Talanta 120 (2014) 289–296

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Two-step microextraction combined with high performance liquid chromatographic analysis of pyrethroids in water and vegetable samples

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ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form
2 December 2013
Accepted 3 December 2013
Available online 17 December 2013

Keywords:
Dispersive liquid microextraction
Dispersive μ-solid phase extraction
Magnetic nanoparticles
Pyrethroids
High performance liquid chromatography

ABSTRACT

Dispersive liquid microextraction (DLME) combined with dispersive μ-solid phase extraction (D-μ-SPE) has been developed as a new approach for the extraction of four pyrethroids (tetramethrin, fenpropathrin, deltamethrin and permethrin) prior to the analysis by high performance liquid chromatography (HPLC) with UV detection. 1-Octanol was used as the extraction solvent in DLME. Magnetic nanoparticles (Fe_3O_4) functionalized with 3-aminopropyl triethoxysilane (APTS) were used as the dispersive in DLME and as the adsorbent in D-μ-SPE. The extracted pyrethroids were separated within 30 min using isocratic elution with acetonitrile:water (72:28). The factors affecting the extraction efficiency were investigated. Under the optimum conditions, the enrichment factors were in the range of 51–108. Linearity was obtained in the range 0.5–400 ng mL^{-1} (tetramethrin) and 5–400 ng mL^{-1} (fenpropathrin, deltamethrin and permethrin) with the correlation coefficients (R^2) greater than 0.995. Detection limits were 0.05–2 ng mL^{-1} (water samples) and 0.02–2.0 ng g^{-1} (vegetable samples). The relative standard deviations of peak area varied from 1.8 to 2.5% ($n=10$). The extraction recoveries of the four pyrethroids in field water and vegetable samples were 91.7–104.5%. The proposed method has high potential for use as a sensitive method for determination of pyrethroid residues in water and vegetable samples.

1. Introduction

Pyrethroids are one of the major classes of pesticides containing a group of hydrophobic esters which have structures that are similar to natural pyrethrins found in the *chrysanthemum* species [1,2]. They have been subdivided into two classes based on their structural differences, toxicological and neurophysiological actions. Structurally (Table 1), type I pyrethroids (permethrin and tetramethrin) lack a cyano substituent, whereas type II pyrethroids (fenpropathrin and deltamethrin) contain the α-cyano group [2]. Pyrethroids are widely used as insecticides in agriculture (field-treatment of crops and protection of stored products), public health (hygienic treatment in houses), forestry, horticulture and veterinary applications (to control exo- and endo-parasites) [3–5]. They are increasingly used in agriculture due to their broad biological activity, slow development of pest resistance and the relatively low mammalian toxicity of most congeners [6]. However, these compounds are considered hazardous to the environment and human health [7]. Their residues may appear in fruits and vegetables and are usually distributed in aqueous environments by leaching and runoff from soil into ground and surface water because of their high solubility in water. The maximum residue limits (MRLs) for pyrethroid residues in various foods have been established to protect consumers by several organizations such as the European Union [8] and the Codex Alimentarius Commission (CODEX) [9]. The MRLs of pyrethroids established by the EU and CODEX in vegetables are in the range of 0.01–0.2 μg g^{-1} and 0.2–5 μg g^{-1} [9,10], respectively. As the MRLs are low, a sensitive analytical method is required for determination of pyrethroid residues.

Sample preparation is the first step in an analytical method and it must provide reliable and accurate results. It is a necessary step, especially for trace analysis of analytes in complex matrices. Nowadays, there is considerable awareness about the environment, therefore sample preparation techniques using solvents with low toxicity that are more environmentally friendly are important [11]. Several microextraction techniques have been developed such as solid-phase microextraction [12–14], liquid-phase microextraction [15,16], stir-bar sorptive extraction [17,18] and micro-solid phase extraction [19,20]. In addition to using less toxic solvents, they are simple and rapid [21].

As describe in this work, a novel adsorbent, magnetic nanoparticles (MNPs), has been applied in sample pretreatment techniques and they can be used as an alternative to the traditional adsorbent materials in solid phase extraction (SPE). The advantages of using MNPs in SPE are based on the properties of MNPs such as high surface area, good stability, ability to disperse in solution and ability to be separated with an external magnetic field [22,23]. In addition,

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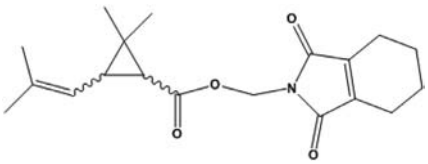
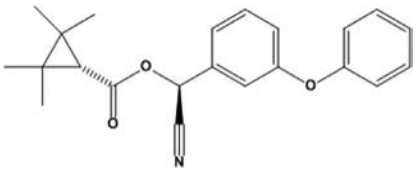
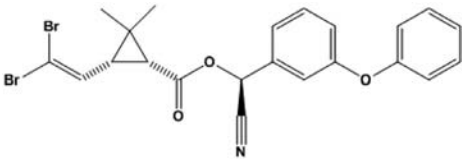
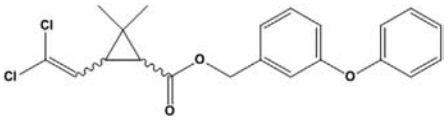
http://dx.doi.org/10.1016/j.talanta.2013.12.005

Table 1
The chemical and physical properties of four studied pyrethroids.

