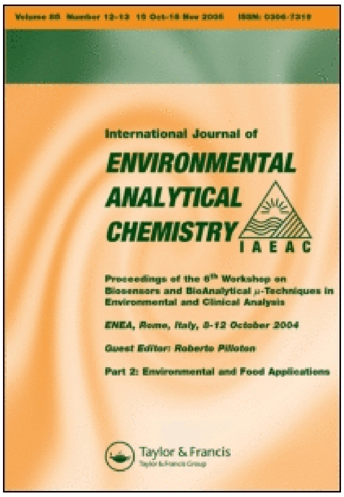
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Pyrethroid soil extraction, properties of mixed solvents and time profiles using GC/MS-NICI analysis

Mohammed A. Ali[a]; Peter J. Baugh
[a] Environmental Analysis Ltd. (EAL), Hastings, East Sussex TH34 4NR, UK

Online publication date: 12 May 2010

To cite this Article Ali, Mohammed A. and Baugh, Peter J.(2003) 'Pyrethroid soil extraction, properties of mixed solvents and time profiles using GC/MS-NICI analysis', International Journal of Environmental Analytical Chemistry, 83: 11, 909 — 922
To link to this Article: DOI: 10.1080/03067310310001608768
URL: http://dx.doi.org/10.1080/03067310310001608768

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., Vol. 83, No. 11, pp. 909–922

Downloaded At: 15:41 17 January 2011

PYRETHROID SOIL EXTRACTION, PROPERTIES OF MIXED SOLVENTS AND TIME PROFILES USING GC/MS-NICI ANALYSIS

MOHAMMED A. ALI[a] and PETER J. BAUGH[b,*]

[a]*Environmental Analysis Ltd. (EAL), 15, Burgess Road,*
Ivyhouse Lane Industrial Estate, Hastings, East Sussex TH34 4NR, UK;
[b]*121, Moss Lane, Timperley, Altrincham, Cheshire WA15 6JG, UK*

(Received 10 July 2001; In final form 17 July 2003)

Ultrasonic extraction was used to develop a suitable binary solvent system for the analysis of synthetic pyrethroid pesticides and mirex on soil. The analysis was carried out by gas chromatography with negative ion chemical ionization mass spectrometry (GC/MS-NICI). In the initial experiments, accurately weighed soil samples were spiked with a mixture of standard solution pyrethroids and mirex and shaken for 24 h to ensure homogeneity, then extracted with solvent. The extracts were evaporated to dryness before the volumetric internal standard was added.

The binary solvents used in this study were various mixtures of hexane : acetone, hexane : dichloromethane (DCM), isooctane : acetone and isooctane : dichloromethane, representing different classes of polarity. The recoveries of all pyrethroids and mirex were satisfactory over three solvent systems: hexane : acetone, hexane : DCM and isooctane : acetone, but results of isooctane : DCM produced low recoveries. The average recovery increased with the extraction time, but the increase was not statistically significant. A 30-min optimum extraction was deemed sufficient for recovering pyrethroids from soil. After 30 min, extraction decreased owing to the re-distribution of the analyte on the soil matrix.

Keywords: GC/MS-NICI; Pyrethroids; Soil; Mixed solvents; Polarity; Extraction

INTRODUCTION

Pyrethroids

The pyrethroid insecticides are a commercially important class of naturally occurring and synthetic compounds, which in 1992 accounted for approximately 20% of the global insecticide market [1]. Their popularity has increased substantially in recent years, and new members are constantly being developed and commercialized. The term pyrethroid is generally applied to the so-called photosynthetic derivatives of natural pyrethrins. Research by Elliott [2] and co-workers, involving the correlation of stereochemical structure with insecticidal activity, led to the discovery of permethrin,

---

*Corresponding author. Fax: +44 (0)161 912 2644. E-mail: PeterBaugh@compuserve.com

ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/03067310310001608768

Downloaded At: 15:41 17 January 2011

cypermethrin and many other important pyrethroids which are insecticidal analogues of cyclopropanecarboxylic acid esters. Further efforts by various research groups worldwide, involving a sequence of isosteric replacements of groups originally present in pyrethrins, have yielded a number of pyrethroids of commercial interest [3,4]. These pyrethroids lack the cyclopropanecarboxylic acid ester bond and are mainly achiral, but they retain the 3-phenoxybenzyl functionality, which is important for activity.

The structurally diverse pyrethroids are applied to crops, forests, soil and animal feeds and are also in household use. The resulting loss of these compounds to the environment, whether as the intact molecules themselves or as their degradation products and/or metabolites, requires the detection of these compounds at the microgram and sub-microgram levels. Pyrethrin and pyrethroid pesticides are non-polar in nature and non-systemic in plants, so that the extractions of these pesticides are rather simple compared to the organophosphate and carbamate pesticides. The extractive solvent and the method used depend on the nature of the sample.

Soil samples are extracted once, or several times, with a single solvent such as hexane, acetone or benzene, or with a binary solvent mixture. Acetone is an appropriate solvent for extracting pyrethroids, together with a wide variety of other lipophilic compounds that co-extract during the process. Because of its permanent dipole, acetone can cause dipole–induced dipole interaction with the numerous π-electrons in pyrethroids. Hexane is non-polar, as are the pyrethroids, and it is not possible for hexane to form dipole interactions with pyrethroids.

The phase distribution of pesticides in a soil is determined by the nature of the adsorptive soil colloids, the physicochemical characteristics of the pesticide and a host of physical, chemical and biological factors, which are determined by the particular soil environment. The electronic structure and the water solubility are important properties of the pesticide. Pesticide adsorption in soils is not a simple, single process [5]; however, in some soils one particular process may predominate. The term “sorption” is often used for the natural process, rather than “adsorption”, because the exact manner in which partitioning to solids occurs is fequently not known [6]. Forces responsible for adsorption reactions are: Van der Waals forces, hydrogen bonding, hydrophobic bonding, ion exchange, charge transfer, ligand exchange and chemisorption. Most of the pesticides currently used are non-ionic and they will tend to be held by organic matter as a result of cation dipole and coordination bonds, hydrogen bonds and Van der Waals forces [7].

