ELSEVIER

Journal of Chromatography A, 760 (1997) 179–192

JOURNAL OF CHROMATOGRAPHY A

Retention profiles of some commercial pesticides, pyrethroid and acaricide residues and their application to tomato and parsley plants[1]

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Received 9 March 1996; revised 1 October 1996; accepted 9 October 1996

Abstract

This work deals with the preconcentration of some water soluble pesticides, pyrethroids and acaricides by polyurethane foams. The retention profiles of the tested species were found quickly and reached equilibrium in a few min. Various parameters – e.g. pH, extraction media, shaking time, salt effect, temperature and sample volume – affecting the preconcentration of the tested species by the unloaded foams and tri-*n*-octylamine and tri-*n*-methylphosphate treated foams were optimized. The unloaded foams were employed in a column mode to study the quantitative retention and recovery of the tested species. The sorption efficiency and recovery of the compounds by the unloaded foam column were found to be up to 99.5%±2.1. The height equivalent of a theoretical plate for the unloaded foam column was found to be in the range 1.9–2±0.2 mm. The sorption mechanisms of the tested compounds by the foams are discussed. Analysis of N, P, Na, K, Cu, Zn, Mn, Fe, humidity, wet and dry mass of tomato and parsley untreated and sprayed for different time intervals – i.e. 24, 72 and 120 h – with Chiorpyrifos, was carried out .

Keywords: Polyurethane foam; Sample preparation; Tomato; Parsley; Environmental analysis; Stationary phases, LC; Thermodynamic parameters; Water analysis; Pesticides; Pyrethroids; Acaricides

1. Introduction

In recent years industrial growth and the need to increase agriculture productivity have resulted in the presence of pollutants in water and air. Since these compounds are present at levels lower than ppb their determination causes problems [1]. Among these substances, pesticides, pyrethroids and acaricides must be watched with particular attention because of their very low limits of tolerability. These compounds are deliberately directed against living organisms and show strong bioaccumulation [1,2].

The most common reported extraction procedures for the water pollutants are liquid–liquid extraction [3], adsorption on activated charcoal [4] and/or cellulose triacetate membrane filters [5], Tenax, Chromosorb 101 and Porapak as trapping materials [6]. Such preconcentration methods are not satisfactory with respect to their capacity for trapping pollutants present at very small amounts and their recovery, and they are also too extensive for routine analysis where many large sample volumes are concentrated on site prior to quantitative analysis [7].

[1] Paper originally submitted for the thematic issue on Pesticide Residues [J. Chromatogr. A, 754 (1996)].

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PII S0021-9673(96)00872-2

Recently, porous polyurethane foam has been used as an inexpensive solid extractor and effective sorbent for the removal of water pollutants [8,9]. The membrane-like structure of the foam together with its efficient sorption properties offered higher concentrating ability and flow-rates compared with other solid granular supports [10]. The present study was aimed at investigating the retention profiles of some pesticides, pyrethroides and acaricides in water at low levels (ppb) by polyether-based polyurethane foams. The influence of Chlorpyrifos on the uptake of some essential elements, e.g. N, K, P, Na, Fe, Zn, Mn and Cu, and on the wet and dry mass and humidity percentage of tomato and parsley plants after different times of spraying was also studied.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical reagent grade. Open pore polyether-type-based polyurethane foams were supplied by K.G. Schaum (Stoffwerk, Kremsmunster, Austria). Foam cubes of approximately 1 cm^3 were cut from polyurethane foam sheets. The foam cubes were dried as reported previously [11]. The foam cubes were loaded with tri-*n*-octylamine (TOA) and tri-*n*-methylphosphate (TMP) by mixing the dried foam cubes with 5% TOA and 5% TMP separately in *n*-hexane (20 cm^3/g dry foam) with stirring for 10 min, respectively, and drying as reported [11]. Stock solutions (1 *M*) of lithium, sodium, ammonium and potassium chlorides were prepared separately in distilled water. Brilton–Robinson buffer (pH 2–12) solutions were prepared by mixing equimolar concentration (0.08 *M*) of boric, acetic and phosphoric acid in distilled water and adjusting the pH with sodium hydroxide (0.04 *M*).

The tested pesticides are Chlorpyrifos, *o,o*-diethyl-*o*-(3,5,6-trichloro-2-pyridyl) phosphorothioate (I); Parathion, *o,o*-diethyl-4-nitrophenyl phosphorothioate (II); Malathion, diethyl-[(dimethoxyphosphinothioyl)thio]butaredioate (III); the pyrethroid Cypermethrin, cyano(3-phenoxyphenyl)methyl-3-(2,2-dichloroethyl)-2,2-dimethylcyclopropanecarboxylate (IV); and the acaricides Dicofol, 2,2,2-trichlor-1-bis(4-chlorophenyl)ethanol (V) and Bromopropylate, isopropyl-4,4-dibromobenzilate (VI). The structures of these compounds are given in Fig. 1.

A stock solution of each compound (100 $\mu g/cm^3$) was prepared by dissolving the exact mass of the compound in ethanol. A series of various concentrations of these compounds was then freshly prepared by diluting their stock solutions with distilled or tap water and a few drops of ethanol whenever it was required to provide a clear solution. The solutions were stored in polyethylene bottles.

2.2. Apparatus

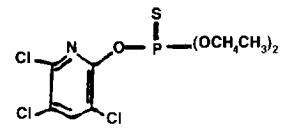
UV absorbance of the tested insecticides was obtained with a Pye Unicam UV-Vis SP8-400 spectrometer with 0.2- and 1-cm quartz cells. An Orion pH meter and glass columns (15 cm×15 mm I.D.) and a Lab-Line Orbit Environ-Shaker Model 35271-1 were also used. A Corning flame photometer (410) and a Pye Unicam SP-9 atomic absorption spectrometer were used to measure the concentration of Na, K, Fe, Mn, Zn and Cu. Calcium was determined by EDTA titration. The Kjeldahl method was used for the determination of the nitrogen content in plant (tomato and parsley) tissues. Hot Box oven Honda spray machine with high pressure and stoppered flasks (50 cm^3 capacity) were used.