Compound	Structure	Molecular formula	Molecular weight (g/mol)	log K_{ow} (Ref.)
Tetramethrin		$C_{19}H_{25}NO_4$	331.4	4.6 [31]
Fenpropathrin		$C_{22}H_{23}NO_3$	349.4	5.6 [32]
Deltamethrin		$C_{22}H_{10}Br_2NO_3$	505.2	6.1 [31]
Permethrin		$C_{21}H_{20}Cl_2O_3$	391.3	6.5 [31]

the sensitivity and capacity of MNPs can be enhanced by chemically modification of MNPs with appropriate functional groups. Bruce et al. modified magnetic/silica core shell nanoparticles with 3-aminopropyl-triethoxysilane and applied to adsorb nucleic acids [24]. The magnetic nanoparticles coated with 3-chloropropyl-triethoxysilane were used as the sorbent for the determination of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples [25].

Recently, an interesting approach for microextraction is the combination of different extraction techniques, known as two-step microextraction. This approach provides better analytical performance than its single-step counterpart, including high selectivity and high enrichment factor which results in high sensitivity. Solid-phase extraction combined with dispersive liquid-liquid microextraction (DLLME) has been reported by Liu et al. for determination of polybrominated diphenyl ethers in different environmental matrices [26]. Dispersive solid-phase extraction (DSPE) followed by DLLME was investigated for the determination of some sulfonylurea herbicides in soil [27]. Liquid–solid extraction coupled with magnetic solid-phase extraction was used for the determination of pyrethroid residues in vegetable samples [28].

In this laboratory, the use of dispersive liquid microextraction (DLME) combined with dispersive micro-solid phase extraction (D-μ-SPE) has been reported for the preconcentration of carbaryl in water samples before its detection by spectrophotometry [29].

This work is aimed at exploring the applicability of the two-step microextraction technique, DLME/D-μ-SPE, for various compounds (analytes) with a wide range of polarity. The studied analytes are the four most widely used pyrethroids (tetramethrin, fenpropathrin, deltamethrin and permethrin). APTS-magnetic nanoparticles were used as the adsorbent in D-μ-SPE. To our knowledge, the use APTS-magentic nanoparticles for the determination of pyrethroids have not been previously reported. As apparent from there the octanol/water partition coefficient values, log K_{ow} [30], the pyrethroid analytes are less polar (that is, more hydrophobic with log K_{ow} ranging from 4.6 to 6.5) than the analyte in our previous work (carbaryl compounds with low log K_{ow} value of about 2.3). The pyrethroids were simultaneously analyzed by HPLC. The effects of various experimental parameters, such as type and volume of the extraction solvent and desorption solvents, amount of the magnetic nanoparticles, extraction time and desorption/sonication time, were studied and optimized. The proposed method was applied to water samples as well as the more complex vegetable samples.

2. Experimental

2.1. Chemicals and reagents

Unless otherwise stated, all chemicals were analytical reagent grade. Pyrethroid standards, namely tetramethrin, fenpropathrin, deltamethrin and permethrin (see structures in Table 1) [31,32], were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Standard stock solutions (100 mg L^{-1} each) were prepared in acetonitrile.

Working standard solutions were freshly prepared by dilution of an appropriate amount of the standard stock solutions in water. All solutions were stored in a refrigerator at 4 °C and protected from light. 1-Octanol (Panreac Sintesis, Spain), toluene (Carlo erba, Italy), and hexane (Lab scan, Thailand) were used as extraction solvents. Acetonitrile (RCI Lab scan, Thailand), methanol (QRëc, New Zealand), and acetone (Lab scan, Ireland) were used as desorption solvents. Magnesium sulfate anhydrous ($MgSO_4$) was purchased from Panreac (Spain). All solutions were prepared in deionized water with resistivity of 18.2 MΩ cm from RiO_s™ Type I Simplicity 185 (Millipore, USA).

2.2. Instrumentation

HPLC experiments were carried out on a Waters HPLC system (Waters Corporation, Milford, USA) consisting of a model 484 tunable absorbance detector, a 515 HPLC pump and a 20 μL Rheodyne injection loop. Waters CWS 32 software was used for the chromatographic data acquisition. The separation was performed on a Waters Atlantis T3 column (150 mm × 4.6 mm i.d., 5 μm) (Dublin, Ireland) at room temperature. Chromatographic analysis was carried out at room temperature using isocratic elution with acetonitrile: water (72:28%, v/v) as the mobile phase. The flow rate was set at

1.0 mL min^{-1} and the eluate was monitored using UV detection at 225 nm. Under the HPLC conditions, the enantiomers of tetramethrin and permethrin can be separated [33,34].

The synthesis and characterization of the APTS-magnetic nanoparticles can be found in previous work [30].