Properties of Mixed Solvents (Polarity Index) [8,9]

Polarity index, P', is a measure of the ability of the solvent to interact with various polar test solutes and is based on experimental GC distribution coefficients for three test solutes on a large number of stationary phases. Each solvent is assigned three classification parameters; proton acceptor (x_e), proton donor (x_d) and strong dipole (x_n). This classification separates solvents into eight groups based on similarity of the x-parameters.

In seeking the best solvent for a given application, it is useful to separate the effects of P' and selectivity on the operation in question (e.g. dissolution of a solid or extraction from a matrix or solid mixture). This can be done by first determining the effect of P' on the operation in question, which is conveniently accomplished by studying the performance of a series of blends of a particular polar and non-polar solvent pair.

Having established the optimum value of P' for a solvent mixture for the operation in question, P'_{m} the effect of solvent selectivity can be explored by using solvents of similar P' but different selectivities. Solvents from the same selectivity group would be unlikely to give significantly improved performance. Solvent selectivity refers to the ability of a given solvent to selectively dissolve one compound as opposed to another, where the polarities of the two compounds are not obviously different.

A single solvent offers limited room for manipulating the system since it alone must meet all process and operational requirements. In other words, it must satisfy all aspects that will lead to an overall viable system. These aspects include selectivity, capacity, solubility, mass transfer, phase separation and costs, among others. Solvent systems composed of at least two components offer more possibility in selection than does a single component. Thus in a two-component system it is possible to modify or change the extractant for optimization [10]. P'_{m} for a solvent mixture (binary) A and B will be given as:

$$P'_{\mathrm{m}} = \phi_{\mathrm{a}} P'_{\mathrm{a}} + \phi_{\mathrm{b}} P'_{\mathrm{b}}$$

where ϕ_{a} and ϕ_{b}, are volume fractions of solvents A and B in the solvent mixture, and P'_{a} and P'_{b}, are the P' values of the pure solvents A and B. If solvent A is non-polar (P' small) and B is polar (P' moderately large), dilution of B by A should not affect the selectivity of B significantly.

Downloaded At: 15:41 17 January 2011

EXPERIMENTAL

Chemicals and Solvents

HPLC-grade hexane, dichloromethane, acetone, isooctane and anhydrous sodium sulphate were obtained from Fisons, Loughborough, UK. All pyrethroid samples used in this study were purchased from Promochem, UK. Mirex and decachlorobiphenyl (DCBP) were obtained from British Greyhound, UK. Common names of each pyrethroid have been used throughout this paper and are as follows:

- Permethrin, 3-phenoxybenzyl-(1*R*,*S*,3*R*,*S*; 1*R*,*S*,3*S*,*R*)-*cis-trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (99.7%).
- Cyfluthrin, (*R*,*S*)-α-cyano-(4-fluoro-3-phenoxybenzyl)-(1*R*,*S*,3*R*,*S*; 1*R*,*S*,3*S*,*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (98%).
- Cypermethrin, (*R*,*S*)-α-cyano-3-phenoxybenzyl-(1*R*,*S*,3*R*,*S*; 1*R*,*S*,3*S*,*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (98.4%).
- Fenvalerate, (*R*,*S*)-α-cyano-3-phenoxybenzyl-(*R*,*S*)-2-(4-chlorophenyl)-3-methylbutyrate (98.2%).
- Deltamethrin, (*S*)-α-cyano-3-phenoxybenzyl-(1*R*,3*R*)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate (99%).
- Mirex, dodecachloropentacyclodecane (99.9%).
- DCBP, decachlorobiphenyl (99%).

The pyrethroids except for fenvalerate have the phenoxybenzyl-dimethylcyclopropanecarboxylate structure with dihalogenoethenyl end groups, Cl or Br (deltamethrin) substituted. The α-cyano group replaces a proton in the methylene constituent of the

Downloaded At: 15:41 17 January 2011

benzyl group in both cyfluthrin and cypermethrin and the former also has fluorine present in the benzyl moiety at the 4 position. Fenvalerate is the exception, having the same cyano-phenoxybenzyl moiety as cypermethrin but linked to 2-(4-chlorophenyl)-3-methyl butyrate. Cyfluthrin comprises four enantiomeric pairs which are only partially resolved by GC and complicate the selected ion chromatographic peak area determination.

Preparation of Pesticide Standard Solutions

All the stock solutions and calibration standards were stored at 4°C while working. Calibration standards and spiking solutions were prepared fresh when required. A stock solution was prepared from each certified pesticide at 1000 mg L^{-1} concentration by accurately weighing 0.100 mg directly into 100-mL volumetric flasks on an Oertling balance and making up with hexane or acetone. From the stock solutions, working calibration standards were prepared with mixtures of the pyrethroids and mirex at varying concentrations: for medium range, 0.25, 0.5, 0.75, 1, 2 and 3 $\mu g\,mL^{-1}$ in hexane with volumetric standard (DCBP) concentration held constant at 50 $\mu g\,L^{-1}$; for low range, 10–200 $\mu g\,L^{-1}$. Spiking solutions consisted of a mixture of the pyrethroids and mirex in acetone each at 1 $mg\,L^{-1}$; a 50 $\mu g\,L^{-1}$ solution of DCBP was prepared in hexane for use at the end of the analytical work-up to act as the volumetric standard for the pyrethroids. A 0.5 $\mu g\,mL^{-1}$ standard solution of a mixture of pyrethroids and mirex was run after every 10 samples as a continuing calibration check.

Soil Properties

The properties of soil used in this study were:

- Texture: loam, coarse 68%; silt 24%; clay 8%
- Organic content: 2.1%
- Moisture content: 12.5%
- pH: 6.5

To determine moisture content, soils were dried at 105°C until a constant weight was achieved. They were then heated to 500°C for 6 h to oxidize volatile organic matter content. Particle size distributions (texture) were determined by dry sieving.

