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Rapid analysis of organochlorine and pyrethroid pesticides in tea samples by directly suspended droplet microextraction using a gas chromatography–electron capture detector

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ABSTRACT

A simple and efficient directly suspended droplet microextraction (DSDME) has been developed to extract and pre-concentrate organochlorine and pyrethrin pesticides from tea samples prior to analysis by a gas chromatography–electron capture detector (GC–ECD). The optimal experimental conditions of DSDME were: 100 μL isooctane exposed for 15 min to 5 mL of the tea aqueous sample stirred at 1100 rpm. For most of the target analytes, the optimal pretreatment of DSDME processes led to no significant interference of tea matrices. The approach was applied to the determination of organochlorine and pyrethroid pesticides in tea samples, with a linearity range of 0.0005–2 μg/mL. The relative recoveries of all the pesticides ranged between 80.0% and 120.8% with relative standard deviations (RSDs) in the range of 0.8–19.9% ($n = 5$). The limits of detections (LODs) ranged between 0.04 and 1 μg/L for all the target pesticides.

1. Introduction

Sample preparation is usually necessary in order to extract, isolate, and concentrate the analytes of interest from complex matrices. Conventional sample preparation techniques, time-consuming procedures, and large amounts of sample and organic solvents, are known to complicate analyses. Modern trends in analytical chemistry have led to the simplification and miniaturisation of sample preparation and have decreased the quantities of organic solvents used [1,2]. Liquid-phase microextraction (LPME), an alternative, miniaturised sample-preparation approach, emerged in the mid-to-late 1990s. LPME is a solvent-minimised sample-pretreatment procedure of liquid–liquid extraction (LLE) in which several microliter volumes of the solvent are required to concentrate analytes from various samples, rather than the hundreds of milliliters needed in traditional LLE. A technique termed single-drop microextraction (SDME) [3–5] was developed in which a microliter drop of water-immiscible organic solvent is suspended on the tip of either a Teflon rod or the needle tip of a microsyringe immersed in the stirred aqueous solution. Compared to classical methods, the consumption of organic solvent observed with SDME is significantly reduced (several hundred or several thousand times), with a much better enrichment of analytes. However, the major practical problem is the dislodging of the microdrop by the stirred aqueous sample.

A novel LPME method named directly suspended droplet microextraction (DSDME) was first introduced by Lu and co-workers in 2006 [6]. Compared to other LPME methods (e.g., SDME), DSDME does not require special equipment, the organic drop is more stable, and the equilibrium is quickly reached. In this method, a stir bar is placed at the bottom of a vial containing an aqueous sample and rotated at a speed required to cause a gentle vortex. If a small volume of an immiscible organic solvent is added to the surface of the aqueous solution, the vortex results in the formation of a single droplet at or near the centre of rotation. The droplet itself may also rotate on the surface of the aqueous phase, thereby increasing mass transfer. Other advantages of DSDME include low cost because it requires only common laboratory equipment, as well as simplicity and fast analysis of trace components in many matrices. The application of DSDME from aqueous matrices has been demonstrated. Sarafraz-Yazdi et al. developed DSDME with gas chromatography–flame ionisation detector (GC–FID) for the determination of two tricyclic antidepressant drugs (TCAs), amitriptyline and nortriptyline, in water, urine [7] and BTEX compounds [8]. The same authors also used the method combined with HPLC for the determination of diclofenac [9] and 3-nitroaniline [10]. The DSDME method had a high enrichment factor and excellent selective clean-up of samples. Good linearity and reasonable relative recovery were also obtained. Subsequently, in 2009, Gao et al. [11]

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addressed the challenges associated with DSDME by utilising a rotating vial instead of a stir bar for mixing samples. Suitable operating conditions (1-octanol as a solvent, 20 min extraction time, 1000 rpm vial rotating speed) were established, and DSDME/GC and DSDME/UV–vis spectrometry analysis methods were used for trace organic compound (nitrobenzene) detection. The analysis of the microextraction method results showed that standard curves for both analysis methods exhibited good linearity and repeatability.

Es'haghi [12] used a novel application of the DSDME method based on a three-phase extraction system which was compatible with HPLC-DAD for determining MDMA (3,4-methylendioxy-N-methylamphetamine) concentrations in hair samples. In this method, MDMA in hair was digested and extracted after treatment. In triple phase DSDME, the acceptor solution was an aqueous phase providing a three-phase system where MDMA was extracted from an aqueous sample, through the thin layer of 1-octanol (organic solvent), and into an aqueous acceptor droplet. Under the optimal conditions, the MDMA was enriched by a factor of 98.11. Linearity ($r = 0.9921$) was obtained in the range of 10–15,000 ng/mL with a detection limit of 0.1 ng/mL. DSDME-microvolume UV–vis spectrophotometry has also been used for the determination of phosphate [13]. The method is based on the extraction of the ion pair formed between 12-molybdophosphate and malachite green onto a microdrop of methyl isobutyl ketone, and subsequent spectrophotometric determination with no dilution. An EF of 325 was obtained after 7.5 min of microextraction. DSDME provides high sensitivity for phosphate determination along with low consumption of both the sample and organic solvent. The method was successfully applied to the determination of dissolved reactive phosphorus in different freshwater samples. Gao et al. [14] developed a simple and novel method of DSDME combined with single drop back-extraction prior to capillary electrophoresis (CE) detection to three alkaloid (BBR, PMT and THP) compounds in aqueous sample. The enrichment factors ranged from 231 to 524 and the LODs varied from 8.1 to 14.1 ng/mL. Human urine samples were spiked with three alkaloid standards to assess the matrix effects. Satisfactory results were obtained.

