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Determination of six pyrethroid insecticides in fruit juice samples using dispersive liquid–liquid microextraction combined with high performance liquid chromatography

Suthasinee Boonchiangma, Wittaya Ngeontae, Supalax Srijaranai*

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

Dispersive liquid–liquid microextraction (DLLME) coupled to high performance liquid chromatography (HPLC) with UV detection was applied for the determination of six pyrethroids (tetramethrin, fenpropathrin, cypermethrin, deltamethrin, fenvalerate and permethrin) in various fruit juices including apple, red grape, orange, kiwi, passion fruit, pomegranate and guava juice. Six pyrethroids were separated within 30 min using a Waters Atlantis T3 column under an isocratic elution of acetonitrile–water (72:28). The parameters affecting extraction efficiency of the DLLME method such as type of disperser and extraction solvent, volume of disperser and extraction solvent and centrifugation time were investigated. Under the optimum conditions, 5.00 mL of sample solution, 300 μL of chloroform as extraction solvent and 1.25 mL of methanol as dispersive solvent gave high enrichment factor in the range of 62–84. Good linearity was obtained from 2 to 1500 μg/L ($r^2 > 0.995$). The mean recoveries of the pyrethroids evaluated by fortification of real samples were in the range of 84–94%. The limits of detection ranging from 2 to 5 μg/L are sufficient to analyze pyrethroid residues at the maximum residue limits (MRLs) established by the European Union (EU) in fruit juices. The proposed method can be applied to direct determination of pyrethroid residues in fruit juices.

1. Introduction

Pyrethroids are synthetic insecticides having chemical structures similar to the natural chemicals, pyrethrins, which are produced by the flowers of pyrethrums, the old world plants of the genus *Chrysanthemum* (*C. cinerariaefolium* and *C. coccineum*) [1,2]. Pyrethroids are hydrophobic esters and most of them contain a cyclopropanecarboxylate residue. They are subdivided into two classes based on their structural differences and neurophysiological actions. Structurally, type I pyrethroids do not contain a cyano substituent (permethrin and tetramethrin) whereas type II pyrethroids contain the α-cyano group (deltamethrin, cypermethrin, fenvalerate and fenpropathrin) (Fig. 1) [3]. In recent years, pyrethroids have been widely used as a new type of insecticide to control pests in agriculture, households, public health, forestry, horticulture and veterinary medicine [4–6]. Pyrethroids have low toxicity compared to other insecticides such as organophosphorus, organochlorine and carbamate [7–9]. The synthetic pyrethroids can cause serious health effects to human such as paraesthesia, headache, dizziness, nausea and skin irritation [10]. Nowadays, the risk of insecticide residues, including pyrethroids, organophosphorus, organochlorines or carbamates, remaining on food consumed is of great interest. The residues are due to overuse, especially when these commodities are freshly consumed, being a significant route to human exposure [11–13]. Therefore, the detection of synthetic pyrethroids is becoming particularly important in protecting the health of consumer from unsafe levels [14]. The maximum residue limits (MRLs) for pyrethroid residues in various foods have been set by several organizations to protect consumers, such as the Codex Alimentarius Commission and the European Union (EU pesticide MRLs, Regulation (EC) No. 839/2008) [6]. The MRLs of pyrethroids established by the EU in fruit is in the range of 0.01–2 mg/kg (see Table 1) [15], for example.

There is an increasing demand to develop sensitive and selective methods for the determination of insecticide residues which are usually present in trace amounts. Thus, the realiable analytical methods coupled with sample preparation and preconcentration techniques are necessary. An ideal sample preparation technique should able to isolate the analytes from sample matrices as well as perform preconcentration of them in one step. Liquid–liquid extraction (LLE) [16] is among the oldest of the preconcentration and matrix isolation techniques in analytical chemistry. However, LLE is time consuming and involves high reagent consumption. Subsequently, solid-phase extraction (SPE) [6,8] and solid-phase

* Corresponding author. Tel.: +66 043 202222; fax: +66 043 202373.
E-mail address: supalax@kku.ac.th (S. Srijaranai).

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Table 1
List of MRLs of studied pesticides in studied fruit juices.