Ultrasonic Extraction [11–14]

Ultrasonic extraction was used to develop a suitable binary solvent system for the analysis of synthetic pyrethroids and mirex on soil. All ultrasonic extractions were performed using an ultrasonic bath (Sonicor Instrument Corporation, Copaique, NY). In the initial experiments, 5 g of soil was accurately weighed and transferred into specially designed conical flask (custom-made in glass blowing shop – B29 socketed neck, cylindrical width/length, 5 × 8 cm with a rounded base), then spiked with 1 mL of mixture of standard solutions containing the pyrethroids and mirex (prepared in acetone, 1 $\mu g\,mL^{-1}$ spike solution–0.2 $\mu g\,g^{-1}$ in 5 g of spiked soil), and placed on a shaker for 24 h to ensure homogeneity. Then the extraction solvent was added. The flask was then submerged in an ultrasonic bath for a period of time, the supernatant was decanted through a glass sinter (porosity 4) capped with anhydrous sodium sulphate (*ca.* 5 g). The extraction procedure was repeated twice and the extracts combined. The extract was evaporated to about 5 mL by rotary evaporation under reduced pressure at 40°C, then transferred into a 15-mL conical vial with a 1-mL mark, and evaporated just to dryness with a gentle stream of clean dry nitrogen. 1 mL of volumetric standard DCBP ($1\,\mu g\,mL^{-1}$ in original soil) in hexane was added to re-dissolve the residue. The final sample extract was transferred to an autosampler vial with a PTFE-lined crimp cap and could be stored at 4°C for at least two weeks.

Excess loss of solutes, such as the pyrethroids (which are largely non-volatile chromatographically on the scale of EPA semi-volatile solutes), in the fairly mild evaporation stage is extremely unlikely and cannot account for the differences in recovery determined for the different solvent systems. For example, permethrin and cyfluthrin, in particular, exhibit extremely low efficiencies of extraction from water or a soil–water mixture when subjected to the more rigorous steam-distillation extraction (SDE) for which the solute $\text{v.p.}_{\text{lower limit}}$ (for extraction) ≥ 100 Pa [15]. The $\text{v.p.}_{\text{pyrethroids}}$ range between *ca.* 10 and 10^3 nPa for cyfluthrin and cypermethrin to 4.5×10^4 nPa [16] for permethrin, factors of *ca.* 10^8 to 10^6 lower than the limit for SDE. It is considered that the extreme involatility of these solutes over-rides any effect that differences in v.p. of the solvents may have on the recovery efficiency of these solutes (differences here may be assumed to arise from a variation in the loss of solutes during the solvent evaporation stage). More important to the observation of any variation in extraction efficiency is the re-adsorption onto soils which is manifested at prolonged ultrasonic extraction times.

Downloaded At: 15:41 17 January 2011

Solvent System Composition

A range of binary solvent system compositions (v/v) between 85 and 15% was tested to observe the effect of the solvent ratio on pyrethroid recovery.

hexane : *acetone*	[**85** : *15*; **65** : *35*; **35** : *65*; **15** : *85*]
hexane : *DCM*	[**85** : *15*; **65** : *35*; **35** : *65*; **15** : *85*]
isooctane : *acetone*	[**85** : *15*; **65** : *35*; **35** : *65*; **15** : *85*]
isooctane : *DCM*	[**85** : *15*; **65** : *35*; **35** : *65*; **15** : *85*]

GC/MS-NICI Analysis

Analyses of the standards and extracts obtained from soil were performed on a Hewlett-Packard 5890A GC interfaced to a VG Trio 1000 quadrupole mass spectrometer (Fisons Instruments, Wythenshawe, Manchester, UK) and equipped with a Hewlett-Packard autosampler, operating in negative ion chemical ionization (NICI) mode employing full scan and selected ion monitoring or recording (SIM/SIR). A 25 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 capillary column with helium head pressure of 5 psi was used to achieve separation using the following temperature programming: initial column temperature, 100°C, hold for 1 min, increase at 35°C/min to 240°C, then increase at 8°C/min to 300°C final temperature, hold for 2 min; the total cycle time was 15 min. All spectra were acquired in the NICI mode (full scan and SIR). The general mass spectrometer conditions were: ion source 250°C; electron voltage 70 eV; photomultiplier voltage 450 V; filament and source currents 4.4 and

TABLE I Characteristic ions of compounds listed according to the retention time in the SIR mode

Compound	*Acquisition window*, min	*Characteristic ions*, ±0.02 u	*Quantitation ion*
Cyfluthrin	6–8	171; **207.07**; 209; 211	**207**
Cypermethrin	6–8	171; **207.07**; 209; 211	**207**
Deltamethrin	8–9.30	**79.04**; 81	**79**
DCBP	7.3–9	495; **497.93**; 499; 501	**498**
Fenvalerate	7.3–9	**167.15**; 169; 211	**167**
Mirex	5.3–7	365; **367.83**; 369; 371	**368**
Permethrin	6–8	171; **207.07**; 209; 211	**207**

345 μA, respectively. When operating in scanning mode, the scanned mass range was 50–550 amu in 0.9 s while in SIR mode, the mass span was 0.02 u in 0.02 s. The voltages of the filter parameters for NICI were periodically optimized using the ion at *m*/*z* 452 generated from the calibration compound, perfluorotributylamine (PFTBA). The linearity and dynamic range of the GC-MS using the SIR or full scan mode was demonstrated by generation of standard curves for each analyte containing five or six levels of concentration that were analyzed in duplicate. Standard deviations were calculated from five replicate injections of the daily calibration standard at 0.5 ng μL^{-1}, using response factors generated from the regression statistics. The limit of detection (LOD) was calculated as three times the standard deviation and this was used to calculate the minimum detection limits (MDLs) for each analyte. A stock solution was prepared from each certified pesticide at 100 mg L^{-1} concentration. From the stock solutions, working calibration standards were prepared with mixtures of the pyrethroids and mirex at varying concentrations in hexane with volumetric standard (DCBP) concentration held constant at 50 μg L^{-1}. GC-NICI-MS calibration curves were based on the peak area using 1–3 of the most intense product ions for each compound (SIR mode). Peak areas were obtained from the mass chromatograms generated for the quantitation ions of each analyte (Table I). Calibration curves were obtained from plots of response factor (pyrethroid peak area/DCBP peak area) against analyte concentration. All the calibration curves in both medium and low concentrations were linear over the entire range with correlation coefficients between 0.995 and 1.0 [11–14]. Spiking solutions consist of a mixture of the pyrethroids and mirex, in acetone at 1 μg mL^{-1}. A 50 μg L^{-1} solution of DCBP was prepared in hexane for use at the end of the analytical work-up to act as the volumetric standard for the pyrethroids.