2.3. DLME and D-μ-SPE extraction procedure

The two-step microextraction (DLME/D-μ-SPE) procedure was carried out as follows: in the DLME step, an aliquot (200 μL) of 1-octanol was injected rapidly into a vial containing 5 mL of standard or sample solution. Then, the vial was sealed and placed on a vortex agitator at 3200 rpm for 3 min. After that, 10 mg of APTS-magnetic nanoparticles were added to the vial and vortexed for 3 min. Subsequently, with the aid of a magnet, APTS-magnetic nanoparticles were deposited at the bottom of the vial and the aqueous part was withdrawn by a syringe. Methanol (150 μL) was added into the vial and sonicated for 5 min to desorb the analytes from the adsorbent. An aliquot of 100 μL was taken and dried under nitrogen gas at room temperature to eliminate organic solvent and redissolved in 30 μL of methanol. Finally, 20 μL was injected onto HPLC system for pyrethroid analysis.

2.4. Determination of pyrethroid in samples

Three water samples were collected from ponds near a vegetable field in Kalasin province (Thailand) and were filtered to remove the sediments before being analyzed as described in Section 2.3.

Vegetable samples, cucumber and cabbage, were purchased from local supermarkets in Khon Kaen province (Thailand). A modified Quick Easy Cheap Effective Rugged Safe (QuEChERS) method was used for the extraction of pyrethroids from the vegetable samples. About 500 g of the edible part of the sample were cut into 1 cm^3 pieces and blended using a commercial food mixer. A 10 g accurately weighed sample was placed in a 50 mL centrifuge tube. A acetonitrile (25 mL) were added and shaken at 250 rpm for 1 h. $MgSO_4$ (ca. 15 g) was added and the sample was vortexed immediately and then centrifuged for 10 min at 2500 rpm. After that, an aliquot of the upper layer (ca. 25 mL) was transferred to a round-bottom flask and then evaporated using a rotary evaporator (at 50 °C water bath) to eliminate acetonitrile. The solution was diluted with water to 10 mL and finally extracted by the two-step microextraction procedure (see Section 2.3).

For spiked samples, standard solutions at different concentrations (three levels) were added to water samples before two-step microextraction. For vegetable samples, standard solutions were added before subjected to QuEChERS and subsequently extracted by two-step microextraction.

2.5. Calculations

The experimental parameters affecting the extraction for both DLME and D-μ-SPE were investigated. The results are expressed in terms of the enrichment factor (EF) and the extraction recovery (%ER) which can be calculated as follows [35]:

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

where EF, C_{sed} and C_o are the enrichment factor, the analyte concentration in the sediment, and the initial analyte concentration in the aqueous phase, respectively.

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

where %ER, V_{sed} and V_{aq} are the extraction recovery, the volume of the sediment phase, and the volume of the aqueous phase, respectively.

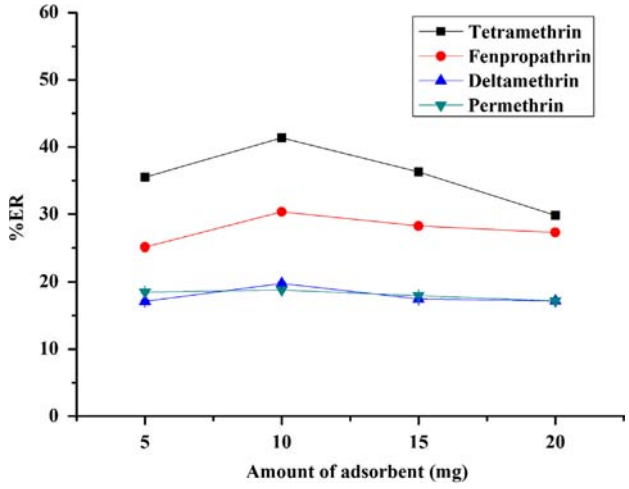


Fig. 2. The effect of amount of APTS-MNPs sorbent; extraction conditions: 1-octanol (200 μL) as extraction solvent, DLME 3 min, D-μ-SPE 3 min, MeOH 150 μL as a desorption solvent, desorption 5 min.