Pyrethroid	MRLs (mg/kg)[a]						
	Apple	Grape	Orange	Kiwi	Passion fruit	Pomegranate	Guava
Tetramethrin	–	–	–	–	–	–	–
Fenpropathrin	0.01	0.01	2	0.01	0.01	0.01	0.01
Cypermethrin	1	0.5	2	0.05	0.05	0.05	0.05
Deltamethrin	0.2	0.2	0.05	0.2	0.05	0.05	0.05
Fenvalerate	0.02 (RR, SS isomer) 0.05 (RS, SR isomer)	0.1 (RR, SS isomer) 0.02 (RS, SR isomer)	0.02	0.02	0.02	0.02	0.02
Permethrin	0.05	0.05	0.05	0.05	0.05	0.05	0.05

–, not reported.
[a] EU pesticide MRLs, Regulation (EC) No. 839/2008 [15].

microextraction (SPME) [2,17,18] have been used to overcome the solvent consumption problem because they are solvent-free methods, but the main drawback of these extraction methods is their very high cost. Stir bar sorptive extraction (SBSE) [19] has been applied for pyrethroid determination, but it is also expensive. Extraction based on surfactant, cloud point extraction (CPE) [20,21] seems to be a good extraction method because it includes both sample preparation and preconcentration. However, CPE often requires salts or acidity (in case of anionic surfactants) to induce the cloud point and high temperature (in case of nonionic surfactants), thus CPE has many parameters to be optimized [16]. Homogeneous liquid–liquid extraction (HLLE) is an extraction method which separates the analyte in the homogeneous aqueous phase into the water-immiscible organic phase [22]. This method uses less solvent and reduces the extraction time. However, it requires reagent addition such as acid, base or salt to separate the analytes in the aqueous phase, so some analytes are destroyed by the addition of acid or base [12,23].

Recently, a new microextraction method, dispersive liquid–liquid microextraction (DLLME), has been developed as an efficient sample preparation and preconcentration method. The advantages of DLLME are the usage of a small volume of organic solvents, ease of operation, rapidity, low cost, high recovery, high enrichment factor and environmentally friendly nature [16,24–26]. The extraction by DLLME is based on the ternary component solvent system (aqueous sample, dispersive solvent and extraction solvent). The appropriate mixture of extraction solvent (organic solvent) and dispersive solvent (water-organic miscible solvent) is rapidly injected into the aqueous sample by syringe. Thereby a cloudy solution is formed. After centrifugation, the analytes are separated into the organic phase (extraction solvent) [12,27,28].

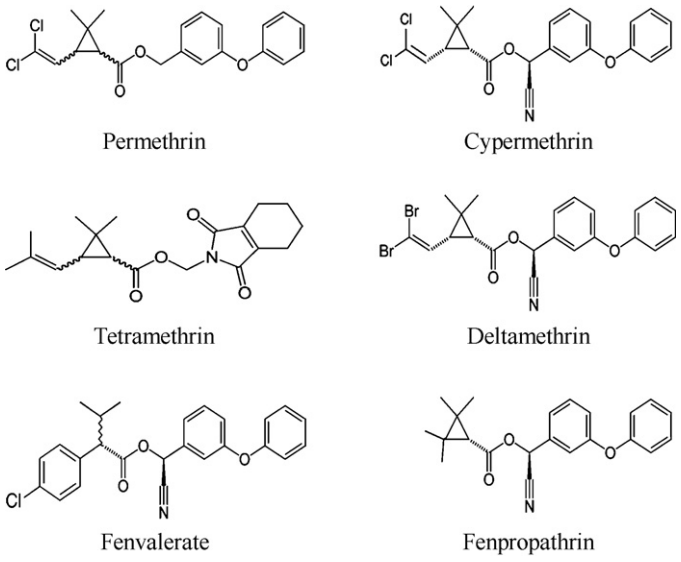

Fig. 1. Chemical structures of six studied pyrethroids.

The analysis of pyrethroid residues requires highly selective and sensitive analytical methods such as chromatography. Gas chromatography (GC) [2,3,7], high performance liquid chromatography (HPLC) [4,9] and capillary electrophoresis (CE) [5] have been used for the analysis of pyrethroids. HPLC is chosen in this study because it provides not only good resolution on the diastereomer of pyrethroids, but also on the enantiomers [3].

The main objective of this study was to develop a simple and sensitive analytical method for pyrethroid residues. DLLME was used as a preconcentration technique for pyrethroids before their analysis by HPLC. Special attention was given to the optimization of DLLME parameters to maximize the extraction efficiency and to allow good ruggedness. The proposed method was then validated and applied for the determination of pyrethroid residues in fruit juices. To our knowledge, this work represents the first time DLLME combined with HPLC has been used as a sensitive and reliable method for the analysis of pyrethroid residues in marketed fruit juice.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of at least analytical reagent grade. Acetonitrile, methanol (Bangkok, Thailand) and acetone (Milan, Italy) were used as dispersive solvents. Chloroform, dichloromethane (Milan, Italy) and hexane (Dublin, Ireland) were investigated as the extraction solvents. De-ionized water was obtained from a Millipore water purification system (Molsheim, France) and acetonitrile was used as the mobile phase. Nitrogen gas (99.99%) for solvent evaporation before analysis by HPLC was obtained from Industrial Nitrogen (Bangkok, Thailand). All pyrethroid standards namely tetramethrin, fenpropathrin, cypermethrin, deltamethrin, fenvalerate and permethrin were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) (see structures in Fig. 1). Standard stock solutions were prepared in acetonitrile at a final concentration of 100 mg/L^{-1}. Working standard solutions were freshly prepared by dilution of an appropriate amount of the standard stock solutions in de-ionized water. All solutions were stored in a refrigerator at 4 °C and protected from light.