DSDME-GC–MS coupled with in injection-port derivatisation was applied to determine different classes of polyphenols in herbal infusions, fruits and functional foods [15]. In injection-port derivatisation, a reaction with bis(trimethylsilyl)trifluoroacetamide (BSTFA) is carried out to convert the polar nonvolatile polyphenols into volatile derivatives. Under the optimal collection efficiency and derivatisation reaction, the recoveries obtained for spiked samples are satisfactory for all the compounds.

The DSDME technique has been utilised by many researchers who have applied it for the analysis of water or other relatively clean samples.

Tea was discovered nearly 5000 years ago and it is the most heavily consumed drink in the world. Pesticide residues in tea leaves raise public concerns as drinking tea is an integral part of the everyday routine for many people. Additionally, pesticide residues may cause acute or chronic adverse health effects. Tea matrix is very "dirty" as it contains pigments, caffeine, sugars, organic acids and other interferences [16]. The effective isolation and/or concentration of target analytes from tea samples is important, making the analytes more suitable for separation and detection [17]. Different methods for the determination of pesticides amounts in tea samples over the calendar years from 2003 to 2011 are detailed in Table 1. Sample preparation techniques (i.e., LLE, SPE and GPC [18,22,24,25,28,34]) are effective clean-up methods which have been widely applied. However, the main drawbacks of the methods are that they tend to be complicated, time-consuming procedures and that they necessitate large amounts of sample and organic solvents. Using harmful chemicals and large amounts of solvents causes environmental pollution, health hazards to laboratory personnel and extra operational costs for waste [1]. Huang and Huang [32] reported on dynamic hollow fibre membrane HFM-LPME for the analysis of organochlorine pesticides (OCPs) in green tea leaves and ready-to-drink tea with GC–ECD detection. The method provides an extract with good enrichment factors along with excellent sample cleanup. In comparison to porous HFM supported LPME, the cost of DSDME is lower, as the fibres are expensive and have a limited lifetime. DSDME has advantages such as ease of operation, freedom from cross contamination, and speed in reaching extraction equilibrium [6].

No report on the extraction of pesticides from tea sample employing the DSDME technique is presently available. In this work we present the use of DSDME to extract 28 organochlorine and pyrethroid pesticides from tea samples. The determination of pesticide amounts was carried out using gas chromatography with electron capture detector (GC–ECD). DSDME extraction parameters (i.e., organic solvent type and volume, stirring speed and extraction time) were systematically optimised and the procedure was then applied to the recovery of organochlorine and pyrethroid pesticides in spiked tea samples.

2. Experimental

2.1. Reagents and materials

All solvents (HPLC-grade) were supplied from Tedia (Fairfield, OH, USA). Stock solutions of 1000 μg/mL for each pesticide (alpha-hexachlorocyclohexane (HCH), beta-HCH, gamma-HCH, delta-HCH, hexachlorobe, heptachlor, aldrin, pp′-DDE, dieldrin, pp′-DDD, op′-DDT, pp′-DDT, s-bioallethrin, bifenthrin, fenpropathrin, cyhalothrin, permethrin, cyfluthrin, flucythrinate, fenvalerate and deltamethrin) prepared in acetone were obtained from Agricultural Environmental Protection Institution in Tianjin, China. Mixed standard working solution was separated into two groups. Mixed working solutions of group 1 (OCPs) and group 2 (pyrethroids) were prepared by dilution of standard stock solution with acetone. All solutions were stored in the dark at 4 °C. Deionised water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Acetone, toluene, n-hexane, isooctane, cyclohexane, acetonitrile and ethyl acetate were HPLC-grade. Cleaner PSA (40–60 μm) was obtained from Agela Technologies.

