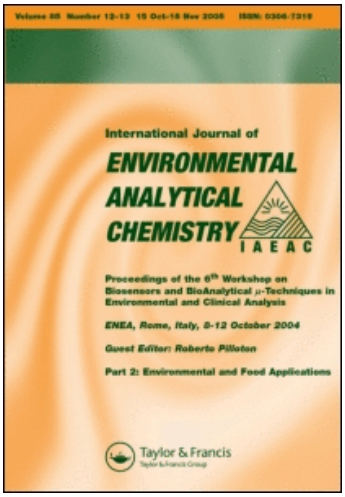

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Monitoring the Supercritical Fluid Extraction of Pyrethroid Pesticides using Capillary Electrochromatography

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MONITORING THE SUPERCRITICAL FLUID EXTRACTION OF PYRETHROID PESTICIDES USING CAPILLARY ELECTROCHROMATOGRAPHY

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Capillary electrochromatography (CEC) is reported for monitoring the extraction of the pyrethroid pesticides fenpropathrin, fenvalerate and fluvalinate by SFE using supercritical CO_2. The optimum SFE conditions obtained for the pyrethroid pesticides from spiked cellulose matrix, were for fenpropathrin 300 atm and 70°C, fenvalerate 300 atm and 60°C and for fluvalinate 200 atm and 75°C. Extracts collected in methanol were subjected to analysis by CEC on a 30 cm × 75 μm i.d. fused silica capillary packed with 5 μm Hypersil ODS (21 cm packed length). Electrochromatograms of the three pyrethroid pesticides were obtained in order of elution thiourea (as the EOF marker), fenpropathrin, fenvalerate and fluvalinate, with mobile phase ACN–25 mM NaH_2PO_4 pH 8.3 (85 : 15), voltage 25 kV, electrokinetic injection 5 kV, 3 sec and detection at 200 nm. The SFE recoveries were > 80% for all three solutes. In addition, enantioseparation of the pyrethroid pesticides was investigated using Me-β-CD and HP-β-CD as chiral additives. The enantioseparation of fenpropathrin was optimised to a methanol–25 mM Tris pH 8.3 mobile phase (75 : 25) containing 70 mM Me-β-CD.

Keywords: Capillary electrochromatography; Supercritical fluid extraction; Pyrethroid pesticides

INTRODUCTION

Synthetic pesticides are important chemicals since they are widely employed to control many forms of insects, weeds and other pests in a variety of agricultural and non-agricultural environments. The global use of pesticides originates from the commercial demands of high agricultural yields. The USA is the world's largest food producer, and producers require careful and timely application of pesticides throughout the year to protect crops. However, the continued over-use of pesticides has led environmentalists to voice concerns about pollution of the hydrological systems and foodstuffs, with water being the principal carrier of pollutants. The need for analytical techniques

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with high levels of sensitivity and selectivity to monitor contamination remains a priority.

Pyrethroid Pesticides

Natural pyrethrins, active constituents of pyrethrum flower extract, have been employed to control pest insects since the discovery of their insecticidal activity in the last century. Synthetic pyrethroids (SPs), originating in 1976 from the modification of the structures of natural pyrethrins, have led to improved physical and chemical properties, with greater biological activity and photostability [1]. Thus pyrethroids constitute another group of insecticides, in addition to organophosphorous, carbamate, organochlorine and other types. Pyrethroids are now employed worldwide as insecticides in agriculture, forestry, public health and domestic applications due to their selective insecticidal activity, rapid biotransformation and excretion by the mammalian catabolic system and most importantly their non-persistence in the environment. Their non-persistence is essentially due to photodegradation, which occurs via decarboxylation, ester bond cleavage, and hydration of the cyano group to carboxamide [2]. However, high toxicity to fish, aquatic species and honeybees is observed for most pyrethroids [3].

Pesticide Analysis by CEC

Only recently has the investigation into the potential use of CEC in the area of pesticide analysis begun in earnest [4]. CEC offers the advantages of low solvent consumption, low sample volume requirements, high separation efficiency and low operational cost relative to LC. Published work to-date in CEC has almost exclusively involved the separation of mixtures of pesticides on reversed phase columns. Fang *et al.* [5] investigated the feasibility of using CEC for the analysis of some pesticide formulation products including the herbicides pendimenthalin and Pendulum 2G (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine). They observed, that not only was CEC better than HPLC in terms of efficiency but was also practical, precise, and accurate in terms of simplicity, recovery and linearity.