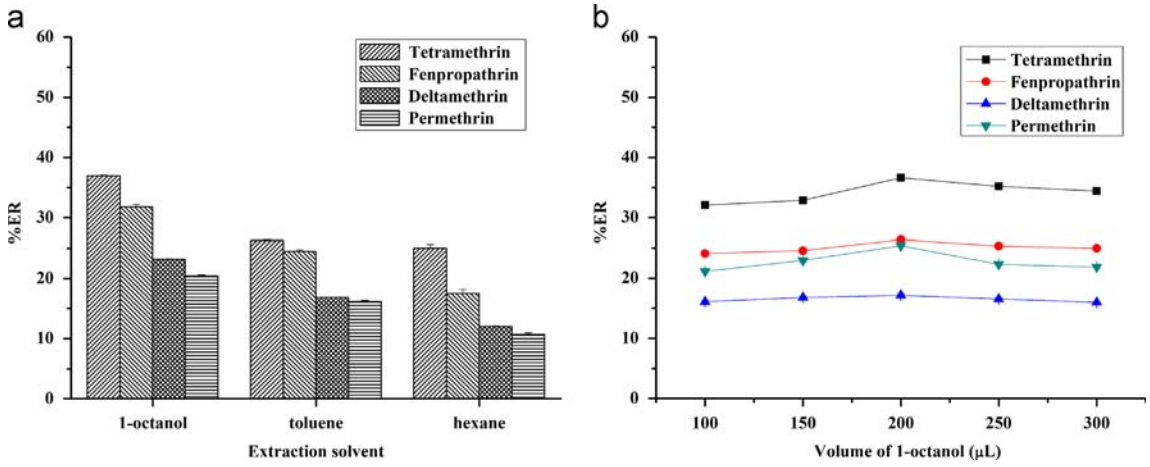


Fig. 1. The dependence of extraction recovery of the pyrethroids on (a) different extraction solvents; extraction conditions: DLME 3 min, D-μ-SPE 3 min, APTS-MNPs 10 mg, MeOH 150 μL as a desorption solvent, desorption 5 min and (b) volume of 1-octanol; extraction conditions: as described in (a) except 1-octanol was used as extraction solvent.

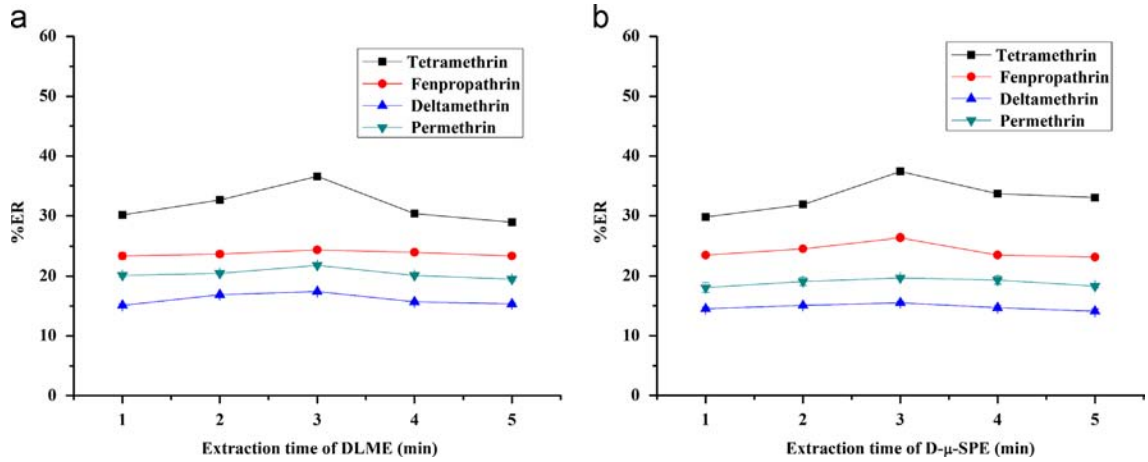


Fig. 3. The effect of extraction time on the extraction recovery of the pyrethroids (a) extraction time for DLME; extraction conditions: as described in Figs. 1 and 2 except APTS-MNPs 10 mg was used (b) extraction time for D-μ-SPE; extraction conditions: as described in Figs. 1 and 2 and (a) except 3 min for DLME.

3. Results and discussion

3.1. Optimization of DLME and D-μ-SPE

Pyrethroids were firstly extracted by DLME. 1-Octanol was rapidly injected into the standard solution. 1-Octanol can disperse into very fine droplets. The pyrethroids can transfer into the 1-octanol phase via hydrophobic interaction. Pyrethroids were subsequently extracted by D-μ-SPE. The aminopropyl group on the surface of the magnetic nanoparticles facilitates the interaction of 1-octanol and pyrethroids by both hydrophobic and hydrophilic interaction. Finally, pyrethroids were eluted by a small volume of methanol before analysis by HPLC. The parameters affecting both DLME and D-μ-SPE were optimized using standard solution of pyrethroids (200 ng mL^{-1}) as described in Sections 3.1.1–3.1.5.

3.1.1. Effect of type and volume of the extraction solvent

For the DLME, the extraction solvent should meet the following requirements: (a) be immiscible with aqueous solution (b) able to dissolve the analytes, and (c) possess low toxicity. To avoid the use of more highly toxic solvents (e.g. CCl_4, $HCCl_3$, H_2CCl_2, etc.), 1-octanol, toluene and hexane were investigated as extraction solvents. As can be seen in Fig. 1 (a), the highest extraction recovery was obtained when using 1-octanol was chosen as the extraction solvent.

The volume of 1-octanol was then varied in the range 100–300 μL in 50 μL intervals. Fig. 1(b) shows the variation of extraction recovery versus volume of 1-octanol. By increasing the volume of 1-octanol, the extraction recovery increased up to 200 μL, and then decreased slightly because of dilution effect. Therefore, 200 μL of 1-octanol was selected as the optimum volume for DLME.