2.3. General procedures

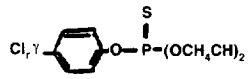
2.3.1. Batch experiments

Influence of shaking time on the retention profiles of the tested compounds on the unloaded and loaded polyurethane foams

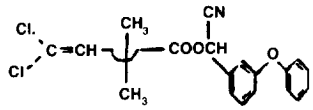
The unloaded and loaded (TOA or TMP) polyurethane foam cubes (0.3+0.004 g) were equilibrated with 100 cm^3 aqueous solution at pH 4–6 of each compound at concentrations of 100 $\mu g/cm^3$ in polyethylene bottles and shaken in a thermostatted mechanical shaker at 20±0.1°C for various time intervals up to 2 h. After shaking, the foam cubes were separated and the amount of the compound remaining in the aqueous phase was determined from its absorbance measurements at the wavelength of maximum absorbance against a blank; the amount of the insecticide retained on the foam was calculated



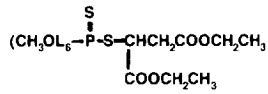
(I)
Chloropyrifos



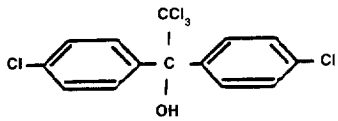
(II)
Parathion



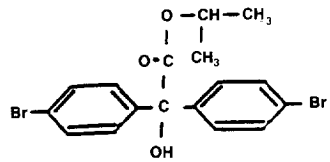
(III)
Cypermethrin



(IV)
Malathion



(V)
Dicofol



(VI)
Bromopropylate

Fig. 1. The structure of the tested organophosphorous insecticides, pyrethroid and acaricides.

using this difference. The extraction efficiency (%E) and the distribution coefficient (D) of the tested species by the unloaded foams were determined employing the equations:

$$\%\text{Extraction}\ (E) = \frac{a_0 - a}{a} \times 100 \qquad (1)$$

and

$$D = \frac{\%E}{100 - \%E} \times \frac{\text{Volume of solution (l)}}{\text{Mass of foam (kg)}} \qquad (2)$$

or

$$D = \frac{\%E}{100 - \%E} \times \frac{\text{Volume of solution (cm}^3\text{)}}{\text{Mass of foam (g)}} \qquad (3)$$

where a_0 = concentration of the tested compound in solution before extraction and a = concentration of the solute in solution after extraction.

Following these procedures, the influence of solution pH, nature of extraction media, temperature, compound concentration and salt concentration ($\leq 0.1\ M$) of different chloride salts (Li, Na, K and NH_4) on the retention profiles of the tested compounds by the unloaded, TOA- and TMP-loaded polyurethane foams were critically determined.

2.3.2. Column experiments

Chromatographic behaviour of the tested insecticides on a column packed with the unloaded foam

Quantitative retention and elution of the tested compounds on the unloaded foam columns were

carried out using the vacuum method of foam packing [11]. Tap or distilled water (0.1–6 dm^3) samples containing 0.05 mg of the tested compound at the pH of maximum retention on the unloaded foams was percolated through the column packed with 3±0.006 g of the unloaded foam at 10 cm^3/min. After squeezing water from the foam material, the compound was recovered from the foam with 100 cm^3 acetone in a Soxhlet extractor for 6 h. The sample quantity was then determined from a preconstructed calibration curve by measuring the absorbance of the extracted acetone solution against a blank.

2.3.3. Plant analysis

Sample preparation

Plant sample (leaves) of tomato and parsley were sprayed with 20 g of commercial Chlorpyrifos (40%, w/w) mixed with 20 dm^3 water ($4:1\times10^4$, w/v) in the open field using a high-pressure sprayer. The treated plant samples were left for periods of 24, 72 and 120 h. Five samples each of untreated and treated leaves were then collected, washed with distilled water until all dust and sand were removed completely and finally dried with a napkin. The leaves were cut into small pieces, washed with water and spread for 24 h at room temperature for drying and grinding into powder form.

Determination of the total nitrogen content

A mass of the dry leaves (0.2–0.3 g) was accurately weighed and placed in a 800 cm^3 Kjeldahl flask; 50 cm^3 of concentrated sulphuric acid containing 1.65 g of salicylic acid were added. Five grams of sodium thiosulphate were added, the mixture was heated for 30 min, cooled and 10 g of a sodium hydrogensulphate–selenium mixture (100:1, w/w) were added and the mixture was digested in the Kjeldahl apparatus. After complete digestion, the mixture was cooled and 300 cm^3 of water and 100 cm^3 of concentrated sodium hydroxide were added. Then the distillate standard sulphuric acid was distilled and titrated and the nitrogen content was determined employing the equation:

$$\%N = \frac{14NV}{10W} \quad (4)$$

where N and V are the normality and volume in cm^3 of sulphuric acid consumed in the titration and W is the mass of the dry leaves in g.

Determination of P, Na, K, Cu, Zn, Mn and Fe by wet ashing

An accurate mass (2–3 g) of the ground plant material was placed in 20 cm^3 of a concentrated sulphuric–perchloric acid mixture (1:1, v/v). The reaction mixture was heated on a hot plate until the acid fumes were completely evolved; the volume of the reaction mixture was reduced to 3–5 cm^3 by evaporation on a hot plate and 50 cm^3 of distilled water were added to the mark. Calibration graphs for phosphorous and molybdenum were made by UV-visible spectrophotometry; for sodium and potassium flame photometry was used, and for copper, zinc, manganese and iron atomic absorption spectrometry was employed. The unknown sample concentration was then obtained from a calibration graph of each element employing the following equation:

$$\%M = \frac{C\ (\text{ppm}) \times \text{solution volume}\ (cm^3)}{10^4 \times \text{sample mass}\ (g)} \quad (5)$$

where M = P, Na, K, Cu, Zn, Mn or Fe and C is the concentration of the element to be determined in ppm.

