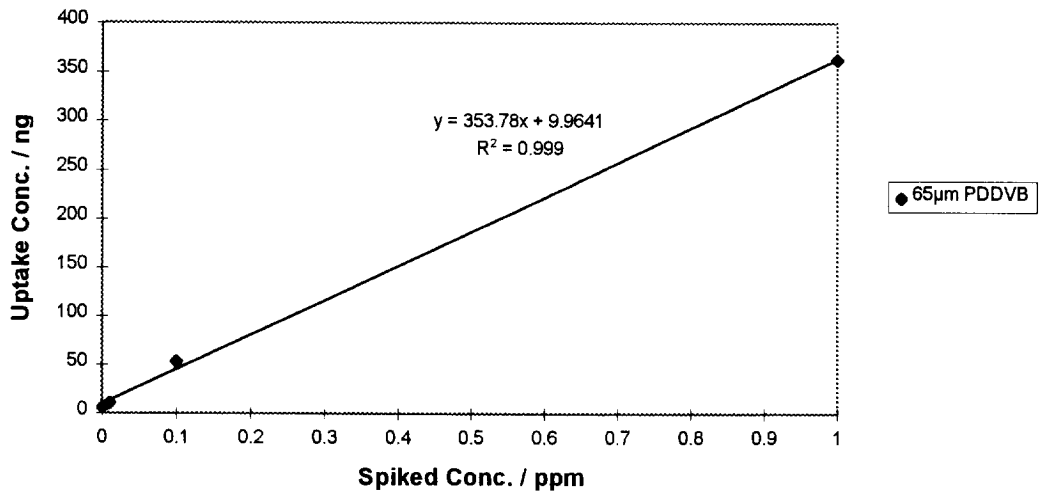

Fig. 3. Uptake of malathion on the 65 µm polydimethylsiloxane–divinylbenzene fibre.

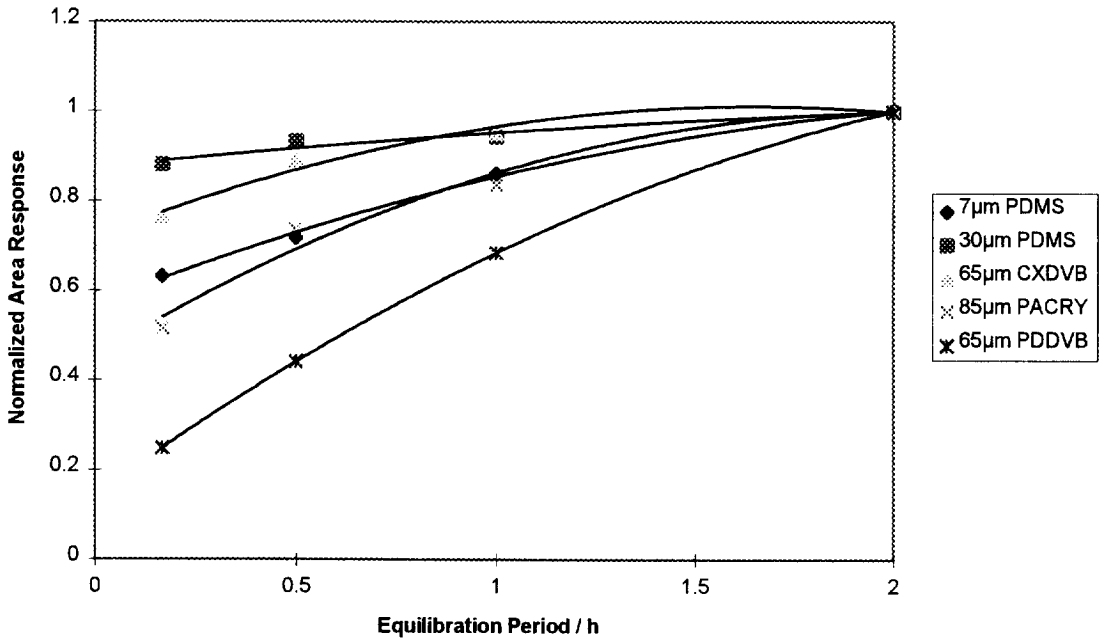

Fig. 4. Equilibrium study of malathion uptake on the fibres.

4. Conclusion

The uptake for malathion and parathion is highest on the 65 μm PDDVB fibre. Although the polyacrylate fibre is more commonly used in SPME, the new combination fibre has proven to be more

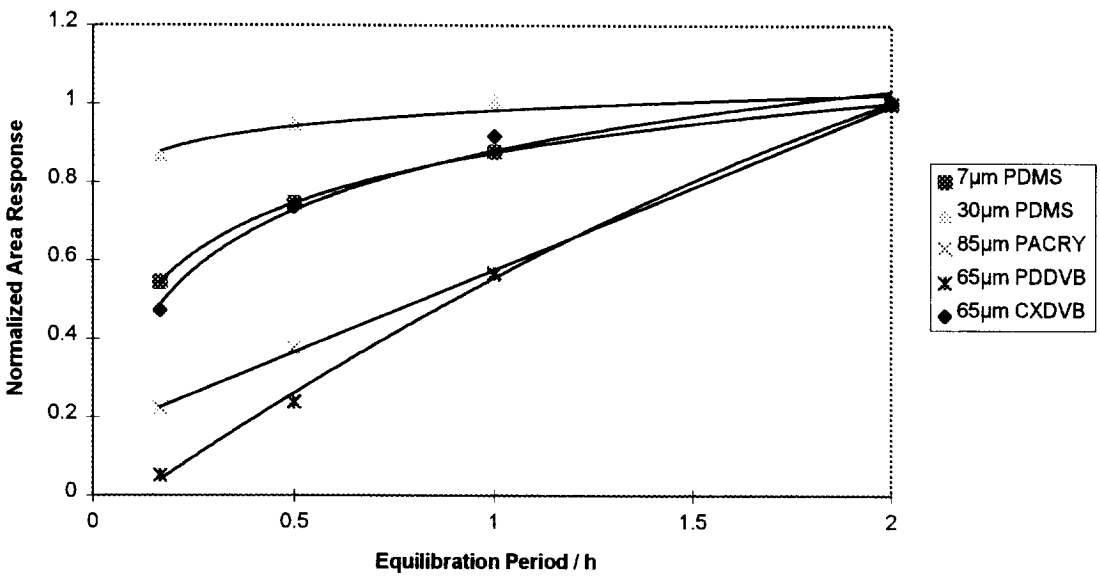

Fig. 5. Effect of equilibration period on uptake of parathion.

efficient for these two organophosphorus pesticides. The extraction time of 30 min is not the optimum extraction period for both malathion and parathion using SPME. However the analysis would be unnecessarily prolonged if an equilibration period of 120 min or greater were used. A period of 30 min was ideal since it was approximately equivalent to the time required for one GC analysis. Furthermore, low detection limits of 0.5 ppb were obtained using the 65 μm PDDVB fibre for both malathion and parathion even though equilibrium was not achieved. This low detection limit was achieved using a flame ionization detector.

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