Dittmann and Rozing [6] demonstrated the power of CEC in the separation of some triazine herbicides including simazine, atrazine, cyanazine and sebutylazine. In their study, the authors compared three different silica-based stationary phases, namely, CEC-Hypersil C_{18}, MOS-Hypersil (a C_8 reversed-phase sorbent) and C_6–SCX Spherisorb (a mixed mode stationary phase containing propyl sulfonic acid and C_6 chains in 50/50 coverage). The separation exhibited good peak shapes, and was achieved in less than 13 min. Interesting selectivity changes were found and the retention of the solutes was observed to be lower on the C_6–SCX and C_8 phases relative to the C_{18} phase, reflecting the hydrophobic nature of the separation.

Mayer *et al.* [7] demonstrated the separation of the pesticide cinosulfuron, from some of its by-products using an ACN–13 mM TFA, pH 3.5 (60/40 v/v) mobile phase on a 25 cm column packed with a 3 μm C_{18} stationary phase. Plate numbers were between 28 000/m and 44 000/m. Yang and El Rassi [8] recently reported the separation of nine phenylurea herbicides (including terbacil, monouron and nebouron) on an ODS-Zorbax capillary column.

Warner and co-workers [9] demonstrated the direct separation and quantification of six insecticidally active pyrethrin esters in extract samples and commercial formulations by CEC on a C_{18} Hypersil phase. The esters were derivatives of cinerin, jasmolin and pyrethrin. A ternary mobile phase of acetonitrile–aqueous buffer–terahydrofuran (55 : 35 : 10) provided the eluotropic solvent strength required to resolve the esters in less than 16 min. The authors concluded that the developed CEC method was a fast, accurate and simple way of quantifying such pyrethrin formulations.

Supercritical Fluid Extraction (SFE) of Pesticides

Solvent extraction, solvent partition and solid-phase extraction have been extensively used, and remain the dominant sample preparation techniques, for chromatographic determination of pesticides. However, solvent extraction remains a costly, laborious technique with excessive organic solvent consumption and waste generation. These disadvantages have led to the development of more effective cleaner tools for pesticide analysis.

As the range of pyrethroid applications has increased in the last 10 years, the need to separate various pyrethroids has emerged, especially for multi-residue analyses. Appreciable levels of pyrethroids have emerged, especially in food commodities from crops, to foods of animal origin (milk, egg, meat), in soils, sediments and in surface waters. In their review, Chen and Wang [10] described the methods for the analysis of pyrethroid residues in various matrices involving the classical liquid extraction approach or solid-phase extraction, with clean up by adsorption or gel permeation chromatography and determination via GC [11–13], or LC [14].

These two chromatographic approaches are the most frequently used in the determination of pyrethroid residues. However, the problem of thermal degradation of pyrethroids in GC analysis inhibits its use as an analytical tool. The degradation resulting from the thermal lability of some pyrethroids has been overcome by employing LC, although the sensitivity achieved with LC (UV detection) is somewhat lower than that provided by GC (FID).

Supercritical fluids, particularly carbon dioxide, which is highly efficient and selective for extractions from complex biological and environmental matrices [15,16], are gaining increasing popularity as replacements for standard solvent extraction techniques. Advantages of supercritical carbon dioxide include its solvating power, low viscosity, rapid mass transfer, low running cost, environmental friendliness and relatively low toxicity. SFE has been investigated as a multi-residue extraction tool for organochlorine, organophosphate, synthetic pyrethroids, and carbamate compounds in fruit and vegetables [17,18]. O'Keeffe *et al.* [19] also demonstrated the use of supercritical fluid extraction as a multi-residue extraction procedure for beta-agonists in bovine liver tissue.

For SFE method development, pressure, temperature and extraction duration are optimised, usually by a multi-factor system in which one factor at a time is varied while the other factors remain constant. Ngunyen *et al.* [20] demonstrated a stepwise approach to develop an SFE method for the analysis of synthetic pyrethroids (SP) on different matrices. By employing an alumina trap and operating the extraction at 50°C, 200 atm for 60 min, recoveries of all SPs from wool samples were satisfactory

(78–101%) over the range of 0.5–5 μg/g levels of these compounds. They also reported that higher pressure (> 200 atm) and temperature (> 50°C) values resulted in poor trapping, isomerisation and possible degradation of some pyrethroid compounds.