3.1.2. Effect of the amount of APTS-magnetic nanoparticles

The effect of the amount of APTS-magnetic nanoparticles was studied using 5.0, 10.0, 15.0 and 20.0 mg amounts of adsorbent. The results are shown in Fig. 2, the extraction recoveries for all the studied pyrethroids except tetramethrin, increased with increasing amounts of the adsorbent (5.0–10.0 mg) and then they remained constant. For tetramethrin, the extraction recovery reached a maximum at 10 mg of adsorbent, then decreased slightly with increasing amounts of adsorbent. This may be due to the stronger interaction of tetramethrin with the adsorbent compared to the others. The desorption solvent (methanol 150 μL) used was not enough to desorb the tetramethrin. Thus, 10.0 mg of the adsorbent was chosen in D-μ-SPE.

3.1.3. Effect of extraction time

The results in Fig. 3(a) show that all the studied pyrethroids except tetramethrin could transfer readily and extraction time had negligible effect on extraction efficiency. For tetramethrin, the extraction efficiency increased with increasing extraction time and the highest efficiency was obtained at 3 min. After that, the extraction efficiency decreased and then constant after 4 min. Therefore, extraction time for D-μ-SPE was chosen at 3 min.

Similar results were obtained for the D-μ-SPE as shown in Fig. 3(b), indicating that the adsorbents could interact with 1-octanol very efficiently within 3 min of extraction and then they kept constant. Therefore, 3 min was selected as the optimum extraction time for D-μ-SPE.

3.1.4. Effect of type and volume of the desorption solvent and desorption time

Desorption of the analytes from the adsorbent was performed by sonication. Different organic solvents were studied including acetone, acetonitrile and methanol. Results in Fig.4(a) show that methanol gave the highest overall extraction efficiency for the target analytes, followed by acetonitrile and acetone. Therefore, methanol was selected as the desorption solvent for the subsequent studies.

The volume of methanol was then investigated by varying in the range from 50 to 250 μL in 50 μL intervals. It can be clearly seen from Fig. 4(b) that when the volume of methanol was increased, the extraction recovery increased up to 150 μL, and then it decreased slightly due to the effect of dilution. Therefore, 150 μL of methanol was selected as the optimum desorption volume.

The desorption time was studied in the range 1–10 min. As shown in Fig. 4(c), the extraction recovery of analytes increased up to 5 min and then decreased slightly. This may be due to the longer sonication time providing heat inside the vial and causing desorption of the analytes from the adsorbent into the aqueous phase, and thus loss of extraction efficiency. As a result, 5 min was selected as the optimum desorption time.

3.2. Reusability of the APTS-magnetic nanoparticle

The adsorbent was rinsed with 5 mL of acetonitrile three times with sonication and then dried at 90 °C for 1 h in an oven before being reused in the next D-μ-SPE. The results are shown in Fig. 5, indicating that the adsorbent still retained over 95% of efficiency for nine times without significant loss of extraction efficiency for