RESULTS AND DISCUSSION

Representative NICI mass spectra and chromatograms for pyrethroids, mirex and DCBP have previously been reported [11–13]. Permethrin, fenvalerate and deltamethrin were totally resolved into two diastereoisomers while cyfluthrin and cypermethrin, which contain a third asymmetric centre, were partially resolved into envelopes of four and three diastereiosomers, respectively. *Cis* and *trans* isomers of permethrin and fenvalerate were quantified separately while the other pyrethroids were quantified using their base peak. In NICI mode using methane as the reagent gas, permethrin, cyfluthrin and cypermethrin, which are esters of dichlorovinylcyclopropane carboxylic acid (CPA), undergo dissociation by electron capture to yield CPA^- anions for which

Downloaded At: 15:41 17 January 2011

m/*z* 207 is the primary quantitation ion and *m*/*z* 209 and 211 are used for diagnostic purposes. In spite of deltamethrin having a similar pyrethroid structure, the base ion is in the low-mass region at *m*/*z* 79 (81) resulting from the favoured fragmentation yielding Br^- ions, where the ion background interference is greatest. The compound also has the characteristic ion at *m*/*z* 137 from the cyclopropane carboxylic acid unit after the loss of the two bromide ions but the intensity ratio of *m*/*z* 79 (quantitation ion) to *m*/*z* 137 (diagnostic ion) is approximately 10 : 1. Fenvalerate undergoes similar dissociation to ion fragments at *m*/*z* 167 (169), the quantitation ion, and *m*/*z* 211 (213) the diagnostic ions, which correspond to the portion of the molecule containing the isopropyl group.

Recovery Studies

The binary solvents used in this study were various mixtures of hexane : acetone, hexane : DCM, isooctane : acetone, and isooctane : DCM. These solvents represent different classes of polarity. Physical properties [polarity index, P' and boiling point, b.p. (°C)] are listed in Table II. Table III and Figs. 1(A)–(H) summarize and illustrate, respectively, the efficiencies of extraction by ultrasonic extraction of the five pyrethroids and mirex employing the four solvent systems selected. Triplicate samples were extracted, concentrated and analyzed. Increasing or decreasing the polarity of the solvent system changes the recovery values. Results for hexane : acetone (Fig. 1(A)) show

TABLE II Properties of solvents used

Solvent	*B.p.*, °C	P'
Acetone	56.3	5.4
Dichloromethane (DCM)	39.8	3.4
Hexane	68.7	0.0
Isooctane	99.2	0.0

TABLE III Percentage recoveries of six pesticides using different solvent systems at the level of 1 mg L^{-1}

Solvent system	*Composition*	P'	*Recovery*, %[a]					
			Permethrin	*Cyfluthrin*	*Cypermethrin*	*Fenvalerate*	*Deltamethrin*	*Mirex*
Hexane : Acetone	85 : 15	0.81	62.63	99.30	117.97	95.21	83.90	66.61
	65 : 35	1.89	59.25	86.37	79.69	64.32	115.42	65.33
	35 : 65	3.51	72.60	84.94	78.95	95.48	103.93	63.83
	15 : 85	4.59	73.71	81.88	81.43	74.94	106.46	64.20
Hexane : DCM	85 : 15	0.51	56.65	36.51	38.80	31.62	42.30	70.19
	65 : 35	1.19	78.10	90.22	84.44	90.10	94.00	75.71
	35 : 65	2.21	91.18	87.84	78.91	87.22	103.24	97.00
	15 : 85	2.89	92.92	93.51	88.20	93.44	79.00	79.27
Isooctane : Acetone	85 : 15	0.47	74.00	85.96	76.38	80.46	95.55	84.24
	65 : 35	1.63	72.55	88.73	105.72	83.53	90.22	92.51
	35 : 65	3.37	90.67	97.98	58.00	86.92	76.52	94.70
	15 : 85	4.53	70.46	78.63	46.85	68.16	57.64	87.62
Isooctane : DCM	85 : 15	0.17	74.62	42.84	55.43	66.33	39.63	69.57
	65 : 35	0.93	77.27	55.56	58.14	71.28	52.18	73.19
	35 : 65	2.07	74.50	61.00	74.40	92.53	56.84	72.63
	15 : 85	2.83	70.78	59.94	65.11	82.74	60.41	73.74

[a] RSD 3–9% ($n = 3$).

Downloaded At: 15:41 17 January 2011

that decreasing P'_m values gave higher recoveries of 99.3–117.9% for cyfluthrin and cypermethrin. When $P'_m > 2.0$, cyfluthrin and cypermethrin recoveries are reasonably constant with an average of 84.33 and 79.96%, respectively, but the recovery of permethrin is lower, 62% when $P'_m < 1$, falling to 59.2% as P'_m increases to 2 but increasing to 72.6 and 73.7% at higher values of P'_m. Figure 1(B) shows that extraction with hexane : acetone gives mixed results compared to Fig. 1(A): mirex shows recoveries independent of P'_m while fenvalerate shows a higher recovery at lower P'_m (66.6%), which decreased at $P'_m < 2$ then reached its highest value (95.4%) at P'_m 3.51, falling to 74.9% at P'_m 4.59.