Determination of the moisture or humidity content

The sample was spread in the container, rapidly weighed, dried in a circulation oven at 70–80°C to a constant mass, cooled in a desiccator, weighed. The humidity and dry matter percentages of the plant leaves were obtained by employing the equations:

$$\text{Moisture}\ (\%) = \frac{\text{Loss in mass on drying}\ (g)}{\text{Initial sample mass}\ (g)} \times 100 \quad (6)$$

$$\text{Dry matter}\ (\%) = \frac{\text{Oven dry mass}\ (g)}{\text{Initial sample mass}\ (g)} \times 100 \quad (7)$$

Ash content

The crucible in a muffle furnace was heated to about 500°C, cooled in a desiccator, weighed and an accurate mass of 1 g of oven-dried sample was transferred into the crucible. The crucible containing the dry sample was placed into a cool muffle furnace

and the temperature was increased to 500°C. After 3 h at 500°C the crucible was removed, allowed to cool in a desiccator, weighed and the ash content was determined by employing the equation:

$$\text{Ash}\ (\%) = \frac{\text{Ash mass (g)}}{\text{Oven dry mass (g)}} \times 100 \qquad (8)$$

Dry ashing

A 0.2-g amount of air-dried ground sample was weighed into an acid-washed porcelain basin, ignited to 500°C for 3 h in a muffle furnace (refer to ashing procedure) and cooled; 5 cm^3 of HCl (1:1, v/v) were added and the sample was covered with a watch glass and heated on a steam bath for 15 min. Then 1 cm^3 of concentrated HNO_3 was added, the sample evaporated to dryness, and heating continued for 1 h; 2 cm^3 of HCl (1:1, v/v) were added, the sample swirled to dissolve the residue, diluted to 20 cm^3 with water and warmed to complete dissolution. Then the sample was filtered through a No. 44 filter paper into a 100 cm^3 volumetric flask and diluted with distilled water to the mark. Blank determination was carried out in the same way.

3. Results and discussion

The use of unloaded polyurethane foams (PuF) in the separation and preconcentration processes led to observation of the potential of their spherical geometrical form (spherical membrane-shaped geometry) and to the proposal of their general use in column operations as a substitute for the traditional granular supports in extraction chromatography. The membrane-like structure of the foams together with the efficient sorption and mass-transfer properties offer higher concentrating abilities and flow-rate compared with other solid supports. Thus, in recent years, considerable progress has been made in the use of polyurethane foam as an inexpensive solid extractor and effective sorbent for the removal of water pollutants.

3.1. Retention behaviour of the tested compounds on the unloaded and loaded foams by batch experiments

Batch experiments using unloaded foams have shown that the retention of Parathion, Malathion, Chlorpyrifos and Cypermethrin was rapid and the equilibrium was reached in less than 50 min, followed by a plateau. Hence, a minimum shaking time of 1 h was adopted in the subsequent work. The results obtained are summarized in Fig. 2. The average values of the half-life ($t_{1/2}$) of the sorption equilibrium calculated from Fig. 2 were found to be in the range 2–3 min.

Similarly, batch experiments using unloaded, TMP- and TOA-loaded polyurethane foams have shown that the extraction of the investigated acaricides Dicofol and Bromopropylate from aqueous solution at pH≤3 is rapid and the equilibrium is reached in less than 1 h, followed by a plateau. A good extraction efficiency and rapid preconcentration of the tested acaricides from aqueous media were obtained with TOA-treated foam as compared to the unloaded and TMP-loaded foams. The average values of the half-life ($t_{1/2}$) of equilibrium sorption on the unloaded, TOA- and TMP-loaded foams were found to be in the range 3–5, 2.5–3 and 3–4 min, respectively. The tri-*n*-octylamine acts as a plasticizer on the polyether foam. Thus, the collection

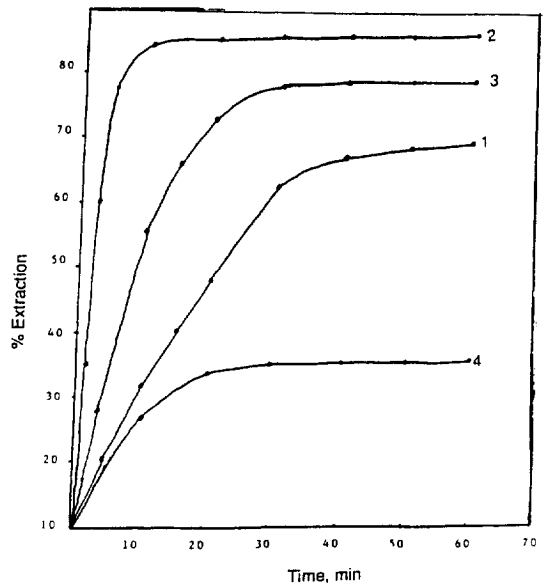


Fig. 2. Effect of shaking time on the sorption profiles of (1) Parathion, (2) Malathion, (3) Chlorpyrifos and (4) Cypermethrin at 100 mg/cm^3 in aqueous solution (100 cm^3) at pH 5–7 and 20±0.1°C using the unloaded foam (0.3±0.004 g).

rates of the compounds with plasticized TOA foams are generally better than with unplasticized ones. This can be attributed to the high mobilities and diffusion rates of the tested acaricides through the open pores and the quasi-spherical membrane structure of the plasticized TOA foam [11,12]. The plasticizer acts as an efficient nonvolatile solvant for the foam plastic itself. These results are in good agreement with the data reported by Braun et al. [13]. The foam membrane acts as a true sorbent where the diffusion rates of the chemical species in the membrane structure are considerably higher than those in bulky solids [14,15].

The influence of the pH on the extraction of each of the tested compounds by the unloaded foams at 100 $\mu g/cm^3$ concentration was examined over the pH range 2–12. The sorption profiles of the investigated compounds by the unloaded foams increased markedly in the pH range 5–7 except for Chlorpyrifos which reached a maximum retention in the pH range 2–4. Malathion displays the lowest removal at pH 9 and the percentage removal slightly increased at higher pH. Lowering the pH tends to protonate the nitrogen atoms of the urethane linkage of the polyurethane foam, Fig. 3, as reported by El-Shahawi [16]. The percentage removal of Dicofol and bromopropylate by the unloaded foams decreased at moderate pH (5–7) and reaches a maximum at pH<3 at which the compounds exist in the neutral form. Thus, the sorption of these compounds involves neutral species and this is consistent with a solvent extraction mechanism [16].