2.2. Instrumentation

HPLC experiments were carried out on a Waters HPLC system (Waters Corporation, Milford, USA) consisting of a 484 tunable absorbance detector, a 515 HPLC pump and a 20 μL Rheodyne injection loop. The Waters CWS 32 software was used to control the

system and process the chromatographic data. The separation was performed on Waters Atlantis T3 (150 mm × 4.6 i.d., 5 μm) (Dublin, Ireland) at room temperature. Chromatographic analysis was carried out using isocratic elution of acetonitrile–water (72:28%, v/v) as mobile phase. The flow rate was set at 1.0 mL/min and the eluate was monitored using UV detection at 225 nm.

A Heraeus Sepatech centrifuge model Labofuge 200 (Osterode, Germany) was used for centrifugation of the extracts in the extraction step.

2.3. Dispersive liquid–liquid microextraction procedure

Fruit juice samples were filtered with Whatman filter paper no. 1 to remove the sediment. A volume of 5.00 mL of filtered sample solution was placed in a 15 mL conical glass tube. The optimum mixture of 1.25 mL of methanol (as dispersive solvent) and 300 μL of chloroform (as extraction solvent) was quickly injected into the sample solution with a syringe to induce the formation of cloudy solution between water/methanol/chloroform in the conical glass tube and then the mixture was gently shaken by hand for 30 s. At this step, the analytes in the aqueous solution were extracted into the fine extraction organic solvent droplets. After that, the mixture was centrifuged at 4000 rpm for 5 min. The dispersive particles in the extraction solvent phase were deposited in the bottom of the conical glass tube. Finally, this extraction solvent phase was collected in a small vial with a syringe and it was blown to dryness under a gentle stream of nitrogen gas at room temperature to eliminate organic solvents (chloroform). The residue was reconstituted in 100 μL of acetonitrile and 20 μL was injected into the HPLC system for pyrethroid analysis.

2.4. Validation study

Linearity was evaluated at nine concentration levels ranging from 0.015 to 8.0 mg/L^{-1}. Instrument precision and repeatability were studied at three concentration series using three replicates of each series and the reproducibility was evaluated for the three replicates at concentration 0.2 mg/L^{-1} on three different days. The precision was expressed as the relative standard deviation (%RSD). Recoveries were determined in three replicates by spiking standard pyrethroid concentrations of 0.02 and 0.05 mg/L^{-1} into the filtered fruit juice samples. Finally, the limit of detection (LOD) was evaluated using a signal to noise (S/N) ratio of 3:1 and limit of quantification (LOQ) was S/N of 10:1.

2.5. Fruit juice samples

Several types of marketed fruit juice samples including apple, red grape, orange, kiwi, passion fruit, pomegranate and guava juice were purchased from local supermarkets. Samples were homogenized and filtered before extraction to remove the sediments. Fruit juice samples were analyzed following the procedure described above (see Section 2.3).

2.6. Calculations

The enrichment factor (EF), defined as the ratio between the analyte concentration after preconcentration (C_{sed}) and the initial analyte concentration (C_0), can be calculated using the following equation [16,26,29]:

$$EF = \frac{C_{sed}}{C_0} \quad (1)$$

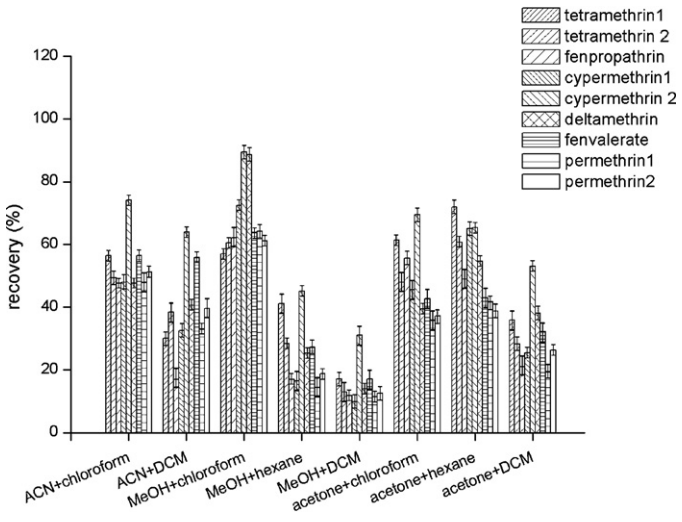

Fig. 2. The effect of extraction and dispersive solvent on recovery of pyrethroids. Extraction conditions: water sample volume (5.00 mL), disperser solvent volume (1.00 mL), extraction solvent volume (200 μL), centrifugation time (5 min), and concentration of each pyrethroid (300 μg/L).