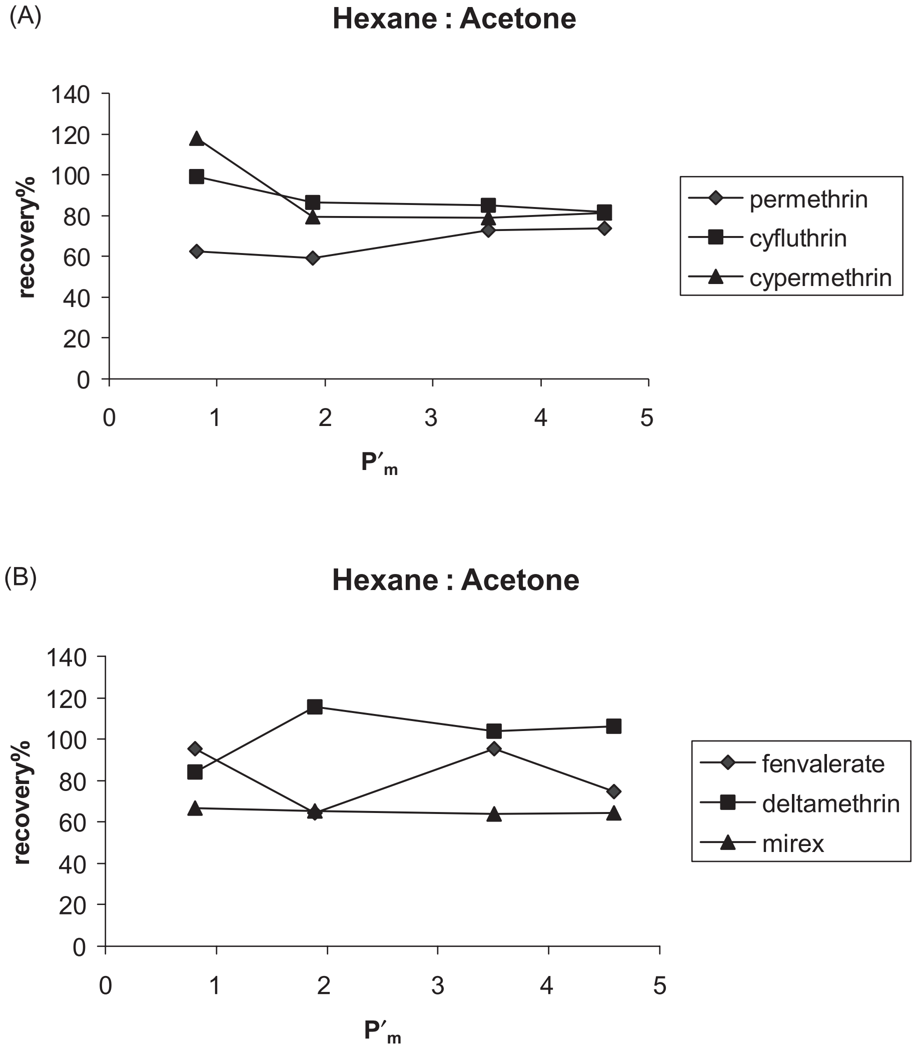


FIGURE 1 (A) Polarity index (P'_m) *vs* percentage recovery (hexane : acetone); (B) polarity index (P'_m) *vs* percentage recovery (hexane : acetone); (C) polarity index (P'_m) *vs* percentage recovery (hexane : DCM); (D) polarity index (P'_m) *vs* percentage recovery (hexane : DCM); (E) polarity index (P'_m) *vs* percentage recovery (isooctane : acetone); (F) polarity index (P'_m) *vs* percentage recovery (isooctane : acetone); (G) polarity index (P'_m) *vs* percentage recovery (isooctane : DCM); (H) polarity index (P'_m) *vs* percentage recovery (isooctane : DCM).