2.2. Sample preparation

Different samples of dry tea (green and black), tea drinks (iced green, iced black and iced jasmine) and tea bags were purchased from a local supermarket. An initial analysis confirmed that tea samples were free of all target analytes. Tea drinks were diluted one time with ultrapure water (dilution ratio 1:1, v/v) before the DSDME procedure. The tea infusions were prepared by introducing the weighed bag (approximately 2 g) to 100 mL of boiled water for 5 min. After cooling, 5 mL of the supernatant solution was extracted with DSDME. Dry tea samples were ground and sieved through a prescription sieve (0.45 mm aperture size). A 0.5 g dry tea sample was weighed into a 50 mL PTFE centrifuge tube. Ten milliliters of MeCN, with 0.05 g PSA added, was vigorously shaken on a Vertex mixer immediately for 2 min. The mixed samples were centrifuged for 5 min at 4000 rpm. A 1.5 mL aliquot of the upper MeCN phase was transferred into 12 mL cylindrical sample vial and the solvent was diluted with 3.5 mL ultrapure water. A 5 mL tea sample solution was extracted with DSDME.

Table 1
Different methods for the determination of pesticides in tea samples.

No.	Date	Pesticides	Sample preparation	Detection	LOD	Linear range	r^2	RSD%	Recovery%	Reference
1	2011	65	Quechers	UPLC/MS/MS	LOQ: 5–10 μg/kg		>0.99	1.5–33.7	70–120	[16]
2	2011	Dinotefuran, thiamethoxam, clothiandin, imidacloprid, acetamiprid and thiacloprid	SPE	LC–MS/MS	0.02 mg/kg	4–100 μg/L	≥0.9991	2.7–7.9	84.3–106.1	[18]
3	2010	13 (ethoprophos, thiometon, terbufos, tefluthrin, probenfos, vinclozolin, isofenphos, phenthoate, chlorfenapyr, propiconazol, EPN λ-cyhalothrin)	SPME (SWCNTs)	GC–MS	0.027–0.23 ng/mL	0.125–25 ng/mL	≥0.9928	2.3–14.6	75.1–118.4	[19]
4	2010	42	Dispersive-SPE	LC–MS/MS	4–50 ng/g	n.r.	>0.99	<15	66–105	[20]
5	2010	6 pyrethrins	SPE	UPLC/MS/MS	LOD: 0.001–0.009 mg/kg LOQ: 0.004–0.03 mg/kg	n.r.	>0.99	2.71–12.93	76.15–101.86	[21]
6	2009	Ethion, endosulfan, dicofol, chlorpyrifos, deltamethrin, hexaconazole, fenpropathrin, propargite, quinalphos and lambdacyhalothrin	LLE (partitioning with hexane (three times 100 mL))	GC (ECD, NPD) HPLC (DAD)	n.r.	n.r.	n.r.	0.5–2.8	89.7–93.0	[22]
7	2009	10 organophosphorus pesticides	DLLME	GC–FPD	0.03–1 μg/kg	0.01–20.0 ng/g.	n.r.	3–7.8	83.3–117.4	[23]
8	2009	lambda-cyhalothrin	LLE	GLC	n.r.	n.r.	n.r.	n.r.	93.8–96.3	[24]
9	2008	33 (organophosphorous, organochlorine and pyrethroid pesticides)	ASE, GPC and SPE	GC–MS	0.005–0.05 mg/kg	0.005–1 μg/mL	>0.999	<20	35.4–108.1	[25]
10	2008	36	HS-SPME, HPGPC	GC × GC/TOF MS	1–28 μg/kg	1.25–200 μg/L	0.9812–0.9999	<24		[26]
11	2007	5 pyrethroid	SBSE (stir bar sorptive extraction-thermal desorption)	GC–MS	4.2–10.5 ng	19.4–1210 ng	0.9960–0.9999	5.0–9.6	98.2–110.1	[27]
12	2007	102	GPC, SPE	GC–MS	0.012–2.45 μg/mL	0.02–127.5 μg/mL	>0.905	3.0–20.8	59.7–120.9	[28]
13	2007	5 organochlorine pesticides	MASD	GC–ECD	0.025–0.23 μg/kg	0.1–2000 ng/mL	n.r.	2.2–8.4	84.04–110.1	[29]
14	2007	Malathion, fenitrothion, dimethoate, chlorpyrifos and pirimiphos-ethyl	LLE, GPC	GC–FID	n.r.	n.r.	n.r.	3.19–4.75	85.4–109.5	[30]
15	2007	10 pesticides (organochlorines, organophosphorus compounds and pyrethrins)	SPME with a 100 μm PDMS fibre-coating	GC–AED	0.03–11.9 ng/mL LOQ: 0.11–39.6 ng/mL	0.1–2000 ng/mL	n.r.	5.4–14.3	73.5–108.3	[31]
16	2006	6 organochlorine pesticides (OCPs)	DHFP-LPME	GC–ECD	<1 μg/L	0.05–50 μg/L	0.031–0.164	<12.57	Absolute recovery 0.02–16.7	[32]
17	2006	82 pesticides – organochlorine, carbamate, organophosphorous, pyrethroid and others	SBSE-TD-LTM	GC–MS	<10 ng/L	n.r.	>0.99	n.r.	n.r.	[33]
18	2005	Bifenthrin	LLE–SPE	GC–ECD	<0.05 mg/kg	0.1–1.0 mg/L	0.9998	1–6	89–108%	[34]
19	2005	21 (organochlorines and pyrethroids)	MSPD	GC–ECD	LOQ: 0.002–0.06 mg/kg	n.r.	n.r.	<7	80–97	[35]
20	2003	Organochlorine pesticides (OCPs)	MAE-SPME	GC–ECD	<0.081 ng/L	0.1–10^3 ng/L.	0.9925–1	<16	39.05–94.35	[36]

n.r., not reported.