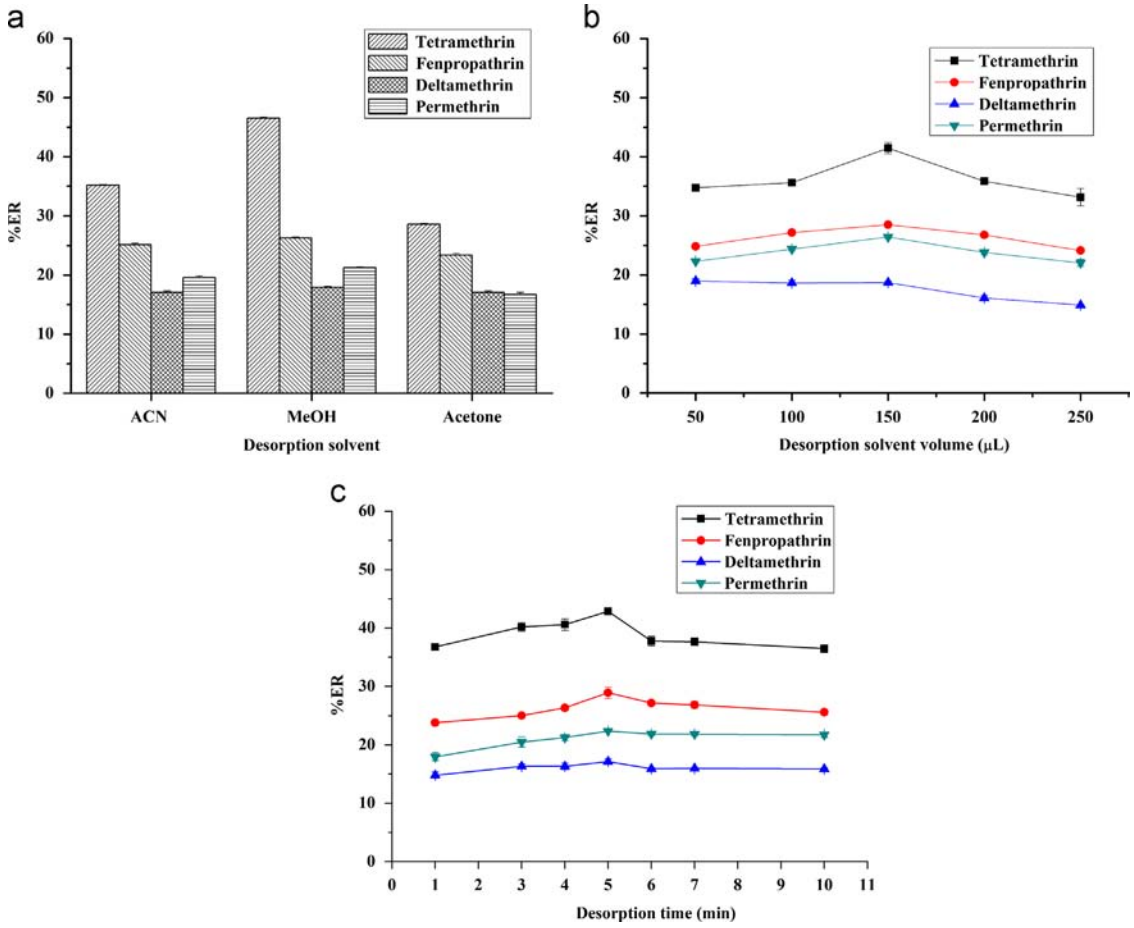


Fig. 4. The effect of type, volume and time of the desorption solvent on the extraction recovery of the pyrethroids (a) desorption solvent; extraction conditions: as described in Figs. 1–3 except extraction time for D-μ-SPE 3 min (b) desorption solvent volume; extraction conditions: as described in Figs. 1–3 and (a) except MeOH was used as desorption solvent (c) desorption time; extraction conditions: as described in Figs. 1–3, (a) and (b) except MeOH 100 μL was used as desorption solvent.

all the pyrethroids, and then decreased presumably due to loss of aminopropyl group on the surface of the magnetic nanoparticles.

3.3. Analytical performance

A series of working solutions containing a mixture of tetramethrin, fenpropathrin, deltamethrin and permethrin at five concentration levels of 10, 30, 50, 200 and 400 ng mL^{-1} were used to prepare calibration curves. For vegetable samples, the calibration curves were performed using matrix match method. For each concentration level, three replicate extractions were performed. The characteristic calibration data are listed in Table 2. Linearity was observed in the range 0.5–400 ng mL^{-1} (tetramethrin) and 5–400 ng mL^{-1} (fenpropathrin, deltamethrin and permethrin) with correlation coefficients (R^2) greater than 0.995.

Limit of detection (LOD) is defined as the concentration that giving the signal-to-noise ratio (S/N) of 3. The LODs of the studied pyrethroids were in the range 0.05–2 ng mL^{-1} for the target pyrethroids which are lower than those given by the US Environment Protection Agency (EPA) method (EPA method 1660). The limits of quantitation (LOQ, S/N=10) for the target analytes were 0.25–5 ng mL^{-1}. The precision is expressed as percent relative standard deviation (%RSD), was carried out using ten and five experiments at the concentration of 200 ng mL^{-1} for mixture of the pyrethroids. The precision were varied from 1.8 to 2.5%RSD for intra-day precision and lower than 9.0%RSD for inter-day precision, respectively. These results show that the proposed method has high sensitivity and precision.

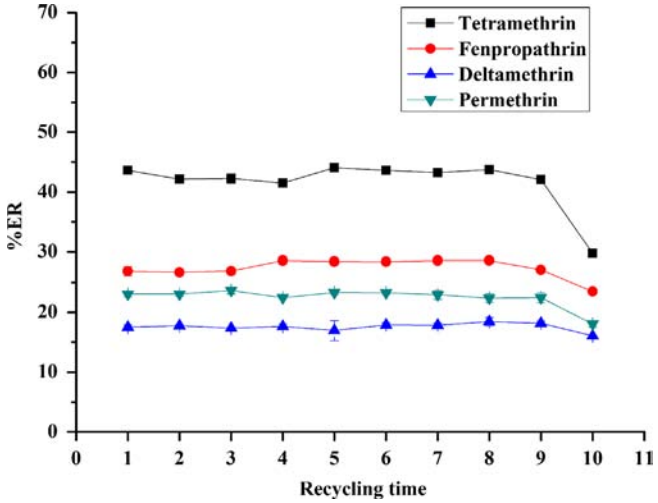


Fig. 5. Reuse of the APTS-MNPs on the extraction recovery of the pyrethroids; extraction conditions: as described in Figs. 1–4.

The enrichment factor (EF) is defined as the ratio between the concentration of the analyte after extraction and its initial concentration in the standard solution. The EFs of this method for tetramethrin, fenpropathrin, deltamethrin and permethrin were 108, 66, 51 and 93, respectively. Note that, tetramethrin has a higher EF than the others. This may due to its high polarity (low log K_{ow}, ca. 4.6) compared to the other analytes (log K_{ow}, ca. 5.6–

Table 2
Analytical performance data for the pyrethroids by the DLME/D-μ-SPE method.