Koinecke *et al.* [21] investigated the SFE of fenvalerate from spiked sea sand samples. A recovery of 100% ± 5 was obtained at a temperature of 60°C and CO_2 pressure of 3.8×10^7 Pa by using 5% methanol as modifier, a diol-modified silica gel trap and ethyl acetate as eluent.

The work reported in this article focuses on the extraction and analysis of three pyrethroid pesticides. The three pyrethroid pesticides, chosen on the basis of availability, chirality and solubility in supercritical CO_2, were fenpropathrin, fenvalerate and fluvalinate, whose structures are shown in Fig. 1.

Initial method development involved studying the separation of the three pyrethroids by CEC on 5 μm ODS stationary phase by varying the pH, the percentage organic modifier and the separation voltage. The aim was to demonstrate the direct analysis by CEC of collected SFE pyrethroid extracts from a spiked cellulose matrix, and to show the further potential of CEC for chiral discrimination of these important pesticides.

EXPERIMENTAL

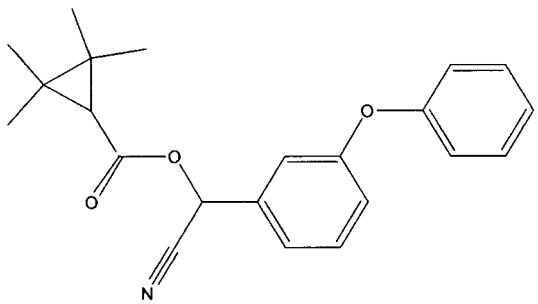
Materials

HPLC grade methanol and acetonitrile were purchased from Labscan (Dublin, Ireland). The buffers sodium dihydrogen phosphate, disodium hydrogen phosphate, Trizma hydrochloride and Trizma base were obtained from Sigma Aldrich (Poole, UK). The pH was adjusted to the desired value using either HCl or NaOH from E. Merck, Darmstadt, Germany. Thiourea, methyl-β-cyclodextrin and hydroxypropyl-β-cyclodextrin were also obtained from Sigma-Aldrich Ltd. (UK). (*R*,*S*)-Fenpropathrin (98.5%, (*RS*)-α-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropane-carboxylate) and (*R*,*S*)-fenvalerate (99.9%, (*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate) were purchased from Riedel-de Haen (Seelze, Germany). (*R*,*S*)-Fluvalinate (77.8%, (*RS*)-α-cyano-3-phenoxybenzyl *N*-(2-chloro-α,α,α-trifluro-*p*-tolyl)-D-valinate) was kindly donated by Novartis (Basle, Switzerland). Hypersil 5 μm ODS particles were purchased from Shandon (Runcon, UK). All water used was Milli Q grade with a resistivity of 18.2 mΩ. Aqueous filter membranes (0.45 μm) were purchased from Millipore Ltd. (Cork, Ireland). Carbon dioxide, supplied by BOC gases (Cork, Ireland), was used as extractant in SFE. Whatman (qualitative grade) filter paper was employed as the spiking matrix, with glass wool from BDH (Poole, UK) used as a packing material for the SFE cells.

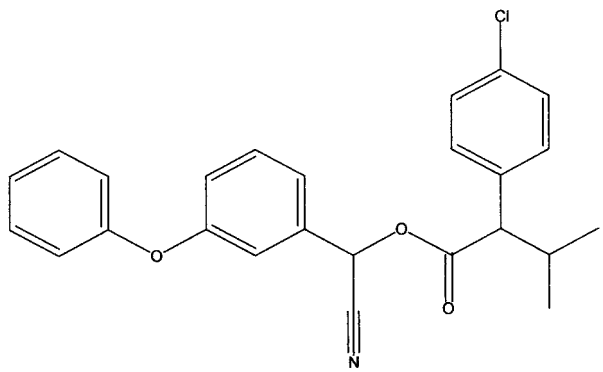
Instrumentation

All CEC separations were obtained with a Beckman P/ACE MDQ instrument (Beckman, Fullerton, CA, USA). The system comprised a 0–30 kV high-voltage power supply, a diode array detector, and the P/ACE software (version 1.6) for system control and data processing. Fused silica capillary (75 μm i.d. and 363 μm o.d.) having a length of 30 cm, 21 cm to detector was used (Composite Metals Ltd.