2.3. Instrumentation

All analyses were conducted with an Agilent Model 6890N GC equipped with an electron capture detector (ECD). The system was equipped with a split/splitless injection inlet and an electronic pressure control. An Agilent Chemstation was used for instrument control and data analysis (Agilent, Palo Alto, CA, USA). The chromatographic conditions were as follows. An A30-m ZB-5 (0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation. Nitrogen was used as the carrier gas (1 mL/min) and the make-up gas (40 mL/min). The inlet was maintained at 290 °C and operated in the splitless mode. The detector temperature was 300 °C. The oven temperature program was: 100 °C for 1 min, raised to 280 °C (20 °C/min) and held for 1 min; then raised to 300 °C (20 °C/min) and held for 5 min.

2.4. DSDME procedure

In this extraction procedure, a cylindrical sample vial (12 mL, O.D. 18.5 mm) with screw top/silicon septa, 10 μL flat-cut syringe (Melbourne, Australia), and a magnetic stir bar of cylindrical type (10 mm × 6 mm O.D.) were used.

A 5 mL sample solution (tea drinks, tea infusion or dry tea MeCN extract dilution) was held in the 12 mL sample vial, and a stirring bar was placed within the sample solution. The magnetic stirrer was turned on and set to 1100 rpm for stirring the extraction mixture. The stirring bar was kept rotating smoothly in order to form a steady vortex. Then, 100 μL of immiscible organic solvent was placed at the bottom of the vortex. The screw cap was kept closed during the extraction process. After 15 min, the screw cap was removed and a portion of the organic droplet was drawn out by microsyringe and placed into a 100 μL inert vial and then automatically injected into the GC–ECD system for analysis.

3. Results and discussion

3.1. Optimisation of directly suspended droplet microextraction method

The different parameters affecting the extraction efficiency such as the organic solvent, the extraction time, the microdroplet volume, and the stirring speed were optimised.

3.1.1. Selection of organic solvent

To achieve acceptable selectivity and extraction efficiency, it is necessary to choose a proper organic solvent. The chosen organic solvent should have a very low solubility in water to avoid dissolution in the aqueous sample and also have low vapour pressure to prevent loss during extraction [7]. Based on these considerations, toluene, n-hexane, cyclohexane and isooctane were investigated (Table 2) [37]. Solvent selectivity was evaluated with 100 μL of extraction solvent and a 5 mL deionised water sample spiked at 1–20 μg/L with all target analytes. These were stirred at 1100 rpm for 10 min. The peak area was selected as the extraction efficiency for each solvent. As shown in Fig. 1, the peak areas of isooctane, cyclohexane and toluene were higher than n-hexane. Among them, cyclohexane was not used as the extractant since the drop inside of tea sample solution was not very stable. Toluene absorbed pigment impurities from tea samples. Isooctane was chosen as the extraction solvent because it has higher viscosity and a more stable droplet.

3.1.2. Organic solvent volume

The volume of the extractor organic droplet has a great effect on the extraction efficiency. In the present work, the volume of the sample solution was kept constant at 5 mL and different microextract (isooctane) volumes of 50, 80, 100, and 120 μL were exposed separately to the tea solution fortified with 1 μg/L organochlorine and 10 μg/L pyrethroid pesticides for 10 min with stirring at 1100 rpm. Most of the analytes presented higher response for 100 μL of isooctane. The use of a larger drop can be transferred with a micropipette easily, but a very large drop causes a decrease in the enrichment factor due to the dilution of the analytes in these large droplets. Smaller volumes of the organic solvent tended to cause instability of the aqueous droplet during agitation. The drop is difficult to collect. Consequently, an optimal 100 μL volume of the organic solvent was chosen for DSDME.

3.1.3. Stirring speed

The agitation of the sample solution enhances microextraction. In DSDME, the stirring speed has a direct influence on both the shape of the droplet and its mass transfer characteristics in the aqueous sample. In general, a proper stirring speed should be convenient for operation and intensify mass transfer effectively [6]. To evaluate the effect of the stirring speed, tea aqueous samples (spiked at 1 μg/L OCPs and 10 μg/L pyrethroid pesticides) were extracted in 100 μL extraction solvent for 15 min at different stirring rates (900, 1000, 1100 and 1200 rpm). As shown in Fig. 2, the peak areas of all analytes increase with increasing stirring speed. It was observed that the stirring speed above 1100 rpm causes instability and dissolution of the solvent droplet. As a result, the 1100 rpm stirring speed was chosen as optimal in our experiments.