The extraction recovery (ER) was used to evaluate the extraction efficiency under the optimum conditions by the following equation:

$$ER = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 \quad (2)$$

where V_{sed} and V_{aq} are the volumes of sedimented phase and sample, respectively.

3. Results and discussion

3.1. Optimization of DLLME

3.1.1. Extraction and dispersive solvent selection

The selection of an appropriate solvent is the most important parameter for the DLLME process because it is the key parameter that affects the performance of this method and the solvent should be compatible with the HPLC mobile phase. Thus, type and volume of solvents were the first parameter to be optimized.

Halogenated hydrocarbons are usually selected as the extraction solvent [28]. In this study chloroform, dichloromethane and hexane were investigated as extraction solvents. Dispersive solvents should be miscible solvents with both aqueous samples and extraction solvents to help the analytes transfer from aqueous phase into organic phase. Acetone, acetonitrile and methanol were studied as dispersive solvents. Thus, nine series of solvents were compared for the extraction of the studied pyrethroids.

The series of solvents were evaluated for extraction using the following model: 5.00 mL of sample spiked with pyrethroids at concentration of 300 μg/L each, 1.00 mL of dispersive solvent and 200 μL of extraction solvent. The extraction efficiency was evaluated by comparison of the recoveries of each analyte. The recovery of each series is shown in Fig. 2. The results reveal that the series of methanol (dispersive solvent) and chloroform (extraction solvent) show the highest extraction recoveries (in the range of 60–90% recovery with the standard deviation between 5 and 8%) when compared with the other series (the highest recovery is 60%). For series of hexane and acetonitrile, the cloudy solution was not formed so neither can be used for extraction. Thus, methanol and chloroform were chosen as the optimum solvents for extraction.

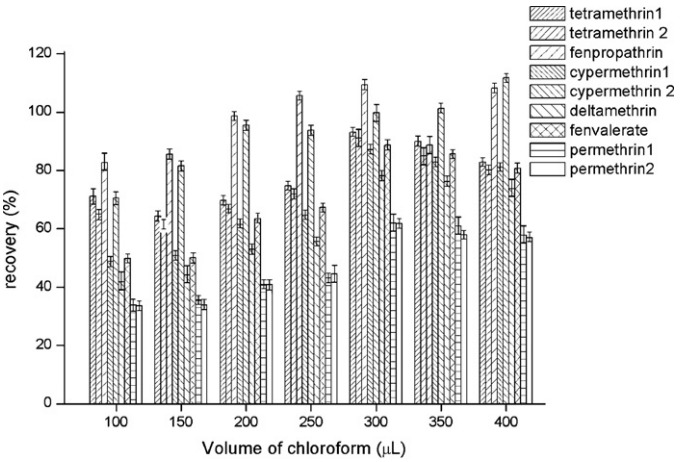

Fig. 3. The effect of extraction solvent volume (chloroform) on the recovery. Extraction conditions: water sample volume (5.00 mL), disperser solvent volume, methanol (1.00 mL), centrifugation time (5 min), and concentration of each pyrethroid (300 μg/L).

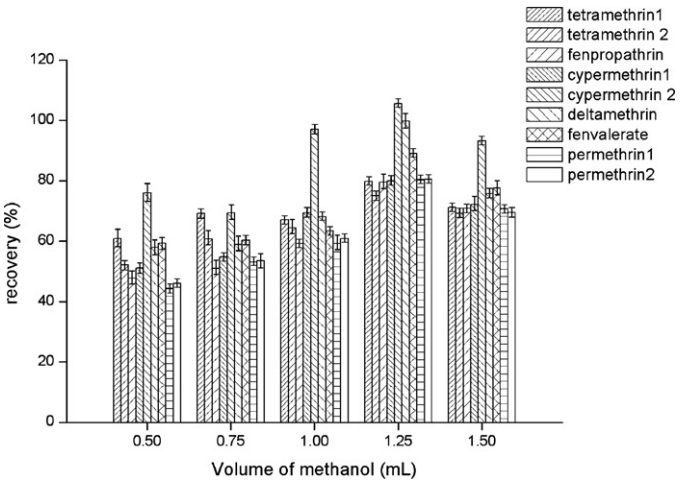

Fig. 4. The effect of dispersive solvent volume (methanol) on the recovery. Extraction conditions: water sample volume (5.00 mL), extraction solvent volume, chloroform (300 μL), centrifugation time (5 min), and concentration of each pyrethroid (300 μg/L).