Fenpropathrin



Fenvalerate



Fluvalinate

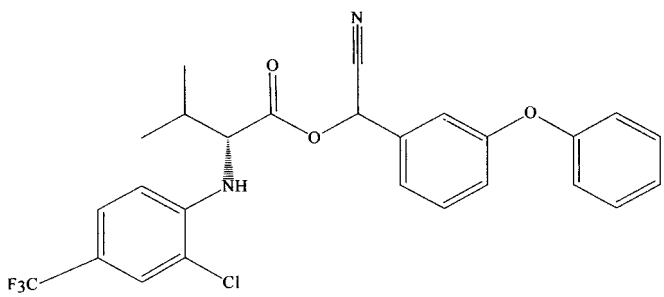


FIGURE 1 Structures of the chiral pyrethroid pesticides.

Worcester, UK). The temperature was controlled at 20°C using a fluorocarbon-based cooling system. The samples were introduced into the capillary at the anodic end (inlet) by electrokinetic injection (10 kV for 10 sec) unless stated otherwise. UV detection was carried out at 200 nm unless stated otherwise.

All supercritical fluid extractions were performed using an ISCO SFX^{TM} 2–10 Supercritical Fluid Extractor (Nebraska, USA), with an initial extraction period

followed by a dynamic extraction period. Linear temperature-controlled restrictors and 10 mL stainless steel extraction cells were used. SFE parameters such as pressure, temperature and extraction time were set and monitored through the display panel.

Experimental Procedures

Mobile Phase and Sample Preparation

A 0.025 M Tris buffer solution was prepared by dissolving 3.92 g of Tris HCl with 3.025 g of Tris base in 1 L deionised water. The pH values of 7.1, 8.0, 8.3 and 9.1 were recorded with a pH meter (Expandable ionAnalyser pH meter EA 920). All eluents were filtered using aqueous 0.45 μm Millipore filter membranes and sonicated (ULTRAsonik NEY) for 10 min to remove dissolved air prior to use.

Individual pyrethroid stock solutions with a concentration of 500 μg/mL in methanol were used to prepare working standards of each, by appropriate dilution with methanol. Stock solutions were stored in a refrigerator at 4°C and wrapped in aluminium foil to prevent degradation.

SFE Procedure

In order to determine pesticide recoveries by SFE, 100 μL of the 500 μg/mL stock pesticide was spiked onto cellulose filter paper (2 cm × 6 cm) and left to air dry for 10 min. It was then packed into a glass extraction vial, held in place with glass wool on either side and then positioned into the extraction cell for extraction. To give an indication of reproducibility, four single SF extractions of each pesticide were undertaken and collected in a 20 mL round bottom flask containing 10 mL of methanol. The sample was then evaporated to dryness and reconstituted in 1 mL of methanol. If the sample were completely extracted from the cellulose matrix it would have a final concentration of 50 ppm. Each extraction was analysed in triplicate by CEC, with the pyrethroids' peak areas from the calibration standards (15, 25, 50, 75, 100 ppm) used to calculate the percentage recoveries of the SFE extracts.

The optimisation of temperature and pressure in the SFE of these pyrethroids was performed. Samples extracted under optimal conditions were subjected to analysis by CEC using the developed methods. The optimised SFE conditions are as follows: fenvalerate was extracted at 300 atm and 60°C, fenpropathrin at 300 atm and 70°C and fluvalinate at 200 atm and 75°C.

The optimum extraction times for the individual pesticides from spiked filter paper were found to be as follows: fenvalerate: 8 min static period, followed by a 15 min dynamic extraction period; fenpropathrin: 4 min static period and 16 min dynamic period; fluvalinate: 16 min static followed by a 12 min dynamic period.

The sc-CO_2 flow rate during the dynamic period was maintained at 0.8 mL/min. Restrictor temperatures were held at 70°C to avoid plugging and enhance collection efficiency. To prevent the restrictor from partially plugging and to remove impurities, the system was cleaned between extractions, by flushing the extraction cell containing methanol soaked filter paper, with supercritical carbon dioxide for 10 min.