Downloaded At: 15:41 17 January 2011

Downloaded At: 15:41 17 January 2011

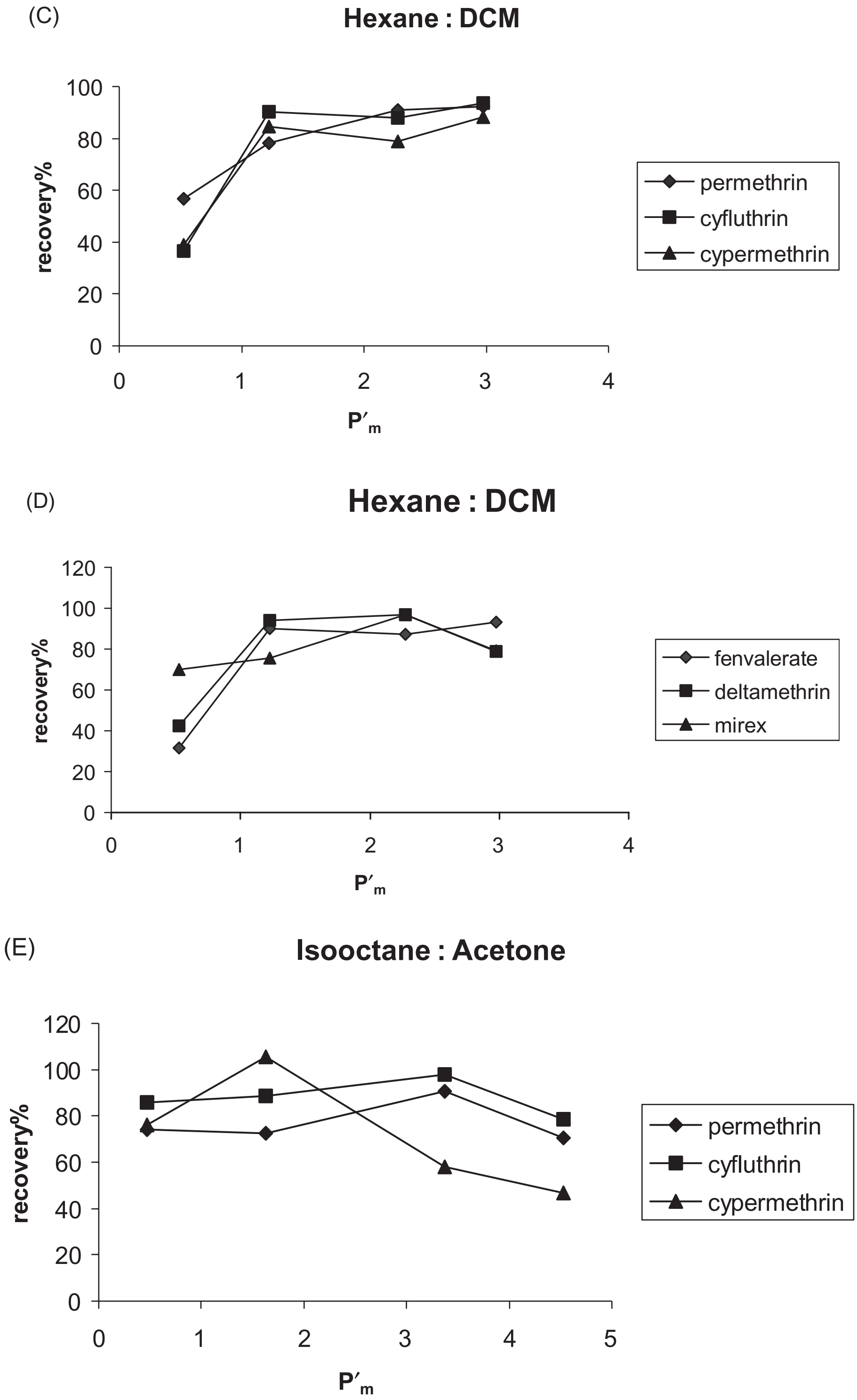


FIGURE 1 Continued.

Downloaded At: 15:41 17 January 2011

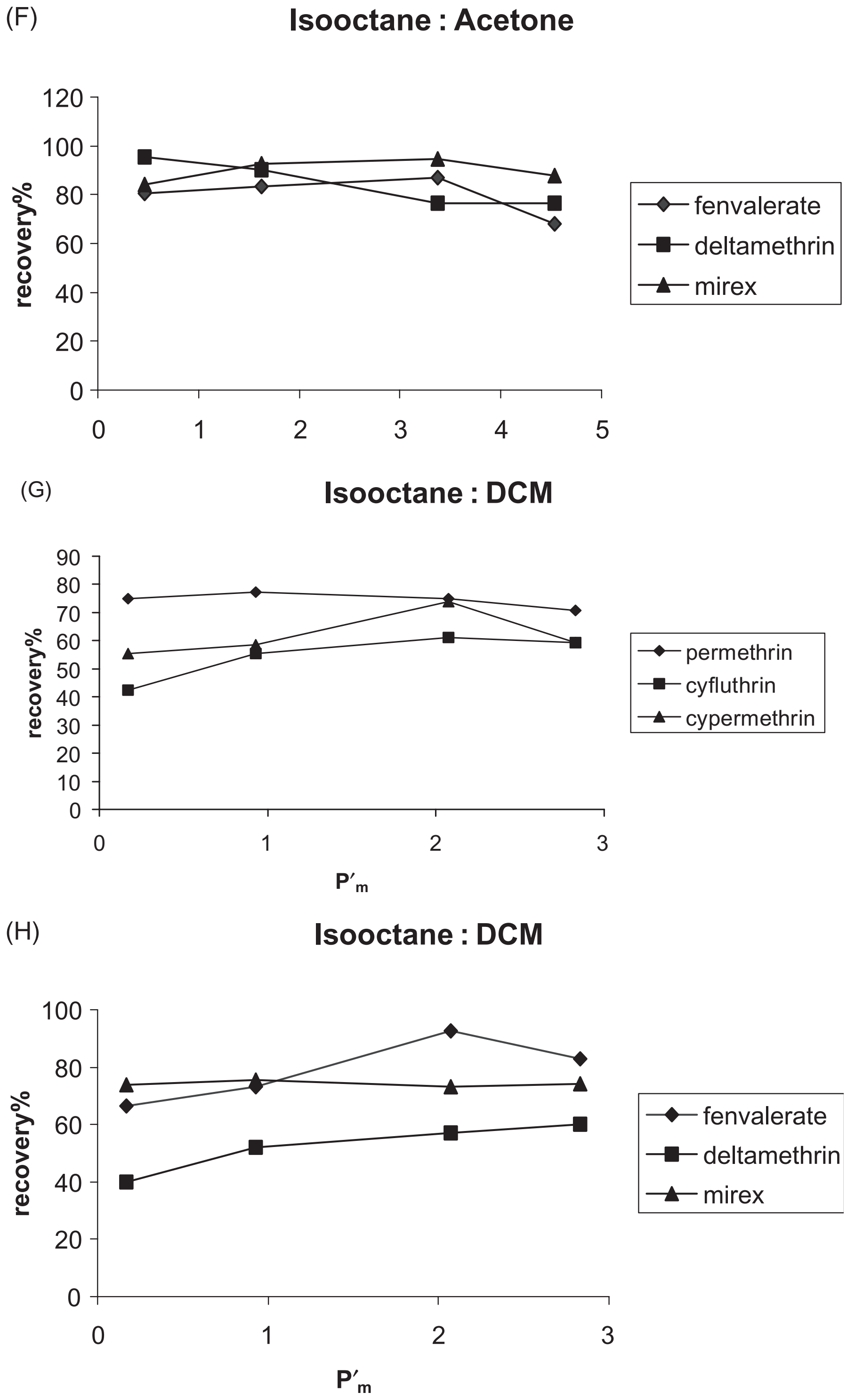


FIGURE 1 Continued.