3.1.2. The effect of extraction solvent volume (chloroform)

In order to study the effect of chloroform volume, experiments were conducted in which the chloroform volume was varied in the range of 100–400 μL in 50 μL intervals and the dispersive solvent volume (methanol) maintained at 1.00 mL. The results are shown in Fig. 3. The extraction efficiency increased with increase of chloroform volume (at volume 100–300 μL, recoveries increase from 35–80% to 60–110% with the standard deviation in the range of 2–7%) while the extraction efficiency was constant at volumes higher than 300 μL. Thus to reduce the organic solvent volume, 300 μL of chloroform was selected as the optimum extraction solvent volume which provided an acceptable recovery.

3.1.3. The effect of dispersive solvent volume (methanol)

To examine the effect of dispersive solvent volume, the chloroform volume in the experiments was maintained at the optimum volume (300 μL) and the methanol volume varied at 0.50, 0.75, 1.00, 1.25 and 1.50 mL. The results are shown in Fig. 4. It is clearly seen that the extraction efficiency increased when increasing the methanol volume (at 0.50–1.25 mL, recoveries increase from 45–75% to 80–100% with the standard deviation between 2 and 5%). However, the efficiency decreased when a large volume of methanol (at 1.50 mL, recoveries decrease to 70–90%) was used. Thus, 1.25 mL of methanol was chosen as the optimum dispersive solvent volume.

3.1.4. The effect of centrifugation time

The centrifugation time was studied at 4000 rpm (data not shown). The result reveals that centrifugation time has little effect on extraction yield because after mixing of the three solvent components (sample, extraction solvent and dispersive solvent) the equilibrium is achieved in few seconds due to the large contact surface between the tiny drops of extraction solvent and sample [30]. Thus, centrifugation was only used to help the cloudy solution to settle to the bottom of the tube. The centrifugation time at 5 min was chosen to ensure that the transfer of droplet to bottom of a centrifuge tube.

3.2. Analytical performance

Using the isocratic elution with the mobile phase acetonitrile and water (72:28%, v/v), the six pyrethroids can be separated within 30 min (Fig. 5). Enantiomers of tetramethrin, cypermethrin and

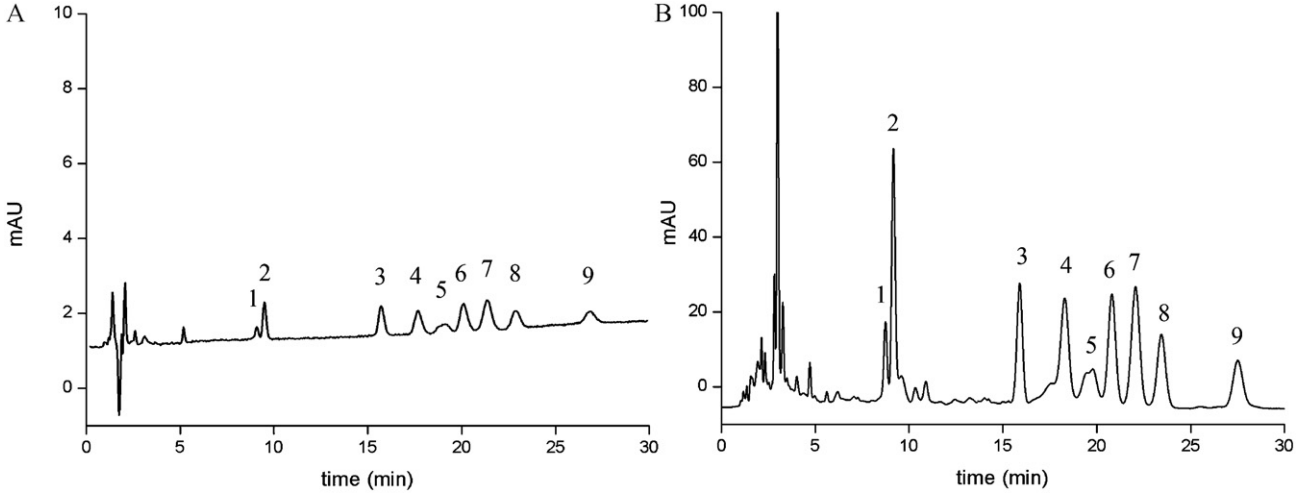

Fig. 5. Chromatograms of six pyrethroid standard solution (50 μg/L) (A) without DLLME and (B) with DLLME using optimum conditions: 1, tetramethrin1; 2, tetramethrin2; 3, fenpropathrin; 4, cypermethrin1; 5, cypermethrin2; 6, deltamethrin; 7, fenvalerate; 8, permethrin1; 9, permethrin2.

Table 2
Analytical performance of the DLLME procedure optimized for the determination of six pyrethroids.