Preparation and Conditioning of Packed Capillary Columns

Capillary columns (75 μm i.d., 21 cm packed length, 30 cm total length) were packed with 5 μm Hypersil ODS in our laboratory, following a procedure similar to that described by Boughtflower *et al.* [22]. Upon preparation, the capillary was flushed with mobile phase (acetonitrile–25 mM Tris pH 8.2 (80 : 20)) for 1 h using an LC pump at 1000 p.s.i. (Shimadzu LC 8A) and then installed in the capillary cartridge. Both the inlet and outlet vials were pressurised to 20 p.s.i. and the voltage set to 20 kV for 40 min until the current stabilised. This procedure was employed whenever a new mobile phase was used. If bubble formation occurred, the capillary was re-connected to the LC pump and flushed with mobile phase for 15 min.

RESULTS AND DISCUSSION

CEC Analysis of Pyrethroid Pesticides

The effects of buffer pH and composition on the separation of the three pesticides are shown in Figs. 2 and 3. In Fig. 2, a reduction in pH from 9.1 to 7.1 led to no significant increase in the separation selectivity for the pyrethroid mixture, as shown by the recorded retention times (t_r) of the solutes. A pH of 8.3 was selected, yielding fast EOF and short analysis times.

From plots of $\log k'$ *versus* acetonitrile concentration, linear relationships were found with regression coefficients r^2 of 0.9978, 0.9998 and 0.9949 for fenpropathrin, fenvalerate and fluvalinate, respectively (Fig. 3). The retention times and separation factors increased with decreasing percentage of organic modifier due to changes in the partitioning of the hydrophobic analytes between the stationary and mobile phases. Enhancing the analyte interaction with the stationary phase yields higher resolution between the closely eluting peaks but at the expense of longer migration times.

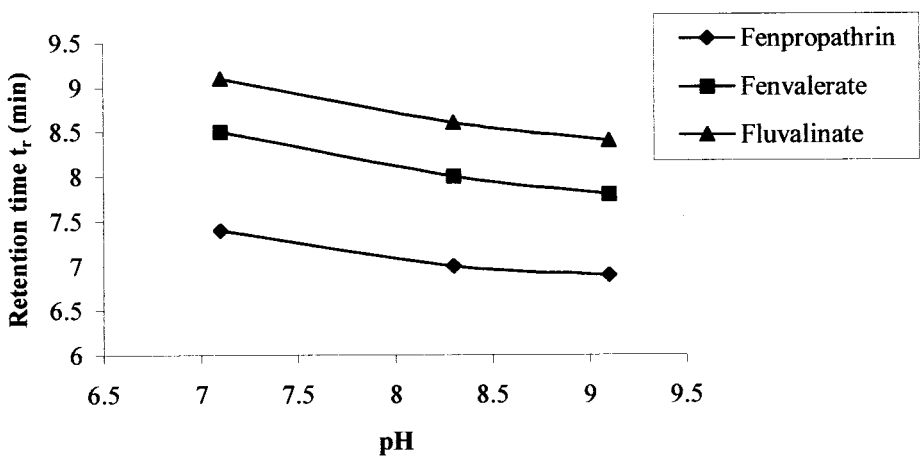


FIGURE 2 The effect of phosphate buffer pH on the retention time of pyrethroid pesticides. Conditions: 30 cm × 75 μm i.d. (21 cm packed length) 5 μm packed Hypersil ODS; mobile phase: acetonitrile–25 mM NaH_2PO_4 (85 : 15); voltage: 25 kV. Electrokinetic injection: 5 kV, 3 s. Sample: fenpropathrin, fenvalerate, fluvalinate in 100% methanol.