3.2. Sorption isotherms

The extraction isotherms of the tested compounds (I–IV) on the unloaded foams were developed over a wide range of equilibrium concentrations (10–100 $\mu g/cm^3$) for each species at 100°C. The pH values of the aqueous solution were adjusted to a pH in the range 4–7, so that the compounds were predominately in the undissociated form. At low concentration the sorption isotherms exhibited a first-order behaviour and tended to plateau at higher bulk solution concentrations. Fig. 4 shows plots of the remaining concentration of the tested insecticides in the aqueous phase versus their concentration retained on the foam material. The sorption of the different species by the unloaded foams increased in the order:

$$\text{Cypermethrin} > \text{Chlorpyrifos} > \text{Parathion} > \text{Malathion} \quad (9)$$

Similar trends for the extraction of the tested

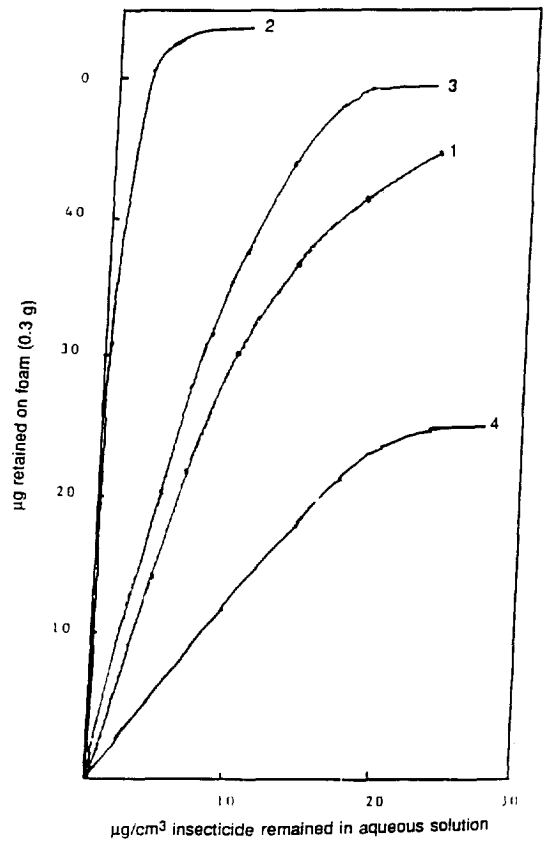


Fig. 4. Extraction isotherm of (1) Parathion, (2) Cypermethrin, (3) Chlorpyrifos and (4) Malathion at concentrations of 10–100 $\mu g/cm^3$ using the unloaded foams (0.3±0.004 g) from a 100 cm^3 aqueous sample at pH 5–7 and 20±0.1°C and 1 h extraction time.

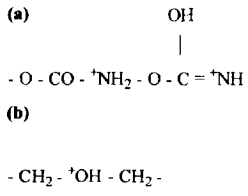


Fig. 3. (a) Protonated urethane, and/or (b) ether oxygen atoms of the polyurethane foam.

compounds were obtained with diethyl ether and for other similar species retained on the polyurethane foams [16]. Therefore, 'solvent extraction' is the most probable mechanism for the sorption of the tested species by the unloaded polyurethane foam [7]. However, it is worth noting that the molecular masses (M_r) of Chlorpyrifos (M_r=345.5), Malathion (M_r=230.3), Parathion (M_r=291.0) and Cypermethrin (M_r=419.6) are also participating factors in the extraction step by the foam. These data are also consistent with the general understanding that the larger the molecular mass of the sorbate the larger the amount of the tested insecticides retained on the foam when the substances concerned are similar in nature [17].

The sorption behaviour of the investigated acaricides (Dicofol and Bromopropylate) from aqueous solution by the unloaded and TMP- and TOA-loaded foams was found also to depend on the concentration. Thus, the extraction isotherms were developed over a wide range of equilibrium concentrations (10–200 $\mu g/cm^3$) for each compound at 20±0.1°C. The pH values of the aqueous solution in these experiments were adjusted at pH≤3. A good linear correlation between the concentration of each compound extracted on the unloaded and TMP- and TOA-loaded foams was achieved. The sorption profiles obtained using the unloaded and loaded foam increased in the order:

$$\text{TOA} - \text{foam} > \text{TMP} - \text{foam} > \text{unloaded foam} \quad (10)$$

The influence of various concentrations of alkali metal (Li^+, Na^+, NH_4^+ and K^+) chlorides at concentrations ≤0.1 M on the sorption percentage of the tested compounds at 80 $\mu g/cm^3$ was studied at the optimum pH extraction. The results obtained on the sorption by the unloaded foams are summarized in Table 1. A significant increase in the distribution ratios of Malathion, Dicofol and Bromopropylate was observed with increasing LiCl or NaCl concentrations from 0.01 to 0.1 M and the following order of extraction was noted:

$$Li^+ > Na^+ > NH_4^+ > K^+ \quad (11)$$

This behaviour is characteristic of the 'solvent extraction mechanism' with the salt acting as salting out and the cation-chelation mechanism excluded [9,16]. The distribution ratios of Malathion increased with the amount of salt added from log D=3.43 and 3.41 to 3.52 and 3.42 for Na^+ and Li^+ ions at 0.05 and 0.1 M (Fig. 5). The added salts (Li^+, Na^+)

Table 1
Logarithm distribution coefficient (D) data for the sorption profiles of the tested compounds using the unloaded foams in the presence of different univalent cations

Cation concentration (M)	Insecticides			Pyrethroid	Acaricides	
	Malathion	Parathion	Cypermethrin	Chlorpyrifos	Dicofol	Bromopropylate
Li^+						
0.01	3.43	2.94	2.70	3.79	3.84	3.61
0.05	3.49	2.58	2.55	3.71	3.60	3.66
0.10	3.52	2.42	2.41	3.59	3.38	3.69
Na^+						
0.01	3.41	2.65	2.91	3.92	3.54	3.50
0.05	3.44	2.40	2.76	3.90	3.37	3.53
0.10	3.42	2.28	2.64	3.90	3.37	3.53
				3.88	3.30	3.55
K^+						
0.01	3.37	2.05	3.60	4.60	2.58	3.92
0.05	3.30	2.02	3.52	4.72	2.62	3.45
0.10	3.19					
NH_4^+						
0.01	3.35	2.03	2.61	4.40	3.37	3.62
0.05	3.32	1.98	2.50	4.45	3.35	3.58
0.10	3.23	1.92	2.42	4.52	3.40	3.54