3.1.4. Extraction time

To investigate the influence of extraction time on the DSDME, 5 mL aqueous tea samples spiked with 1 μg/L OCPs and 10 μg/L pyrethroids were extracted in 100 μL extraction solvent under different extraction time intervals (5, 10, 15, 20 min) at a stirring rate of 1100 rpm. Fig. 3 shows the effect of the extraction time on the method efficiency. By increasing the extraction time, the peak area related to the analyte concentrations increased up to 15 min, after which most of the analytes decreased with increasing extraction time. The extract concentrations of op′-DDT and pp′-DDT increased with the increase of the extraction time.

A long extraction time of microextraction to reach complete equilibrium may result in drop dissolution and a high rate of drop loss. The exposure time can be chosen such that it is just sufficient for obtaining satisfactory precision. Based on the results, 15 min was selected as the optimal extraction time.

3.2. Method analytical performance

Based on the method described above, the following are the optimal conditions of DSDME: 5 mL tea sample solution, isooctane organic solution, 100 μL microextract volume, 15 min extraction time, and 1100 rpm stirring speed.

The method was validated in terms of its linearity and the limits of detections (LODs) under the optimal conditions. A calibration study was performed by spiking blank tea samples with analytes over the concentration range of 0.0005–2 μg mL^{-1}. The results are shown in Table 3. LODs at an S/N of 3 were 0.04 μg/L for α-HCH, hexachlorobe, γ-HCH, aldrin, pp′-DDE, dieldrin, pp′-DDD, 0.08 μg/L for β-HCH, δ-HCH, heptachlor, s-bioallethrin, 0.1 μg/L for op′-DDT, PP′-DDT, 0.15 μg/L for cyhalothrin-I, cyhalothrin-II, 0.3 μg/L for bifenthrin, fenpropathrin, 0.5 μg L^{-1} for cyfluthrin-I, cyfluthrin-II, cyfluthrin-III, flucythrinate-I, flucythrinate-II, fenvalerate-I, fenvalerate-II, deltamethrin-I, deltamethrin-II and 1 μg/L for permethrin-I, permethrin-II. All calibration curves had good linearity with correlation coefficients ranging from 0.9864 to 0.9978.

Table 2
Characteristics of organic solvents.

Solvent	Density, g/cm^3	Solubility in water, g/L	Surface tension, dyn/cm	Viscosity C.P. 30 °C	Log $P_{o/w}$
Isooctane	0.86	0.001	28.7	7.7	4.09
Toluene	0.87	0.53	28.5	0.59	2.69
n-Hexane	0.659	0.013	18.4	0.31	3.9
Cyclohexane	0.779	Insoluble	24.99	0.98	3.18

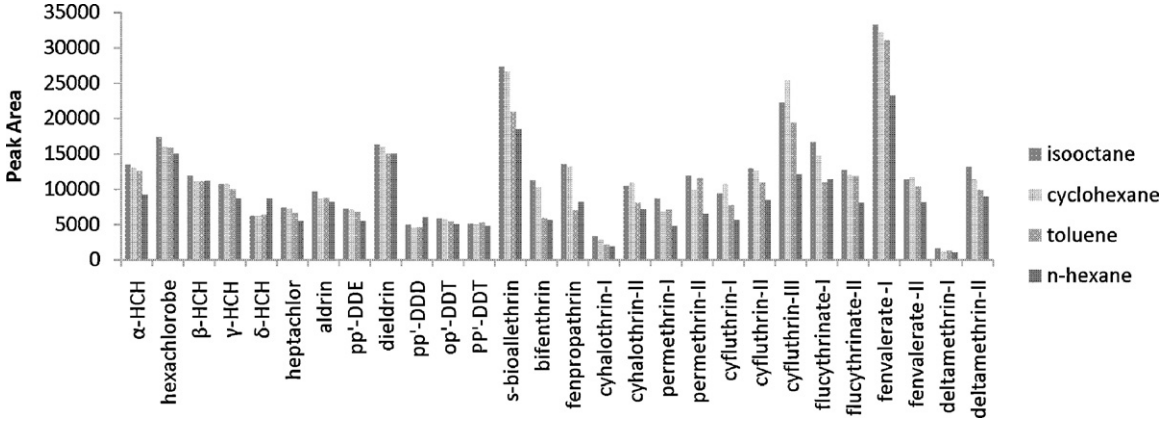

Fig. 1. Comparison of the extraction efficiency of different organic solvents on DSDME ($n = 3$).