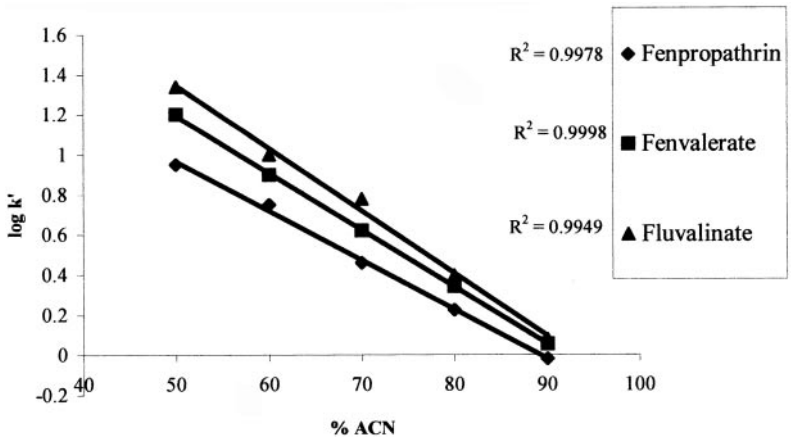


FIGURE 3 Plot of the logarithm of capacity factor, k', of pyrethroid pesticides *versus* the acetonitrile content. Conditions: 30 cm × 75 μm i.d. (21 cm packed length) 5 μm packed Hypersil ODS; mobile phase: acetonitrile–25 mM NaH_2PO_4 pH 8.3; voltage: 25 kV. Electrokinetic injection: 5 kV, 3 s. Sample: fenpropathrin, fenvalerate, fluvalinate in 100% methanol.

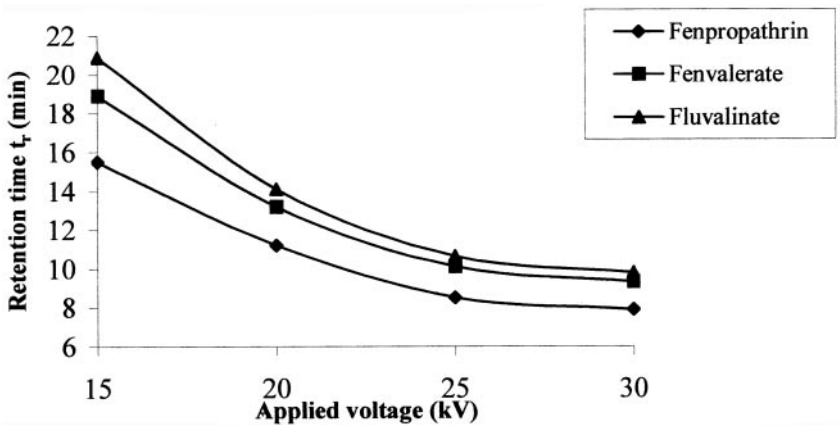


FIGURE 4 The effect of applied voltage on the retention time of pyrethroid pesticides. Conditions: 30 cm × 75 μm i.d. (21 cm packed length) 5 μm packed ODS; mobile phase: acetonitrile–25 mM NaH_2PO_4 pH 8.3 (85 : 15). Electrokinetic injection: 5 kV, 3 s. Sample: fenpropathrin, fenvalerate, fluvalinate in 100% methanol.

Thus, the volume ratio of acetonitrile to phosphate buffer was kept at 85% to achieve fast separations of the three pesticides.

The effect of applied voltage on the pesticide separation is shown in Fig. 4. As the voltage decreased from 30 to 15 kV the separation between the solutes increased. However, longer analysis times and broader peak shapes resulted; 25 kV was selected as the separation voltage. A typical separation, obtained with a mobile phase consisting of acetonitrile–25 mM NaH_2PO_4 pH 8.3 (85 : 15), for a mixture of the three insecticides, is shown in Fig. 5. Some retention time variation occurs from capillary to capillary, with these CEC capillaries prepared in-house.

As mentioned earlier, fenpropathrin, fenvalerate and fluvalinate standards were each analysed in triplicate by CEC. Calibration curves were constructed by plotting peak