Downloaded At: 15:41 17 January 2011

Results obtained from recovery profiles (Figs. 1(A) and (B)) of pyrethroids and mirex indicate that the chemical structure plays a major role in solvent–solute interactions. It was found that the relative importance of hydrogen bonding and dipole interactions are determined by the functional groups within molecules rather than the overall molecular structure [7]. Because pyrethroids in general have a similar chemical structure (being esters of cyclopropanecarboxylic acid), cyfluthrin, cypermethrin, permethrin and, to some extent fenvalerate all show the same polarity index–recovery curve profiles, while the mirex curve profile is different.

The results shown in Fig. 1(C) indicate that hexane : DCM mixtures are as capable as hexane : acetone of extracting pyrethroids and mirex from soil. As P'_{m} is increased, the amount of pyrethroids extracted is also increased and it appears that this system is more efficient than hexane : acetone for extracting permethrin, cyfluthrin and cypermethrin. Figure 1(C) shows that at $P'_{\mathrm{m}} > 2$ the three pyrethroids show higher mean recoveries (87.36, 90.5 and 83.8%) than in hexane : acetone mixtures (68.5, 84.3, and 79.9%). In Fig. 1(D) the same trend continues with deltamethrin (recovery 92%) and fenvalerate (recovery 83.6%) but mirex shows higher recoveries at intermediate $P'_{\mathrm{m}} > 2.27$ (97%), and a decrease to 79.2% as the P'_{m} further increased.

Extraction with the isooctane : acetone system (Figs. 1(E) and (F)) gives two similar recovery profile curves for permethrin and cyfluthrin. At $P'_{\mathrm{m}} < 2$, permethrin and cyfluthrin exhibited lower average recoveries (73.3, 88.8%) but with increasing P'_{m}, the amount extracted increased (90.6 and 97.9% at P'_{m} 3.37) but it decreased again to 70.4 and 78.6%, respectively. Cypermethrin shows a similar trend except the highest recovery was at $P'_{\mathrm{m}} = 1.63$ (105.7%). As in Fig. 1(A), the recovery of mirex is again largely independent of P'_{m}, with an average recovery of 89.8%, while deltamethrin and fenvalerate exhibited the highest recoveries at $P'_{\mathrm{m}} < 0.5$ and P'_{m} 3.37, respectively (95.5 and 86.9%).

With the isooctane : DCM system (Figs. 1(G) and (H)), the recoveries follow the same trend as in the case of isooctane : acetone; the recoveries obtained were significantly lower than those obtained from the previous systems. The only pyrethroid that exhibited recoveries above 80% was fenvalerate ($P'_{\mathrm{m}} > 2$), permethrin exhibited an average recovery of 74.7% and cypermethrin an average recovery of 63.25%. Cyfluthrin and deltamethrin average recoveries were only 54.8 and 52.22%, respectively, while mirex gave an average recovery of 72.22%.

The recoveries of the pyrethroids and mirex were satisfactory for three of the solvent systems used, namely, hexane : acetone, hexane : DCM and isooctane : acetone, but the results for isooctane : DCM indicated that this solvent system was less efficient. Hexane : DCM is the most suitable solvent system for extraction considering the difference in P' values of the two solvent components. Because of the high boiling point of isooctane (b.p. 99°C), resulting in prolonged evaporation times, solvent systems involving this component were rejected.

Time Profile

The objective of this study was to determine the optimum conditions for efficient extraction in term of percentage recovery as a function of sonication time. Table IV summarizes the recoveries and Figs. 2(A) and (B) illustrate the time profile curves for the five pesticides and mirex, represented by the extracted amount as a function of the extraction time. The time profiles drawn for permethrin, cyfluthrin

TABLE IV Percentage recoveries[a] at different extraction times

Compound	*Extraction time*, min			
	10	*20*	*30*	*45*
Permethrin	49.4	61.8	77.0	63.9
Cyfluthrin	45.2	57.0	70.1	57.0
Cypermethrin	51.7	63.1	73.8	64.6
Fenvalerate	51.6	65.8	69.3	66.9
Deltamethrin	63.2	88.5	97.1	96.5
Mirex	54.4	62.9	84.0	61.0

Solvent system hexane : DCM (50 : 50, v/v).
[a] RSD 2.4–4.5% ($n=4$).