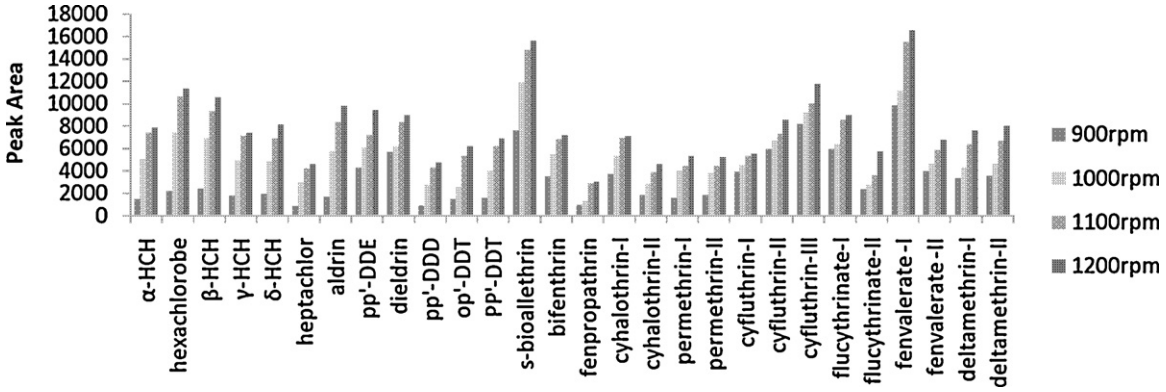

Fig. 2. Plot of different stirring rates on the extraction efficiency of DSDME for organochlorine and pyrethroid pesticides.

3.3. Recovery study

The DSDME technique was applied for the determination of organochlorine and pyrethroid pesticides in tea matrix samples. Tea samples, including dry tea (green and black), tea drinks (iced green, iced black and iced jasmine) and tea bags, were purchased from a local supermarket. The samples were treated as indicated above. Recovery experiments were carried out using 5 mL of the tea drink or tea infusion and 0.5 g dry tea, which were spiked with 100 μL of a standard mixture of organochlorine and pyrethroid pesticides using a microsyringe. Samples were mixed well and were allowed to stand in room temperature for at least half an hour before starting the extraction procedure. The DSDME was applied under the described optimal conditions. Typical chromatograms of

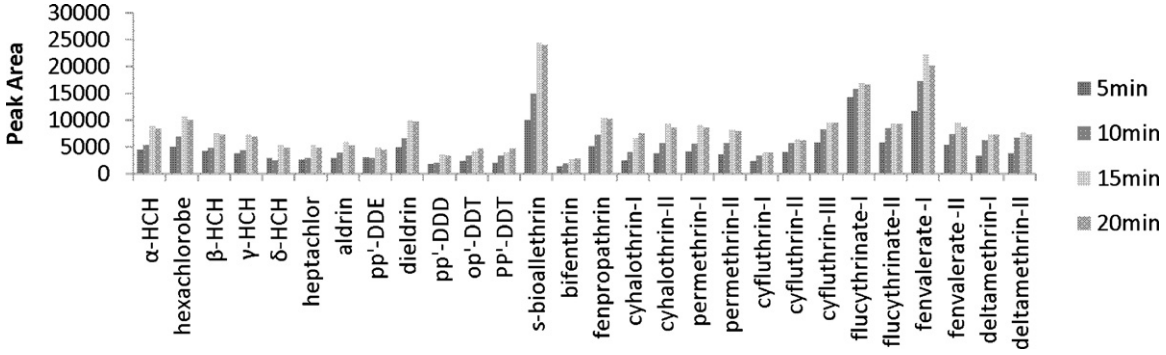

Fig. 3. Plot of different extraction times on the extraction efficiency of DSDME for organochlorine and pyrethroid pesticides.

Table 3
Linear equation, correlation coefficients (γ), linear range and LOD of DSDME method.