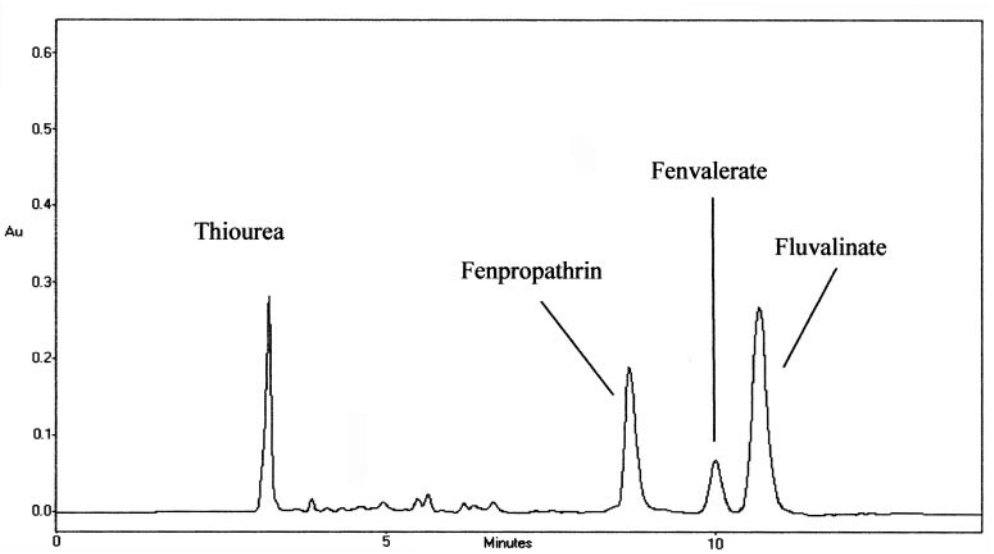


FIGURE 5 Electrochromatogram of the three pyrethroid pesticides in order of elution: fenpropathrin, fenvalerate, fluvalinate, with thiourea as the EOF marker. Conditions: 30 cm × 75 μm i.d. packed (21 cm packed length) 5 μm Hypersil ODS; mobile phase: ACN–25 mM NaH_2PO_4 pH 8.3 (85 : 15); voltage: 25 kV; electrokinetic injection: 5 kV, 3 s. Sample: thiourea, fenpropathrin, fenvalerate and fluvalinate in 100% methanol.

area as a function of analyte concentration. The response by CEC with UV detection (200 nm) was found to be linear ($r^2 > 0.9934$) for all the pyrethroid pesticides over the concentration range of 15–100 ppm.

All pesticide extractions performed on the cellulose matrix were single extractions (i.e. only one extraction event). The single extractions were repeated four times for each pesticide. An extraction yielding a final concentration of 50 ppm represents 100% recovery. The mean SFE recoveries were 84.6, 86.0 and 81.4% for fenpropathrin, fenvalerate and fluvalinate, with relative standard deviation (RSD) at less than 5% for all pesticides. Fenpropathrin, fenvalerate and fluvalinate yielded LODs of 4.7, 3.8 and 2.1 μg/mL, respectively, calculated as previously reported [23]. The LOQs were 14.3, 11.7 and 6.6 μg/mL, respectively.

Ngunyen *et al.* [20] reported the SFE extraction recoveries of pyrethroid pesticides (i.e. tetramethrin, permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin) from wool. Under optimum conditions, fenvalerate yielded an 83% recovery with all others in the range from 78 to 101%. Atienza and Jimenez [24] described a method for the supercritical CO_2 extraction of fortified fluvalinate residues in honey and subsequent analysis by LC. Recoveries from honey samples fortified at 0.5 and 10 mg/kg was 94 and 53%, respectively.

No literature concerning the SFE of fenpropathrin or the CEC of pyrethroids could be found. Hence, the supercritical fluid extraction of the three pyrethoid pesticides and their analysis in CEC is the first time these analytical techniques have been employed in tandem for the pesticide quantification. The results obtained in this research for the extraction of fenvalerate are similar to those obtained by Ngunyen *et al.* [20] at 86.0%. Fenpropathrin extraction at 84.6% is also quite satisfactory. However, the lowest percentage extraction was achieved for fluvalinate at 81.4%.

This is unexpected given the fact that the pesticide bears a trifluoro group, expected to aid the solubilisation of the pyrethroid in supercritical CO_2. The less than quantitative recovery of the pyrethroids may be due to possible thermal degradation of the pesticides under supercritical fluid conditions or losses in collection. As the above recoveries of pesticides are the result of a single extraction from cellulose paper, the incomplete extraction of pesticide could have resulted from the matrix. However, secondary and tertiary extractions on the same spiked cellulose matrix failed to confirm this.

In addition to single extraction studies, the simultaneous SFE of the three pyrethroids from the cellulose matrix, at an extraction pressure of 300 atm and a temperature of 65°C, was also demonstrated using CEC.