Pyrethroid	Linear equation	Linear range (ng mL^{-1})	Correlation coefficient (R^2)	Precision (%RSD)		LOQ (ng mL^{-1})	EF	LOD (ng mL^{-1})	
				Intra-day ($n=10$)	Inter-day ($n=5\times3$)			This method	EPA method
Tetramethrin	$Y=9003.45X+172.30$ ($Y=83.65X-23.1863$)[a]	0.5–400 (200–10000)	0.9957 (0.9966)	2.1	6.2	0.25	108	0.05 (200)	2
Fenpropathrin	$Y=3795.43X+107.4$ ($Y=57.46X-18.7514$)	5–400 (500–10000)	0.9978 (0.9973)	2.3	7.4	3	66	0.5 (500)	nr
Deltamethrin	$Y=6005.32X+110.6$ ($Y=119.00X-58.9820$)	5–400 (500–10000)	0.9964 (0.9977)	1.8	9.0	3	51	0.5 (500)	nr
Permethrin	$Y=8057.08X+173.21$ ($Y=86.64X-22.3428$)	5–400 (500–10000)	0.9984 (0.9982)	2.5	8.6	5	93	2 (500)	2

nr, not reported.

[a] Values obtained from the standard without DLME/D-μ-SPE method are reported in parentheses.

Table 3
Comparison of the proposed method and some other methods for pyrethroids determination.

Method	Analytes	Sample	Adsorbent (mg)	EF	Linear range	LOD	Reuse (time)	% recovery	Ref.
Magnetic solid-phase extraction (MSPE)	- Lambda-cyhalothrin - Cypermethrin - Deltamethrin - Esfenvalerate - Permethrin - Bifenthrin	Vegetable (chiness cabbage and celery) samples	30	nr	5.0–500.0 ng g^{-1}	0.69–1.2 ng g^{-1}	8	76.0–99.5	[28]
SPE with SiO_2 microspheres	- Fenpropathrin - Cyhalothrin - Fenvalerate - Bifenthrin	Water samples	300	nr	0.1–5.0 ng mL^{-1}	0.004–0.08 ng mL^{-1}	nr	88.9–110.4	[36]
Magnetic carbon-nanotubes	- Beta-cyfluthrin - Cyhalothrin - Cyphenothrin	Tea samples	40	nr	0.05–25 μg g^{-1}	0.01–0.18 μg g^{-1}	nr	82.2–94.4	[37]
DLME/D-μ-SPE	- Tetramethrin - Fenpropathrin - Deltamethrin - Permethrin	Field water and vegetable (cucumber and cabbage) samples	10	51–108	0.5–500 ng mL^{-1}	0.05–2.0 ng mL^{-1} (water samples) 0.2–2.0 ng g^{-1} (vegetable samples)	9	91.7–104.5	Proposed method

nr, not reported.

6.5), resulting in the additional interaction via hydrophilic interaction between tetramethrin and aminopropyl group on surface of the adsorbent. The others may exhibit hydrophobic interaction only. In addition, the extraction efficiency of the two-step of DLME and D-μ-SPE is much higher than a single step, direct D-μ-SPE method, by 15 times.

The analytical characteristics of the proposed method have been compared to the other reported methods (SPE and HPLC), as summarized in Table 3. In terms of linearity, LODs and recovery, the proposed DLME/D-μ-SPE provides superior performance compared to the other reported methods. In addition, the proposed method uses less adsorbent and less organic solvent than the others.

3.4. Application to the real samples

The proposed method was applied to the determination of pyrethroids in field water (I, II and III) and vegetable samples (cucumber and cabbage). Pyrethroids were not detected in any of the studied samples. The accuracy of the method was evaluated by recovery. The recoveries of pyrethroids were studied by spiking the pyrethroids at three concentrations (1, 10 and 100 ng mL^{-1} for tetramethrin and 5, 30 and 100 ng mL^{-1} for the other pyrethroids) into the samples before the determination by the proposed DLME/D-μ-SPE. Table 4 summarizes the results of recovery. High recovery was obtained in the range of 91.7–104.0% (field water samples) and 91.7–104.5% (vegetable samples). Fig. 6(a) and (b) shows the typical chromatograms of the blank samples and the spiked samples. The high recovery indicated a negligible matrix effect on two-step DLME/D-μ-SPE efficiency in different sample matrices. Therefore, the proposed method has potential for applicability for the detection of pyrethroids in real samples.

4. Conclusions

This work demonstrates a sensitive and reliable method that includes the use of magnetic nanoparticles for simultaneous analysis of pyrethroids at trace concentration level. The method consists of the preconcentration of four pyrethroids using two-step microextraction method followed by analysis by HPLC. Dispersive liquid microextraction (DLME) combined with dispersive μ-solid phase extraction (D-μ-SPE) provided high extraction efficiency for preconcentration of pyrethroids with the enrichment

Table 4
Recoveries obtained in the determination of pyrethroids in spiked field water I, II, III and vegetable samples ($n=3$).