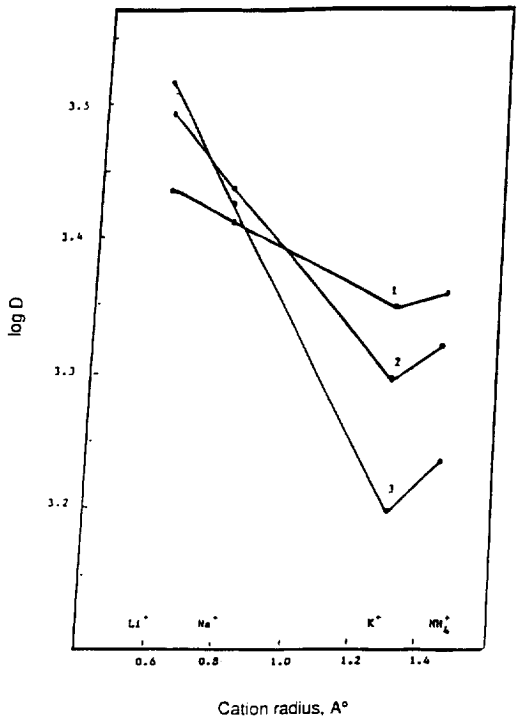


Fig. 5. Effect of extraction media on the sorption profile of Malathion using unloaded foam at 1 h shaking time, with (1) 0%, (2) 5% and (3) 10% of ethanol–water (v/v). Other conditions are as in Fig. 2.

increased the sorption profiles of the tested compound into the polyether foams by reducing the number of water molecules available to solvate the organic compound which would, therefore, be forced out of the solvent phase into the foam. In such cases some amount of the free water molecules are preferentially used to solvate the ions added [18]. Hence, the influence of these salts can be explained by the salting-out effect and 'solvent extraction' is the most probable mechanism [9].

The retention behaviour of Cypermethrin and Chlorpyrifos by the unloaded foams (Table 1) decreased with increasing concentration of the alkali metal Li^+, Na^+, K^+ and NH_4^+ chlorides, and the following order of sorption

$$K^+ > Na^+ > NH_4^+ > Li^+ \quad (12)$$

was achieved at 0.1 *M* salt concentration. Therefore, the ion dipole interaction of NH_4^+ with the oxygen sites of polyurethane foam might highly predominate in the sorption profiles of Cypermethrin and Chlorpyrifos.

According to the 'cation-chelation mechanism' the presence of K^+ ions should facilitate the extraction of Cypermethrin and Chlorpyrifos by the foam more than the other alkali metal ions (NH_4^+, Na^+ or Li^+) because of the better fit of this ion into the central cavity of the oxygen-rich helix in the polyurethane foam. The sorption profiles of Cypermethrin and Chlorpyrifos are in good agreement with the data recently reported by Palagyi et al. [15]. Therefore, the 'cation-chelation mechanism' is the most probable mechanism for the sorption of these species. In accordance with this mechanism, the polyalkenoxy chains of the PuF sorbent form a clathrate with suitable simple cations [16].

In batch experiments the influence of temperature (35, 45 and 55°C) on the sorption profiles of the tested species (I–IV) by unloaded foams was determined at the pH of maximum extraction of each compound. The percentage extractions and the distribution ratios of the tested compounds increased slightly with increasing temperature and similar trends to that obtained at 20°C were achieved. Assuming no precipitation or chelation and the extracted species to be neutral, then the equilibrium constant *K* for the equation

$$\text{compound}_{(\text{aqueous})} \Leftrightarrow \text{compound}_{(\text{foam})} \quad (13)$$

is equivalent to the distribution ratio, *D*. Thus by plotting $\ln D$ vs. T and employing the equation:

$$\ln K = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (14)$$

the values of the standard enthalpy change ΔH^0 and the standard entropy change ΔS^0 were obtained (Table 2). The ΔS^0 for Malathion and Parathion were found to be -20 ± 2 and -38 ± 4 J/mol deg, while for the Cypermethrin and Chlorpyrifos the ΔS^0 values were found to be -16 ± 1.8 and -19 ± 2 J/mol deg, respectively, for the sorption into the unloaded foam. The high molecular mass of the Cypermethrin ($M_r = 416.6$) may account for its higher value of ΔS^0. The observed decrease in the ΔS^0 of Malathion and Parathion is possibly due to the presence of the P=S group which could reduce the

Table 2
Thermodynamic data for the sorption of the tested insecticides and acaricides by (a) unloaded, and (b) TOA-loaded foams

	ΔH^0 (kJ/mol)		ΔS^0 (J/mol deg^{-1})	
	a	b	a	b
Malathion	24±2		20±2	
Parathion	26±1.2		38±4	
Cypermethrin	28±1.8		16±1.8	
Chlorpyrifos	25±2.1		19±2	
Dicofol	20.12±2	22.7±2.3	27.9±2.9	33±2
Bromopropylate	23.2±2.6	27.2±3	30±3	42±3

Conditions: extraction from aqueous solution (100 cm^3) at pH 3 and temperature range 20–55°C.

ion-dipole interaction with the oxygen sites of the polyurethane foam. This also would reduce the degrees of freedom of movement of the tested organic compounds in the polyurethane foam, as previously reported [18–20].

The polymeric nature and/or the different functional groups or heteroatoms in the foam may also take a part in the sorption process of both Malathion and Parathion. These data are also consistent with the solvent extraction mechanism and are in good agreement with the data previously reported by Schumack and Chow [19]. The values of ΔH^0 were found in the range 24–28±2.1 kJ/mol. Raising the temperature may facilitate the partition of the tested species through the polyurethane foam via urethane linkage and/or ether oxygen atoms.