Downloaded At: 15:41 17 January 2011

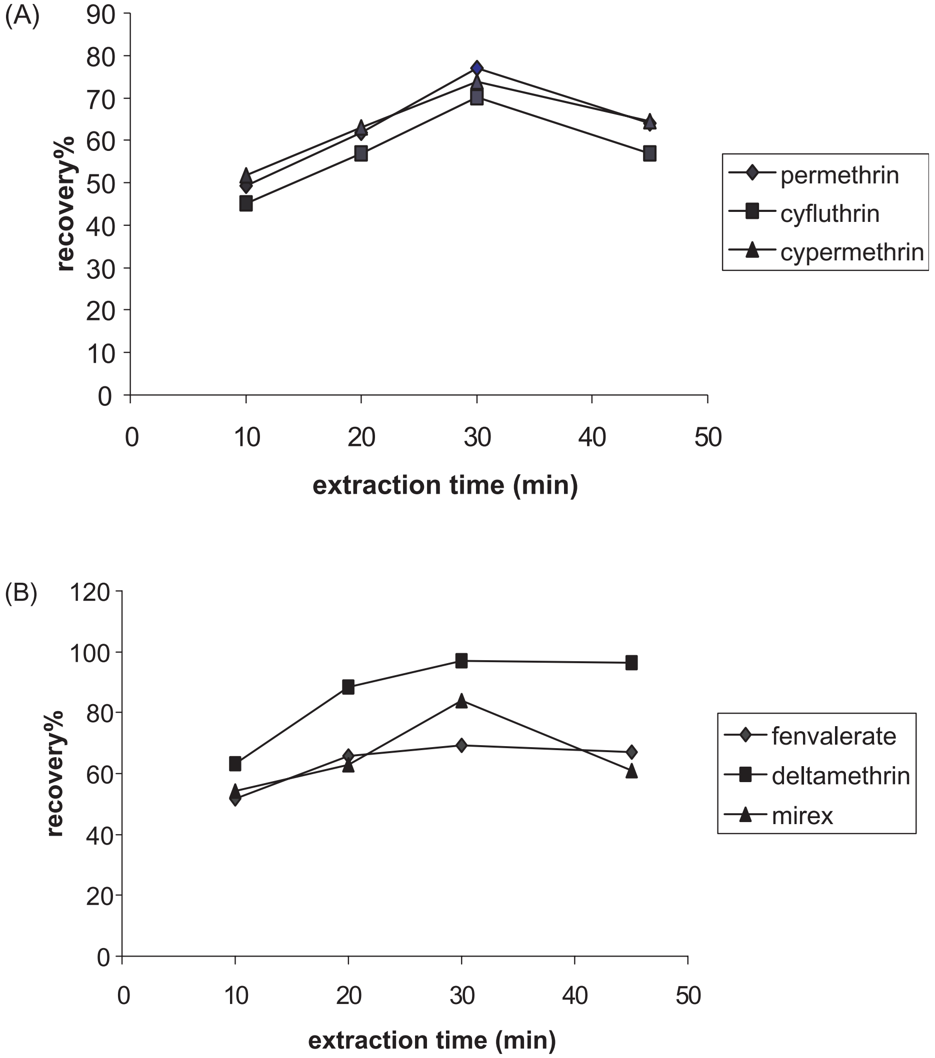


FIGURE 2 (A) Time profile curves for permethrin, cyfluthrin and cypermethrin; (B) time profile curves for fenvalerate, deltamethrin and mirex.

and cypermethrin (Fig. 2(A)) were shown to be the same. The amount extracted first increases with sonication time and then decreases after 30 min. When comparing the time profile in Fig. 2(B) an apparent plateau is observed for fenvalerate and deltamethrin after 20 min, but mirex followed the trend shown in Fig. 2(A). The experiments show a decreasing amount of extracted pyrethroids after 30 min, confirming that a redistribution process takes place continuously between the solid phase (soil) and the solvent.

CONCLUSIONS

An ultrasonic extraction technique was used to develop a suitable binary solvent for analysis of synthetic pyrethroids and mirex on soil. It was found that pyrethroids were readily extractable from soils over a wide range of compositions of the binary solvent system. The hexane : DCM binary system was considered to be the most appropriate because in addition to the high percentage recovery, DCM has a higher solubilizing capacity to pyrethroids. Normally, an intermediate mixture of the two component system will maximize the solubility.

The average recovery increased with the extraction time, but the increase was not statistically significant after 30 min, thus 30 min was deemed the optimum extraction time for recovering pyrethroids from soil. After 30 min, extraction decreased owing to a redistribution of the analyte to the soil matrix.

In recent years chlorinated solvents (DCM and chloroform) have come under close environmental scrutiny. Analysts may find themselves in the position that they can no longer use a solvent. which they may have relied on for many years in well-established methods [11–14]. It is advisable to identify suitable alternative solvents that meet the performance requirements of the method, or use an alternative technology that reduces or eliminates the use of solvents. Factors such as toxicity, flammability, volatility and cost should be considered when solvents are used.

Downloaded At: 15:41 17 January 2011

References

[1] T.R. Perrior, *Chem. Ind.*, 883–887 (1993).

[2] M. Elliott, In: N.F. Janes (Ed.), *Recent Advances in the Chemistry of Insect Control*, pp. 73–102. Special Publication No. 53, The Royal Society of Chemistry, London (1985).

[3] I.A. Fleet, J.J. Monaghan and D.B. Gordon, *Analyst*, **121**, 55–59 (1996).

[4] Yashio Katsuda, *Pesticide Sci.*, **55**, 775–782 (1999).

[5] J.C. Westall, In: W. Stumm (Ed.), *Adsorption Mechanisms in Aquatic Surface Chemistry*, pp. 3–32. Wiley Interscience, New York (1987).

[6] C.N. Sawyer, P.L. McCarty and G.F. Parkin, *Chemistry for Environmental Engineering*, 4th Edn. McGraw-Hill, New York (1994).

[7] H. Tan Kim, *Principles of Soil Chemistry*, 3rd Edn. M. Dekker, New York (1998).

[8] L.R. Snyder, *J. Chromatogr. Sci.*, **16**, 223–234 (1978).

[9] V.J. Barwick, *Trends Anal. Chem.*, **16**, 293–309 (1997).

[10] R. Blumberg, *Liquid–Liquid Extraction*. Academic Press, London (1988).

[11] M.A. Ali, *Methods and Analysis for Pyrethroids in the River Ecosystems*. MSc Dissertation, University of Salford (1993).

[12] M. Yasin, *Environmental Monitoring of Pesticides in Components of River Systems*. PhD Thesis, University of Salford (1996).

[13] P.M. Hancock, M. Yasin, P.J Baugh, G.A. Bonwick and D.H. Davies, *Intern. J. Environ. Anal. Chem.*, **67**, 81–95 (1997).

[14] M.A. Ali and P.J. Baugh, presented at the British Mass Spectrometry Society, 23rd Annual Meeting, University of Warwick (1998); *Intern. J. Environ. Anal. Chem.* (2003), this issue.

[15] Puziah Abdul-Latif, *Instrumentation and Methodology for the Monitoring of Synthetic Pyrethroids (Mothproofing Pesticides) in Water Courses*. PhD Thesis, University of Salford (1994).

[16] M.A. Kamrin, *Pesticide Profiles: Toxicity, Environmental Impact and Fate*, CRC/Lewis Publishers, Boca Raton, FL (1997); In: C.S. Tomlin (Ed.), *The Pesticide Manual*, 11th Edn. British Crop Protection Council and Royal Society of Chemistry, London, (1997) and subsequent editions in the series.

Downloaded At: 15:41 17 January 2011