Pyrethroid	Linear range (μg/L)	Linear equation	Correlation coefficient (r^2)	LOD (μg/L)	LOQ (μg/L)	Enrichment factor
Tetramethrin1	5–1500	$y = 8224x - 191.37$	0.9995	5	10	84
Tetramethrin2	2–1000	$y = 20{,}405x + 205.60$	0.9959	2	5	80
Fenpropathrin	2–1000	$y = 20{,}238x + 85.11$	0.9983	2	5	65
Cypermethrin1	2–1500	$y = 19{,}934x + 248.69$	0.9998	5	10	72
Cypermethrin2	5–1500	$y = 11{,}786x - 273.48$	0.9993	5	10	62
Deltamethrin	2–1000	$y = 22{,}963x + 199.10$	0.9993	2	8	74
Fenvalerate	2–1000	$y = 29{,}381x + 261.18$	0.9993	2	8	76
Permethrin1	2–1500	$y = 19{,}250x + 302.28$	0.9996	2	10	71
Permethrin2	5–1500	$y = 15{,}690x + 338.71$	0.9995	5	10	77

Table 3
Recoveries of the pyrethroids standard spiked in fruit juice samples and intra-, inter-day precisions.

Pyrethroid	Recovery (%)		Precision (%RSD)			
	Spiked level (μg/L)		Intra-day ($n = 3$)		Inter-day ($n = 3 \times 3$)	
	20	50	t_R	Peak area	t_R	Peak area
Tetramethrin1	87.9 ± 2.3	88.6 ± 1.4	0.00	0.89	0.65	4.73
Tetramethrin2	85.8 ± 2.5	88.4 ± 1.8	0.02	3.14	0.67	5.25
Fenpropathrin	90.3 ± 1.6	92.3 ± 2.2	0.09	1.73	0.76	4.13
Cypermethrin1	85.2 ± 2.5	90.1 ± 1.7	0.04	0.83	0.77	4.45
Cypermethrin2	86.4 ± 1.9	94.0 ± 2.1	0.10	2.46	0.79	5.57
Deltamethrin	86.8 ± 2.3	88.3 ± 2.3	0.04	0.60	0.83	0.98
Fenvalerate	84.5 ± 1.4	89.5 ± 1.8	0.06	0.42	0.90	0.69
Permethrin1	88.2 ± 1.3	94.0 ± 2.9	0.04	2.19	0.85	2.43
Permethrin2	90.5 ± 1.6	88.2 ± 1.3	0.08	3.61	0.98	4.40

5.00 mL of juices is in range 5.16–5.26 g.

Table 4
Comparison of the proposed method and some other methods for pyrethroid determination in fruit juice samples.

Extraction method	Instrument-detector	Analyte	Sample	Extraction solvent	Disperser solvent	Sample size	LOD	Linear range	Recovery	EF	Ref.
UA-DLLME	GC–FID	Cypermethrin, permethrin	Pear juice	30 μL C_2Cl_4	3.5 mL MeOH	5 mL	3.1, 2.2 μg/kg	0.009–1.52 μg/g	92.1–107.1%	344–351	[13]
DLLME	GC–GC–MS	24 Pesticides (permethrin, cypermethrin)	Apple juice	100 μL CCl_4	0.4 mL acetone	5 mL	0.43, 2.2 μg/L	0.013–0.2 mg/kg	60–105%	42–58	[30]
SPME	GC–MS	54 Pesticides (fenpropathrin)	Orange, peach, pineapple juices	1 mL ethyl acetate	–	1 mL	0.9 μg/L	0.01–0.1 mg/L^{-1}	90–97%	–	[32]
DLLME	HPLC–UV	Fenpropathrin, deltamethrin, fenvalerate, permethrin, cypermethrin, tetramethrin	7 Fruit juices	300 μL chloroform	1.25 mL MeOH	5 mL	2–5 μg/L	0.002–1.5 ng/L	84–94%	62–84	Proposed method

permethrin could be separated and detected. It is clearly seen from Fig. 5A and B that DLLME is an effective method for preconcentration of pyrethroids. Fig. 5A shows the chromatogram of the pyrethroids (50 μg/L each) without DLLME, while Fig. 5B shows the chromatograms of the same mixture of pyrethroid (50 μg/L each) with DLLME. The signal intensities, i.e. sensitivity, increased significantly.

The linear regression equation and the other relevant results are given in Table 2. The results show an excellent linearity for all analytes with correlation coefficients (r^2) higher than 0.995. LODs and LOQs of six pyrethroids based on signal to noise ratio (S/N) of 3 and 5 were in the range of 2–5 μg/L and 5–10 μg/L, respectively. LODs of the proposed method are below the MRLs established by the European Union (EU, Regulation (EC) No. 839/2008) as summarized in Table 1. Since, the MRLs of pyrethroids for processed fruit, such as fruit juice, have not been established yet, the MRLs corresponding to the recommended values for the original matrices (in this case is fresh fruit) can be applied [31].