The values of the standard entropy change ΔS^0 and the standard enthalpy change ΔH^0 for the tested acaricides on the unloaded and TOA-treated foams are also summarized in Table 2. The ΔS^0 for the Dicofol and Bromopropylate were found to be in the range −27–30±3 J/mol deg, for extraction into the unloaded foams and −33–42±3 J/mol deg, for sorption into the TOA foams. The decrease in the entropy change with the use of the TOA foam is believed to be due to the hydrogen bonding reducing the degree of freedom of movement of the organic compound in the polyether foam, as reported [20]. These results are consistent with the solvent-extraction mechanism. The bonding of the organic compound with the foam was estimated to be about 10 kJ/mol, which is lower than the intermolecular H-bonding (30 kJ/mol) [16,19]. Raising the temperature may facilitate the formation of intermolecular H-bonding between the hydrogen group of the tested acaricide and the polyurethane foam via nitrogen and/or oxygen atoms.

The influence of the sorption media on the preconcentration of the tested compounds by the foams was examined at the optimum pH by the addition of various proportions of ethanol (0–10%). The sorption percentages of Malathion and Parathion were decreased by the addition of ethanol up to 10%. Representative results are summarized in Fig. 6. This behaviour is probably due to the formation of different association in the aqueous solution [20]. These data are also consistent with the fact that with a compound of low dielectric constant, the degree of extraction should increase with increasing polarity of the polar phase [16]. Thus the 'solvent extraction mechanism' is the most probable mechanism for the sorption of Malathion and Parathion. In contrast, the sorption profiles of Cypermethrin and Chlorpyrifos increased with increasing ethanol concentration.

The effect of ethanol (0–10%) on the sorption percentage of the tested acaricide by the unloaded and TMP-loaded foams was determined. The sorption profiles of compounds V and VI by the unloaded foams are given in Fig. 7. The extraction of the compounds by the unloaded foams increased by the addition of ethanol (up to 10%) to the aqueous solution. Similar trends were also obtained with TMP-loaded foams. Dicofol and Bromopropylate species in the aqueous solution are well solvated in the presence of ethanol and so it is difficult for these ions to form ion-pairs in the aqueous solution. Thus, the solvent extraction mechanism is the most probable mechanism.

3.3. Chromatographic behaviour of the tested insecticides on polyurethane foam columns

Static experiments on the sorption behaviour of the tested pesticides, pyrethroid and acaricides (I–VI) from the aqueous solution with the unloaded foams suggest the possible application of the foam in the column extraction mode. Distilled or tap-water samples (0.1–6 dm^3) containing 0.05 mg of each compound were percolated separately through the foam columns at a flow-rate of 10–15 cm^3/min at the pH of maximum extractibility. More or less complete retention of the tested compounds was

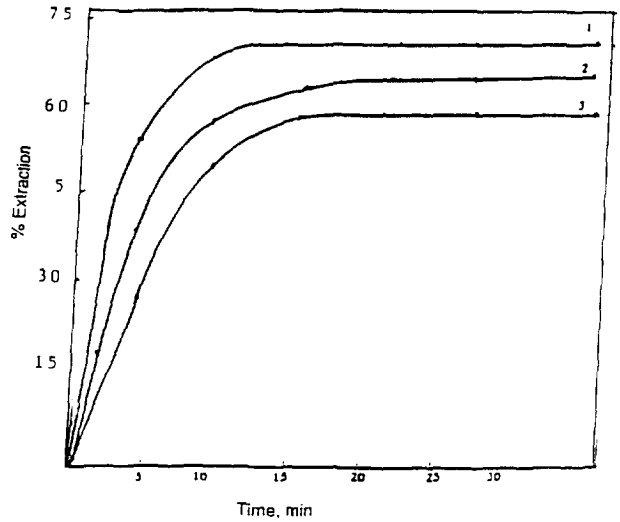


Fig. 6. Effect of extraction media on the sorption profile of Malathion using the unloaded foam at 1 h shaking time, with (1) 0%, (2) 5% and (3) 10% of ethanol. Other conditions are as in Fig. 2.

achieved by the foam column. After squeezing water from the foam, the retained compounds were recovered quantitatively from the foam material with 100 cm^3 acetone in a Soxhlet extractor and determined spectrophotometrically at the optimum wavelength. Satisfactory recovery percentages (99.5%±2.1) of the tested compounds from the aqueous media by the proposed foam column method are summarized in Table 3.

The dependence of the sorption profiles of the tested species by the proposed unloaded foam column on the flow-rate (2–25 cm^3/min) and sample volume (0.1–6 cm^3) was investigated. An aqueous sample (2 dm^3) containing 0.05 mg Parathion was percolated through the foam column at various flow-rates up to 25 cm^3/min. Complete retention of Parathion was obtained at a flow-rate up to 15 cm^3/min. The extraction efficiency decreased significantly to 76% at a flow-rate of 20–25 cm^3/min from a 6 dm^3 aqueous sample solution. On the other hand, on increasing the sample volume from 2 to 6 dm^3 at a flow-rate <15 cm^3/min, no significant decrease on the retention percentage was observed.

To determine the performance of the untreated foam column by the chromatogram method a quantitative retention of Dicofol (0.01 mg) in 0.5 dm^3 aqueous solution at optimum pH of extraction was achieved followed by elution with 200 cm^3 acetone–HCl (1:1, v/v) from the unloaded foam column at a flow-rate of 5 cm^3/min. The height equivalent to a theoretical plate (HETP) was obtained from the elution curves using the equation [9]

$$N + \frac{L}{\mathrm{HETP}} = \frac{8V_{\max}^2}{w_e}, \tag{15}$$

where N = number of theoretical plates, V_{max} = volume of elute at the peak maximum, w_e = width of the peak at $1/e$ of the maximum solute concentration and L = length of the column foam bed in mm. The HETP values were found to be equal to 1.9±0.2 and 2±0.2 mm at flow-rates of 15 and 20 cm^3/min, respectively.