Enantioseparations by CEC with Cylodextrin Additives

A consideration made in selecting the pyrethroid pesticides in this research was the presence of chiral centres. This allowed the study of chiral solutes in SFE–CEC analysis. Although this research did not focus on the selective extraction of enantiomers in SFE, chiral separations were investigated by using ODS stationary phase and cyclodextrin additives in the mobile phase. All the enantioseparation studies were performed using methanol as the organic modifier.

The separation of fenpropathrin with a methanol–25 mM Tris pH 8.3 mobile phase (75 : 25) yielded a capacity factor, k', of 7.4 on Hypersil 5 µm ODS tationary phase. The enantiomeric separation of fenpropathrin was then studied by adding Me-β-CD to the mobile phase, over the range from 10 to 70 mM (Fig. 6). Optimum resolution (R_s) of

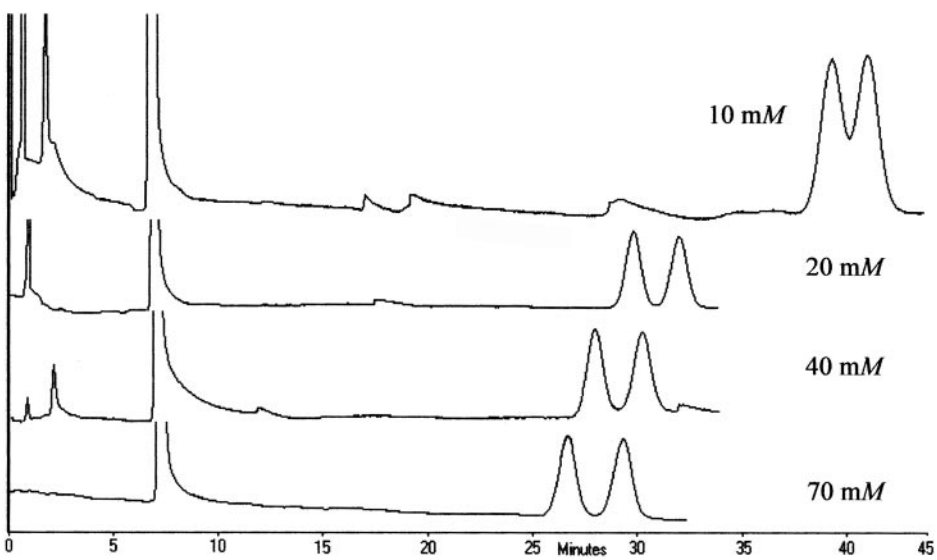


FIGURE 6 Overlay of the electrochromatograms of the separation of fenpropathrin with increasing Me-β-CD concentration. Experimental conditions: mobile phase: methanol–25 mM Tris pH 8.3 (75 : 25) (10, 20, 40, 70 mM Me-β-CD); column: 30 cm × 75 µm i.d. (21 cm packed length) 5 µm packed Hypersil ODS; voltage: 25 kV; temperature: 20°C; detection: 214 nm; electrokinetic injection: 5 kV, 3 s. Sample: thiourea and fenpropathrin in 100% methanol.

1.40 and separation (α) of 1.14 was obtained at 70 mM cyciodextrin, with an increase in CD concentration above this leading to decreased resolution.

Fenvalerate, however, only showed slight resolution ($R_s = 0.42$) at 80 mM Me-β-CD, with higher concentrations of CD leading to complete loss of discrimination.

The choice of cyclodextrin is important in obtaining adequate chiral separation. The ODS packed capillary was flushed electrokinetically (25 kV for 2 h) with MeOH–25 mM Tris pH 8.3 (75 : 25) with 20 mM of an alternative cyclodextrin, HP-β-CD. Under these conditions, fenpropathrin yielded a resolution of 0.53, compared to a resolution of 1.35 for Me-β-CD under the same conditions. No chiral discrimination was achieved for fenvalerate using HP-β-CD. Fluvalinate failed to show any resolution for Me-β-CD or hydroxy-propyl-β-CD (HP-β-CD), under these conditions.

Future Work

The use of SFE and CEC couples the strengths of both these techniques i.e. low running cost, low solvent consumption and increased efficiency in the extraction and analysis of the selected pesticides. Future research is expected to focus on the enantioseparation of chiral pesticides using open tubular CEC and indeed on the use of chip-based CE and CEC devices.

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