Analyte	Linear regression equation[a]	Correlation coefficient[b]	Linear range (μg/mL)	LOD (μg/L)[c]
α-HCH	$A = 3 \times 10^6 C - 761$	0.9978	0.0005–0.1	0.04
Hexachlorobe	$A = 5 \times 10^6 C - 156$	0.9993	0.0005–0.1	0.04
β-HCH	$A = 1 \times 10^6 C + 30$	0.9981	0.001–0.2	0.08
γ-HCH	$A = 2 \times 10^6 C + 3540$	0.9939	0.0005–0.1	0.04
δ-HCH	$A = 2 \times 10^6 C + 83$	0.9933	0.001–0.1	0.08
Heptachlor	$A = 78{,}313C + 2049$	0.9930	0.001–0.3	0.08
Aldrin	$A = 3 \times 10^6 C - 3565$	0.9975	0.0005–0.1	0.04
pp′-DDE	$A = 3 \times 10^6 C + 1155$	0.9987	0.0005–0.1	0.04
Dieldrin	$A = 4 \times 10^6 C + 350$	0.9945	0.0005–0.1	0.04
pp′-DDD	$A = 1 \times 10^6 C + 553$	0.9951	0.0005–0.1	0.04
op′-DDT	$A = 90{,}209C - 310$	0.9938	0.001–0.2	0.1
PP′-DDT	$A = 9 \times 10^6 C + 1317$	0.9929	0.001–0.2	0.1
s-bioallethrin	$A = 1 \times 10^6 C - 4871$	0.9913	0.001–0.125	0.08
Bifenthrin	$A = 4 \times 10^6 C - 3058$	0.9972	0.004–0.5	0.3
Fenpropathrin	$A = 4 \times 10^6 C - 6025$	0.9929	0.004–0.5	0.3
Cyhalothrin-I	$A = 1 \times 10^6 C - 1306$	0.9923	0.002–0.25	0.15
Cyhalothrin-II	$A = 9 \times 10^6 C - 12{,}231$	0.9864	0.002–0.25	0.15
Permethrin-I	$A = 38{,}079C - 244$	0.9977	0.016–2	1
Permethrin-II	$A = 25{,}283C - 1146$	0.9926	0.016–2	1
Cyfluthrin-I	$A = 1 \times 10^6 C - 5482$	0.9935	0.008–1	0.5
Cyfluthrin-II	$A = 1 \times 10^6 C - 7556$	0.9951	0.008–1	0.5
Cyfluthrin-III	$A = 3 \times 10^6 C - 13{,}415$	0.9920	0.008–1	0.5
Flucythrinate-I	$A = 30{,}622C + 303$	0.9978	0.008–1	0.5
Flucythrinate-II	$A = 3 \times 10^6 C - 16{,}374$	0.9905	0.008–1	0.5
Fenvalerate -I	$A = 5 \times 10^6 C - 21{,}975$	0.9910	0.008–1	0.5
Fenvalerate -II	$A = 1 \times 10^6 C - 5932$	0.9949	0.008–1	0.5
Deltamethrin-I	$A = 31{,}180C - 1406$	0.9954	0.008–1	0.5
Deltamethrin-II	$A = 3 \times 10^6 C - 14{,}193$	0.9962	0.008–1	0.5

[a] A, peak area and C, concentration of analytes (μg/L).
[b] Correlation coefficient was calculated by analysis tea aqueous samples fortified level between 0.0005 and 1 μg/mL.
[c] LOD was calculated for a three signal to noise ratio (S/N = 3).

organochlorine and pyrethrin pesticides are shown in Fig. 4a and b. The detection results of organochlorine and pyrethroid pesticides in tea samples are shown in Table 4. The relative recovery (defined as the ratios of the peak areas of the analyses in the spiked real samples and the peak area of the analyses in pure distilled water sample spiked with the same amount of the analyte [38]) were between 80.0 and 120.8%. The RSDs were 0.8–19.9%. The results indicated that the DSDME method was feasible for the

Table 4
Relative recoveries and precision of the DSDME technique for tea samples spiked with the analyte ($n = 5$).

Analytes	F_1[a]	Tea drinks		Tea infusion		F_2[b]	Dry tea	
		Relative recovery%	RSD%	Relative recovery%	RSD%		Relative recovery%	RSD%
α-HCH	0.1	97.3	3.6	88.7	3.2	5	98.5	4.6
Hexachlorobe	0.1	83.9	6.2	104.9	16.3	5	99.0	7.7
β-HCH	0.25	95.8	6.4	86.7	2.2	13	94.2	19.4
γ-HCH	0.1	97.3	5.5	87.4	2.0	5	96.4	3.3
δ-HCH	0.1	102.3	4.1	87.3	3.5	5	91.0	9.1
Heptachlor	0.25	80.0	8.1	96.3	12.4	13	97.1	9.9
Aldrin	0.1	77.7	5.6	120.8	19.6	5	100.6	7.9
pp′-DDE	0.1	105.3	16.4	99.0	9.3	5	94.3	10.7
Dieldrin	0.1	88.2	4.0	104.1	12.4	5	102.1	7.8
pp′-DDD	0.1	92.3	16.0	113.7	8.3	5	90.8	14.6
op′-DDT	0.25	83.5	7.5	100.0	16.9	13	92.2	13.2
PP′-DDT	0.25	82.8	5.1	112.4	9.2	13	93.4	13.2
s-bioallethrin	1	90.1	7.3	90.1	6.2	5	88.7	3.7
Bifenthrin	4	82.1	17.1	74.7	19.9	20	89.3	2.9
Fenpropathrin	4	86.9	12.4	98.3	9.7	20	88.1	6.9
Cyhalothrin-I	2	94.4	10.7	96.2	10.0	10	84.0	5.1
Cyhalothrin-II	2	93.6	8.0	96.7	12.3	10	91.5	5.8
Permethrin-I	16	92.6	7.0	94.1	13.9	80	81.4	9.6
Permethrin-II	16	91.8	7.8	98.0	7.3	80	89.5	0.8
Cyfluthrin-I	8	88.4	5.8	96.6	13.7	40	83.1	13.6
Cyfluthrin-II	8	88.5	5.2	98.3	11.4	40	92.8	14.9
Cyfluthrin-III	8	87.8	5.0	96.4	14.0	40	87.8	14.3
Flucythrinate-I	8	89.6	18.4	102.6	9.9	40	88.7	4.2
Flucythrinate-II	8	86.0	12.1	87.2	7.5	40	95.0	10.7
Fenvalerate-I	8	86.6	11.0	88.3	1.1	40	88.0	14.9
Fenvalerate-II	8	84.1	19.7	83.2	16.0	40	94.0	8.5
Deltamethrin-I	12	86.0	12.3	92.0	15.6	60	100.9	7.4
Deltamethrin-II	12	83.9	10.7	88.3	0.8	60	90.9	11.7

[a] Fortification level (μg/L)in tea drinks and tea infusion samples.
[b] Fortification level (μg/kg) in dry tea sample.