The unloaded foam column performance was also calculated from the breakthrough capacity curve method for Parathion (Fig. 8). An aqueous solution (5 dm^3) of Parathion (50 $\mu g/cm^3$) was percolated through the column at 10 and 20 cm^3/min and the height equivalent to the theoretical plates was calculated by employing the equation:

$$N = \frac{V_1 V_2}{(V_1 - V_2)^2} = \frac{L}{\mathrm{HETP}}, \tag{16}$$

where V_1 = volume of the effluent at the centre of the

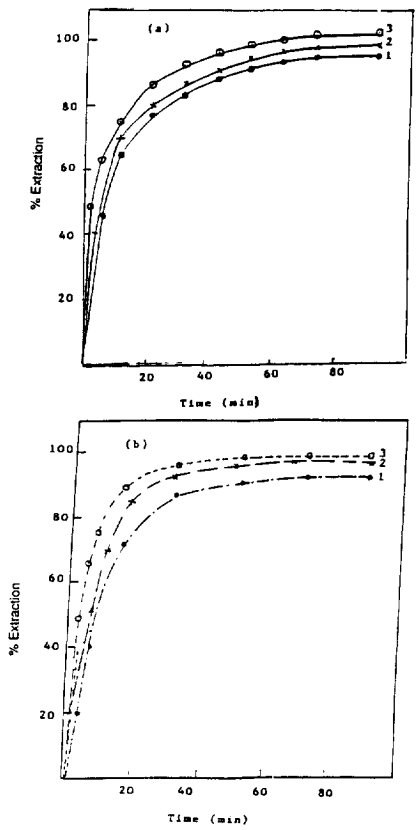


Fig. 7. Effect of extraction media on the sorption profile of (a) Dicofol and (b) Bromopropylate using unloaded foams at pH<3 and 1 h extraction time. Ethanol concentrations are: (1) 0%, (2) 5% and (3) 10%. Other conditions are as in Fig. 2.

Table 3
Extraction and recovery of the tested compounds from 3 dm^3 distilled and tap water by the proposed unloaded foam column[a]

Compound	Recovery (%)		Wavelength (nm)
	Distilled water	Tap water	
Parathion	95.6±0.4	95.9±0.4	274
Malathion	93.5±0.5	99.5±2.1	206
Cypermethrin	94.2±0.4	95.7±0.7	273
Chlorpyrifos	96.5±0.6	97.2±0.4	206
Dicofol	97±1.2	94.9±2.1	248
Bromopropylate	97.2±2.2	95.1±1.7	242

[a] Average±S.D. for five measurements.

S-shaped part of the breakthrough capacity curve where the concentration is one-half of the initial concentration and V_2 is the volume at which the effluent has a concentration of 0.1578 of the initial concentration. The volume of HETP obtained by this method was found to be in the range 2.1±0.2 mm at flow-rates of 10 and 20 cm^3/min. These values are in good agreement with the data obtained from the chromatogram methods at a flow-rate of 10 cm^3/min.

The proposed foam column method has been successfully employed for the separation of the binary mixtures Malathion–Cypermethrin and Parathion–Cypermethrin insecticides from different volumes (0.1–2 dm^3) of the aqueous media. A mixture containing 0.05 mg Malathion (or Parathion) was separated from 0.05 mg of Cypermethrin at pH 1.5 and 0.1 *M* lithium chloride. Sorption of Malathion (or Parathion) took place while Cypermethrin was not retained on the foam column and collected quantitatively in the eluent. Malathion (or Parathion) was then recovered from the column by 100 cm^3 acetone in a Soxhlet extractor, as described before.

3.4. Capacity

Break-through capacity was defined as the amount of the compound that could be retained on the column when the solution of the tested compound was allowed to pass through it at a reasonable flow-rate (5–10 cm^3/min) until the compound was first detected in the effluent solution. Practically, this capacity was determined from the actual volume that was collected just before the appearance of the compound in the effluent solution minus the free-column volume. The resulting value was multiplied by the concentration of the marginal solution. After reaching the break-through volume, percolation of the test solution was continued until the effluent solution concentration reached that of the feed aliquot. The curves of Fig. 8 present the break-through volume and the volume needed to reach feed saturation for Parathion (50 μg/cm^3) at the optimum pH at flow-rates of 10 and 20 cm^3/min. The break-through and the overall capacities of the proposed column packed with 1 g dry foam for the retention of Parathion were 0.4 and 0.35 mg insecticide per g of

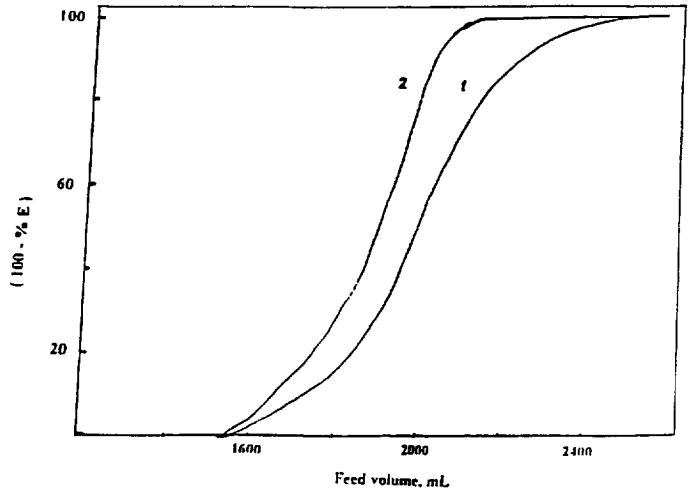


Fig. 8. Breakthrough capacity curves of the sorption profiles for Parathion at flow-rates of (1) 10 cm^3/min and (2) 20 cm^3/min using the unloaded foam column.

the unloaded foam at 10 and 20 cm^3/min, respectively.

3.5. Effect of Chlorpyrifos treatment on tomato and parsley plants

Total trace-element analysis of tomato and parsley plants was performed before (1) and after spraying with Chlorpyrifos in water for 24 (2), 72 (3) and 120 (4) h. The results are summarized in Tables 4 and 5 for tomato and parsley, respectively. The overall average concentration pattern of the essential elements N, K, P, Na, Fe, Zn, Mn and Copper in tomato is summarized in Table 4.