The precision (expressed as percentage of relative standard deviation, %RSD) and the accuracy (expressed as the mean percentage recovery between the amounts found and those added) are shown in Table 3. The recoveries obtained from two levels of spiked concentration of pyrethroids (20 and 50 μg/L each) in fruit juice samples were in the range of 88.9–94.5% and 92.1–98.3%,

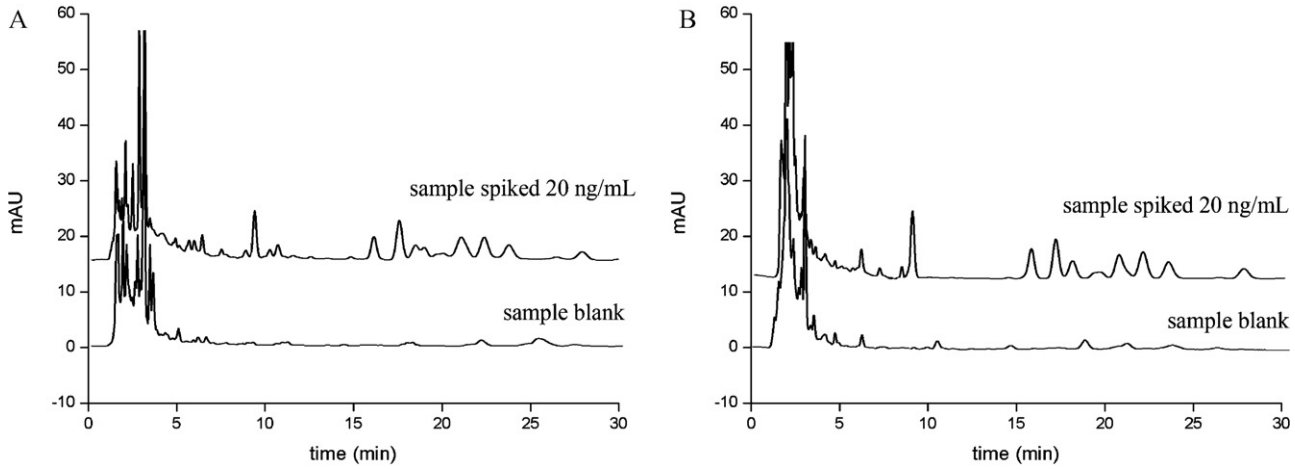

Fig. 6. Chromatograms of sample blank and sample spiked pyrethroids (20 μg/L): (A) orange juice sample and (B) kiwi juice sample.

respectively. The obtained recoveries were slightly lower for low level assayed, especially for cypermethrin1, cypermethrin2 and permethrin 1. The %RSD of peak area was lower than 3.61% for intra-day precision and lower than 5.57% for inter-day precision. It can be concluded that this method provides both good accuracy and precision.

It is known that matrix components affect the detection of the analytes either by inhibiting or enhancing the analyte signal, thus matrix-matched calibration was used. In this work, two fruit juices (guava and kiwi juices) were selected as representatives for the evaluation. The matrix effect in aqueous solvent and in representative juice samples were evaluated by comparing the slopes of the calibration curves. The paired *t*-test ($p = 0.05$) showed insignificant differences between the results obtained from aqueous solvent and fruit juice samples (data not shown). It is indicated that no significant difference between the matrices.

3.3. Analysis of fruit juice samples

The proposed analytical method was applied to determine six pyrethroid insecticides in fruit juice samples. Different matrices of samples were studied including apple, red grape, orange, kiwi, passion fruit, pomegranate and guava juice. In this study, the samples were only filtered to eliminate the suspended solids before extraction using DLLME and analysis by HPLC. The six pyrethroids studied were not found in the studied fruit juices at quantification level of this method. Fig. 6 depicts the typical chromatograms of juice sample blanks and sample spiked pyrethroids after DLLME, showing no interference peaks. Table 4 summarizes the details of DLLME along with the obtained analytical performances of the proposed method and the other methods which used for pyrethroid determination in fruit juice samples. However, the obtained LODs are comparable and below MRLs.

4. Conclusions

DLLME coupled with HPLC was developed and validated for the simultaneous determination of six pyrethroids namely tetramethrin, fenpropathrin, cypermethrin, deltamethrin, fenvalerate and permethrin. Using HPLC, a common instrument available in most laboratories, is an alternative to the mostly used GC for the analysis of pyrethroids. DLLME provided high efficacy for extraction with the obtained enrichment factor ranging from 62 to 84. The proposed method has been successfully applied to the analysis of pyrethroid insecticides in various fruit juice samples with good recoveries in the range of 84–94%.