Fungicides	Spiked ($ng\ mL^{-1}$)	Field water I			Field water II			Field water III			Spiked ($\mu g\ kg^{-1}$)	Cucumber		Cabbage	
		Measured ($ng\ mL^{-1}$)	%R	% RSD	Measured ($ng\ mL^{-1}$)	%R	% RSD	Measured ($ng\ mL^{-1}$)	%R	% RSD		%R	% RSD	%R	% RSD
Tetramethrin	0	–									0	–			
	1	0.97	96.5	3.6	1.0	102.7	4.7	0.98	97.9	5.6	0.01	101.8	5.3	92.5	6.7
	10	9.2	91.7	2.6	9.2	92.16	2.2	9.3	92.8	2.0	1	98.3	5.5	100.4	3.0
	100	97.6	97.6	1.1	99.4	99.42	1.6	1.6	97.4	1.4	100	96.7	1.1	98.52	1.9
Fenpropathrin	0	–									0	–			
	5	4.9	97.6	3.6	4.8	96.8	4.9	5.0	100.5	3.0	0.50	100.6	6.1	94.5	3.4
	30	28.3	94.2	4.2	29.2	97.4	3.3	28.1	93.8	4.0	3	100.5	2.4	102.6	1.2
	100	97.7	97.7	1.2	97.7	99.7	1.2	96.0	96.0	3.4	100	98.3	1.3	98.6	1.4
Deltamethrin	0	–									0	–			
	5	5.2	104.0	3.3	5.0	99.9	3.4	5.2	104.0	2.9	0.50	103.5	2.6	104.5	3.6
	30	29.4	98.1	4.0	30.1	100.4	2.0	27.9	93.2	3.9	3	91.7	5.7	98.8	2.7
	100	99.2	99.2	1.3	99.0	99.0	1.7	100.2	100.2	1.5	100	97.5	2.0	102.3	4.0
Permethrin	0	–									0	–			
	5	4.7	94.7	3.2	4.9	98.8	5.3	5.0	99.0	4.0	0.50	95.3	6.1	100.8	4.8
	30	28.4	94.6	4.5	28.4	94.8	4.4	28.4	94.7	4.5	3	98.1	4.5	95.72	5.2
	100	93.1	93.1	1.3	92.9	92.9	1.7	93.0	93.0	1.4	100	95.8	3.0	97.4	2.0

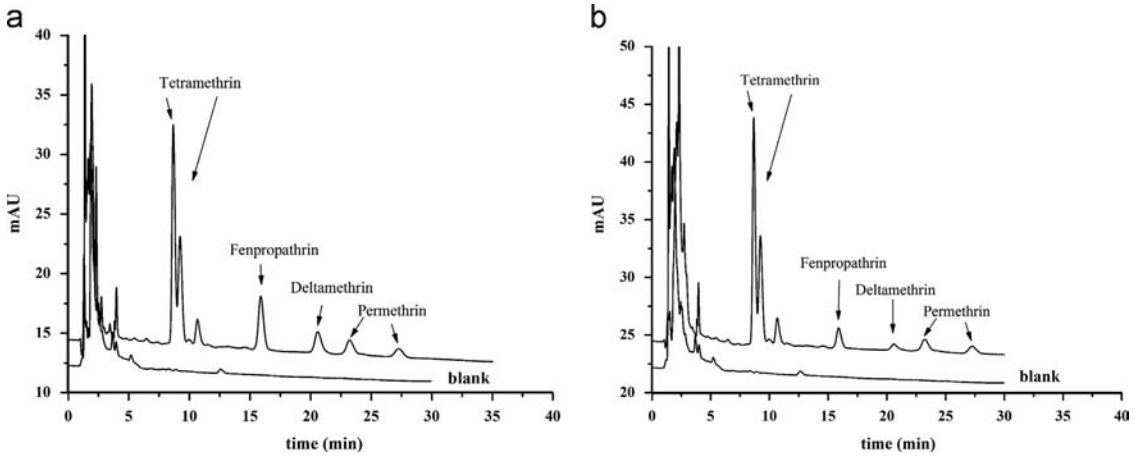


Fig. 6. Chromatograms of blank samples and spiked samples (100 $ng\ mL^{-1}$ each of pyrethroids): (a) field water I sample and (b) cucumber sample.

factors between 51 and 108. The limits of detection were in the range 0.05–2.0 $ng\ mL^{-1}$ (water samples) and 0.02–2.0 $ng\ g^{-1}$ (vegetable samples) which are lower than the MRLs established by CODEX in vegetables. The two-step microextraction (DLME /D-μ-SPE), has advantages of ease of operation, short extraction time, and lower consumption of toxic organic solvents making it more environmentally friendly. In addition, the APTS-magnetic nanoparticle can be readily reused nine times with high extraction efficiency. It has been successfully applied to the analysis of pyrethroids in field water and vegetable samples with good recoveries in the range of 91.7–104.5%.

Acknowledgments

This paper is dedicated to Prof. Dr. Kate Grudpan (Chiang Mai University, Thailand) in celebration of his 60th birthday. The Development and Promotion of Science and Technology Talents Projects (DPST) is gratefully acknowledged for financial support to S. Mukdasai. The valuable suggestions from Prof. Richard L. Deming (California State University of Fullerton, USA) are also acknowledged. One of the author (C. Thomas) would like to thank the National Research Council of Thailand for the research funding in applications of magnetic nanoparticle for better health and quality of life.

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