Table 4
Total trace element of tomato before and after spraying with Chlorpyrifos in water (0.04%, w/v)[a]

S. No.	Type	Content (%)				Concentration (ppm)			
		N	K	P	Na	Fe	Zn	Mn	Cu
1	Tomato before spray	3.45±0.52	0.80±0.08	0.43±0.10	0.31±0.04	100.±3.40	12.0±2.40	55.5±2.80	41.0±3.10
2	Tomato after spray 24 h	3.16±0.60	0.86±0.12	0.46±0.26	0.36±0.05	110.±2.80	11.5±1.80	61.0±2.90	26.0±2.20
3	Tomato after spray 72 h	3.22±0.32	0.87±0.22	0.45±0.14	0.29±0.09	080.±4.00	12.0±1.20	45.0±2.10	30.0±2.80
4	Tomato after spray 120 h	3.36±0.40	0.75±0.11	0.46±0.10	0.32±0.07	055.±3.20	12.0±1.30	40.0±2.60	16.0±1.20

[a] Average of three measurements.

Table 5
Total trace element of plant parsley before and after spraying with Chlorpyrifos in water (0.04%, w/v)[a]

S. No.	Type	Content (%)				Concentration (ppm)			
		N	K	P	Na	Fe	Zn	Mn	Cu
1	Parsley before spray	3.10±0.29	1.90±0.07	0.39±0.20	1.50±0.10	72.5±3.20	30.5±2.90	31.0±2.40	07.0±1.20
2	Parsley after spray 24 h	3.67±0.29	1.97±0.07	0.43±0.34	1.48±0.07	70.0±2.80	32.5±1.60	33.5±1.90	07.0±1.10
3	Parsley after spray 72 h	3.81±0.30	2.60±0.08	0.43±0.50	0.92±0.08	60.0±2.10	34.0±3.00	35.0±1.80	08.0±1.10
4	Parsley after spray 120 h	3.75±0.24	2.52±0.10	0.50±0.60	1.05±0.06	65.0±1.80	34.0±2.20	35.0±2.10	08.0±0.90

[a] Average of three measurements.

Table 6
Wet mass, dry mass and humidity of tomato before and after spraying with Chlorpyrifos in water (0.04%)[a]

S. No.	Sample	Wet mass (g)	Dry mass (g)	Humidity (%)
1	Tomato before spray	11.78±0.70	02.13±0.11	81.90±6.22
2	Tomato after 24 h spray	14.81±0.90	02.08±0.07	86.10±4.90
3	Tomato after 72 h spray	17.78±0.40	07.53±0.60	81.00±5.20
4	Tomato after 120 h spray	17.57±0.42	03.43±0.10	78.40±3.20

[a] Average of five measurements.

For iron (55–110±4 ppm), manganese (40–61±2.9 ppm) and copper (16–41±3.1 ppm), the concentration pattern follows the sequences 2>1>3>4, 2>1>3>4 and 1>3>2>4, respectively. The observed decrease of these elements is possibly attributed to the great ability of Chlorpyrifos and its modes of action [21] to penetrate through tomato plant tissues and complexing with these metal ions. Accumulation of Chlorpyrifos complex species may also decrease the uptake of these metal ions. No significant changes in the uptake of zinc (12±0.4 ppm) and nitrogen (3.2–3.4±0.6%) were observed.

In plant parsley (Table 5) the distribution of phosphorous (0.39–0.50±0.2%) and copper (7–9±1.2 ppm) before and after spray follows the sequence 4>3>2>1, while for nitrogen (3.1–3.8±0.3%) and potassium (1.9–2.6±0.1%) the uptake follows the order 3>4>2>1.

In the case of sodium (0.9–1.5±0.1%) and iron (60–72.5±3.9 ppm) the distribution follows the sequence 1>2>4>3, while for zinc (30.5–34±3 ppm) and manganese (31–35±2.4 ppm), the uptake follows the sequences 4>3>2>1 and 3>4>2>1, respectively. The uptake of phosphorous and copper increased with increasing spray time of Chlorpyrifos, while the uptake of sodium and iron decreased. These results may be attributed to the influence of Chlorpyrifos on the plant tissues.

Tables 6 and 7 show the effect of Chlorpyrifos on the percentages of humidity, wet mass and dry mass for tomato and parsley plants. In tomato (Table 6) the percentages of humidity (78.4–86.1%), dry mass (2.1–7.5%) and wet mass (11.8–17.8%) distribution patterns follow the sequences 2>1>3>4, 3>4>1>2 and 3>4>2>1.

In parsley plant (Table 7), a more or less similar observation on the humidity (78.4–81%), dry mass (2.3–3.8%) and wet mass (12.3–17.6%) was observed. The distribution patterns follow the sequences 2>3>1>4, 4>2>1>3 and 4>2>3>1.

These results suggest a similar mode of action of Chlorpyrifos on the humidity percentages of plant tomato and parsley. A more or less similar mode of action of Chlorpyrifos on the dry and wet mass was found for tomato and parsley tissues untreated and treated with Chlorpyrifos for different periods of time (0–120 h).

4. Conclusion

Loaded and unloaded foams in batch and column modes can be applied to trap trace amounts of insecticides, pyrethroids and acaricides from water. The retained species can be separated with an appropriate eluent, provided that there is a suffi-

Table 7
Wet mass, dry mass and humidity of parsley before and after spraying with Chlorpyrifos in water (0.04%)[a]

S. No.	Sample	Wet mass (g)	Dry mass (g)	Humidity (%)
1	Parsley before spray	12.29±0.20	2.55±0.40	79.00±5.20
2	Parsley after 24 h spray	15.61±0.30	2.97±0.40	81.00±2.90
3	Parsley after 72 h spray	14.32±0.62	2.34±0.12	79.00±3.40
4	Parsley after 120 h spray	17.57±0.75	3.80±0.25	78.00±4.20

[a] Average of five measurements.

ciently large difference in the optimum condition of extraction of each compound. The study of the tested compounds shows that Parathion, Malathion and acaricides are extracted in their neutral form by a simple solvent extraction mechanism. This conclusion is supported by the short time required for the extraction equilibrium and the salting-out phenomenon. The molecular mass of the sorbate and the strong hydrogen bonding between the tested acaricides with the polyether foam have also a great influence on the extraction process. Moreover, the plasticization of the foam with TOA offers a wider range of modifications than normal granular solids. The good hydrodynamic properties of the foam sorbents give unique advantages in rapidity, versatility and preconcentration of the tested compounds. The foam provides advantages because it is low cost, easily separable and non-polluting. The foam membrane offers unique advantages because of its high flow-rates, effective separations and preconcentrations of different species from fluid systems when large sample volumes are analyzed.

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