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References

[1] V. Casas, M. Llompart, C. García-Jares, R. Cela, J. Chromatogr. A 1124 (2006) 148–156.
[2] Z.M. Chen, Y.H. Wang, J. Chromatogr. A 754 (1996) 367–395.
[3] M.R. Moya-Quiles, E. Muñoz-Delgado, C.J. Vidal, Chem. Phys. Lipids 79 (1996) 21–28.
[4] K.B. Kim, M.G. Bartlett, S.S. Anand, J.V. Bruckner, H.J. Kim, J. Chromatogr. B 834 (2006) 141–148.
[5] F. Ye, Z. Xie, X. Wu, X. Lin, Talanta 69 (2006) 97–102.
[6] J. Cheng, M. Liu, Y. Yu, X. Wang, H. Zhang, L. Ding, H. Jin, Meat Sci. 82 (2009) 407–412.
[7] Z. Sharif, Y.B.C. Man, N.S.A. Hamid, C.C. Keat, J. Chromatogr. A 1127 (2006) 254–261.
[8] S. Zawiyah, Y.B. Che Man, S.A.H. Nazimah, C.K. Chin, I. Tsukamoto, A.H. Hamanyza, I. Norhaizan, Food Chem. 102 (2007) 98–103.
[9] E. García, A. García, C. Barbas, J. Pharm. Biomed. 24 (2001) 999–1004.
[10] L. Chiu-Hwa, Y. Cheing-Tong, V.K. Ponnusamy, L. Hong-Ping, J. Jen-Fon, Anal. Bioanal. Chem. 401 (2011) 927–937.
[11] R.R. González, A.G. Frenich, J.L.M. Vidal, Talanta 76 (2008) 211–225.
[12] A. Kruve, A. Künnapas, K. Herodes, I. Leito, J. Chromatogr. A 1187 (2008) 58–66.
[13] J. Du, H. Yan, D. She, B. Liu, G. Yang, Talanta 82 (2010) 698–703.
[14] Y. Liang, S. Zhou, L. Hu, L. Li, M. Zhao, H. Liu, J. Chromatogr. B 878 (2010) 278–282.
[15] Regulation (EC) No. 839/2008 of the European Parliament and of the Council, European Union, Brussels. http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=substance.selection.
[16] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[17] P.P. Vázquez, A.R. Mughari, M.M. Galera, Anal. Chim. Acta 607 (2008) 74–82.
[18] A. Sanusi, V. Guillet, M. Montury, J. Chromatogr. A 1046 (2004) 35–40.
[19] A. Juan-García, Y. Picó, Guillerina Font, J. Chromatogr. A 1073 (2005) 229–236.
[20] J.B. Chen, W.J. Zhao, W. Liu, Z.M. Zhou, M.M. Yang, Food Chem. 115 (2009) 1038–1041.
[21] W.J. Zhao, X.K. Sun, X.N. Deng, L. Huang, M.M. Yang, Z.M. Zhou, Food Chem. 127 (2011) 683–688.
[22] X. Zhao, X. Liu, Z. Zhao, X. Huang, M. Zhang, H. Wang, X. Wang, J. Sep. Sci. 32 (2009) 2051–2057.
[23] M.R. Jamali, Y. Assadi, R.R. Kozani, F. Shemirani, E-J. Chem. 6 (4) (2009) 1077–1084.

[24] Z.M. Liu, X.H. Zang, W.H. Liu, C. Wang, Z. Wang, Chin. Chem. Lett. 20 (2009) 213–216.
[25] A.V. Herrera-Herrera, M. Asensio-Ramos, J. Hernández-Borges, M.Á. Rodríguez-Delgado, Trends Anal. Chem. 29 (2010) 728–751.
[26] S.S. Caldas, F.P. Costa, E.G. Primel, Anal. Chim. Acta 665 (2010) 55–62.
[27] P. Hashemi, F. Raeisi, A.R. Ghiasvand, A. Rahimi, Talanta 80 (2010) 1926–1931.
[28] M. Rezaee, Y. Yamini, M. Faraji, J. Chromatogr. A 1217 (2010) 2342–2357.
[29] M. Bernardo, M. Gonçalves, N. Lapa, B. Mendes, Chemosphere 79 (2010) 1026–1032.
[30] S.C. Cunha, J.O. Fernandes, M.B.P.P. Oliveira, J. Chromatogr. A 1216 (2009) 8835–8844.
[31] G.L. Bienvenida, G.R. Juan, M. Milagros, M.D. Antonio, F.A. Amadeo, J. Agric. Food Chem. 55 (2007) 10548–10556.
[32] S. Cortés-Aguado, N. Sánchez-Morito, F.J. Arrebola, A. Garrido Frenich, J.L. Martínez Vidal, Food Chem. 107 (2008) 1314–1325.