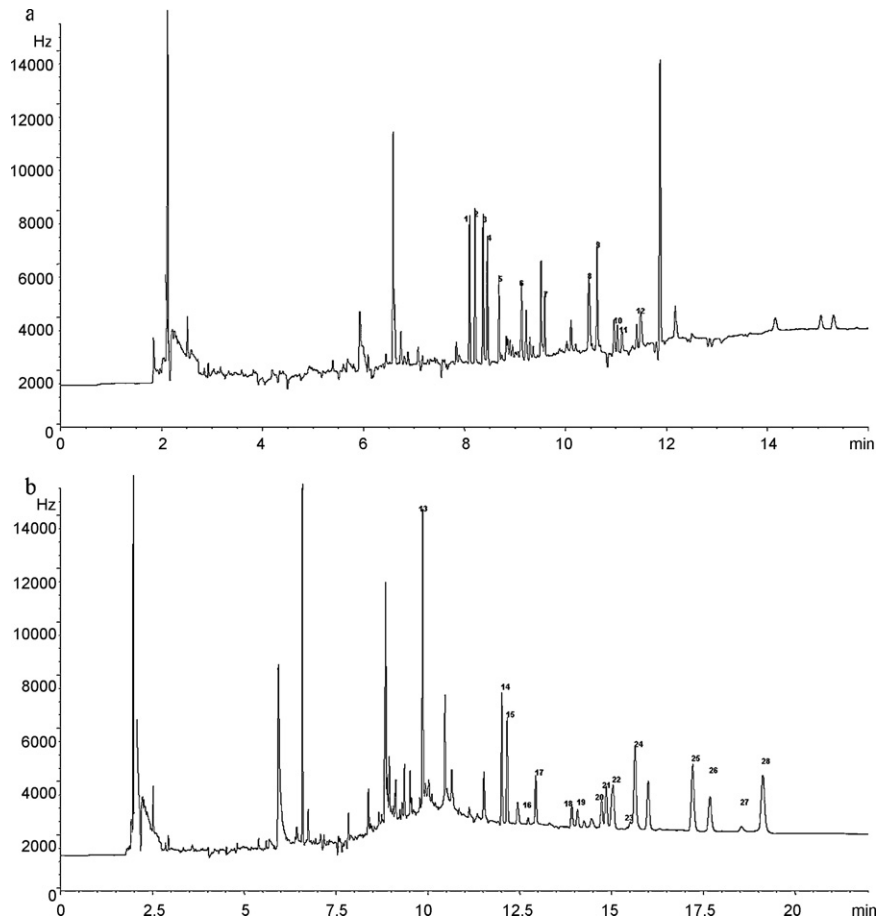

Fig. 4. Chromatograms of GC–ECD obtained by DSDME with 12 kinds of organochlorine (a) and 16 types of pyrethroid (b) pesticides in tea sample. (1) α-HCH, (2) hexachlorobe, (3) β-HCH, (4) γ-HCH, (5) δ-HCH, (6) heptachlor, (7) aldrin, (8) pp′-DDE, (9) dieldrin, (10) pp′-DDD, (11) op′-DDT, (12) pp′-DDT, (13) s-bioallethrin, (14) bifenthrin, (15) fenpropathrin, (16) cyhalothrin-I, (17) cyhalothrin-II, (18) permethrin-I, (19) permethrin-II, (20) cyfluthrin-I, (21) cyfluthrin-II, (22) cyfluthrin-III, (23) flucythrinate-I, (24) flucythrinate-II, (25) fenvalerate-I, (26) fenvalerate-II, (27) deltamethrin-I, (28) deltamethrin-II.

determination of organochlorine and pyrethroid pesticides in tea samples.

4. Conclusions

In this work, a sensitive and effective analytical method for the quantitative determination of organochlorine and pyrethroid pesticides residues in tea samples using DSDME coupled with GC–ECD was developed. The optimal DSDME method showed satisfactory validation parameters in terms of linearity, relative recovery, accuracy, and limits of detection. Compared with the alternative conventional sample-preparation method, DSDME-GC–ECD offers advantages, such as simplicity of assembly, ease of operation, lower consumption of organic solvent, high extraction efficiency, low matrix effects relatively and low detection limit. DSDME possesses great potential in the fast analysis of trace compounds in many complicated matrices.

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