Research Article

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Development of a solventless stir bar sorptive extraction/thermal desorption large volume injection capillary gas chromatographic-mass spectrometric method for ultra-trace determination of pyrethroids pesticides in river and tap water samples

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Abstract: Stir bar sorptive extraction (SBSE) has been developed in 1999 to efficiently extract and preconcentrate volatile compounds, and many applications have been found after that. This technique conforms to the principles of green chemistry. Here, we used an autosampler with an online thermal desorption unit connected to CGC-MS to analyze pesticides. This study describes the development of a highly sensitive extraction method based on SBSE for simultaneous determination of ultra-trace amounts of four pesticides λ -cyhalothrin, α -cypermethrin, tefluthrin, and dimefluthrin in environmental water samples. This method was compared to the standard liquid–liquid extraction. In this study, a totally solventless SBSE was applied to river and tap water samples for the extraction and preconcentration of four pesticides. PDMS-coated SBSEs of 10 mm $\times$ 1 mm thickness were used for this purpose, and SBSEs were directly placed into a large-volume injector of a CGC-MS for thermal desorption of the analytes. In all extractions, deltamethrin was used as an internal standard. This method showed linearity in the range of 1.0–200.0 ng L⁻¹ for cyhalothrin, tefluthrin, and dimefluthrin and 10.0–800 ng L⁻¹ for cypermethrin. Preconcentration factors of 179, 7, 162, and 166 were obtained with very low limits of detection of 0.32, 3.41, 0.36 and 0.69 ng L⁻¹ for cyhalothrin, cypermethrin, tefluthrin and dimefluthrin, respectively. These detection

limits are thousands of times lower than that of the standard method of liquid–liquid extraction. Reproducibility of the method, based on the relative standard deviation, was better than 7.5% and recoveries for spiked tap and river water samples was within the range of 87.83–114.45%. The application of PDMS-coated SBSE coupled with CGC-MS equipped with a large volume injector thermal desorption unit can be used for ultra-trace analysis of environmental water samples. Solventless SBSE offers several advantages over conventional traditional liquid–liquid extraction such as being very fast and economical and provides better extraction without requiring any solvents; so it can be considered as a green method for the analysis of pesticides.

Keywords: pesticides, stir bar sorptive extraction, thermal desorption, simultaneous determination, capillary gas chromatography-mass spectrometry, water analysis

1 Introduction

Sample preparation is one of the most important steps in the chemical analysis. Especially, it is of most importance at trace level analysis, which needs not only preconcentration of the analytes but also a cleanup step to eliminate interferences [1]. Sample preparation by traditional extractions such as Soxhlet and liquid–liquid extraction (LLE) are tedious, time consuming, and need large amounts of toxic organic solvents. Hence, innovative approaches are being investigated to find extraction techniques with higher efficiency, less chemicals consumption, less extraction time, and being more environmentally friendly and safer, among others [2]. Most of these techniques are based on the miniaturization of traditional methods, so they are called microextraction techniques (MEs). In all MEs, the volume of the extracting phase is considerably reduced in comparison with the sample volume; as a result, extraction takes place based on establishing equilibrium of analytes between adsorbents or

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sorbents and target sample, rather than exhaustive extraction. Liquid-phase microextraction, solid-phase microextraction (SPME), and stir bar sorptive extraction (SBSE) are the most used sorbent-based methods of MEs. These techniques benefit from low sample requirement, automation of devices, and high speed [3]. SPME and SBSE are similar in extraction principle; however, SBSE has higher capacity due to more amount of sorbent phase, and hence, it is more sensitive, more robust, and can be applied to ultra-trace detection of inorganic compounds as well as organics in various real matrices. For liquid samples, it also needs no previous sample preparation neither a solvent with the ability of extraction of several analytes simultaneously in a single step [4,5]. Due to these advantages, SBSE have wide applications in many areas such as food, flavor, environmental, life, and biomedical sciences for the analysis of variety of analytes [6]. After extraction, SBSE can be introduced directly into the analytical system equipped with a thermal desorption (TD) or liquid desorption (LD) system [7]. A wide range of analytes such as polycyclic aromatic hydrocarbons, chlorinated solvents, pesticides, polychlorinated biphenyls, odor compounds, organotins, and preservatives were extracted by means of SBSE [8–10]. Stir bar with polydimethylsiloxane (PDMS) coating is the most applied polymeric phase, which is in use for SBSE extraction [11] and is known worldwide as Twister[®], made by GERSTEL GmbH & Co KG (Mülheim, Germany). Because PDMS is a viscous liquid polymer, diffusion coefficients of the analytes are several orders of magnitude higher than that of solid coatings; so, higher uptake is obtainable for this coating when extracting volatile/semi-volatile compounds [12]. Because of thermal stability, it can be used in a broad range of temperatures, and also Twister can be directly inserted into an injection port of a gas chromatograph (GC) at elevated temperature without risk of bleeding. This also makes results more reproducible.

Pesticides are well-known contaminants of water samples such as drinking and ground waters due to widespread use of them for agricultural purposes [13]. Accumulation of pesticides in the environment has hazardous effects in food chain and consequently to animals and humans. So the amount of various pesticide residues in environmental and drinking water samples are important to be determined [14,15]. The maximum contamination level (MCL) of each pesticide in drinking water depends on its solubility; however, European Union regulations recommend MCL of $0.1 \mu\text{g L}^{-1}$ for the most individual pesticides and $0.5 \mu\text{g L}^{-1}$ as total [16]. Besides LLE, a number of ME techniques have recently been applied for preconcentration of pesticides before their gas chromatographic detection, including SPME [17], dispersive liquid–liquid microextraction

[18], air-assisted liquid–liquid microextraction [19], microwave-assisted dispersive liquid–liquid microextraction [20] and salt and pH-induced solidified floating organic droplets homogeneous liquid–liquid microextraction [21]. However, except SPME, these techniques are not entirely solvent free and have multistep procedures. On the other hand, SPME fibers generally suffer from drawbacks such as relatively high cost, fragility, a low limited selectivity, and swelling of the coatings in chlorinated solvents [22].

λ -Cyhalothrin, α -cypermethrin, tefluthrin, and dimefluthrin are classified as pyrethroids, which are mainly used to control the population of insects. They are synthetic pyrethrins with high hydrophobicity and high octanol–water partition coefficients. The solubility of λ -cyhalothrin, α -cypermethrin, tefluthrin, and dimefluthrin in water are 0.8, 4.0, 20.0 and $2,000 \mu\text{g L}^{-1}$ respectively. Because of high toxicity of pyrethroids for fishes, bees and soil microorganisms, monitoring of them in the environment even at very low concentrations ($<0.5 \mu\text{g L}^{-1}$) is extremely important [23–25]. SBSE has already been applied for trace determination of pesticides such as endosulfan, chlordane, methoxychlor, ethion, and bromopropylate and also some pyrethrin pesticides [26,27] (except for dimefluthrin) in water samples before their capillary gas chromatography/mass spectrometry (CGC/MS) determination with satisfactory results [28–30]. These researches were performed more than 15 years ago, with some older versions of the instruments and software, including earlier thermal desorption unit (TDU) and Twister[®]. Therefore, the aim of this study is to investigate the ability of Twister[®] SBSE in combination with thermal desorption CGC-MS for efficient extraction and simultaneous determination of ultra-traces of four pyrethroids, i.e., λ -cyhalothrin, α -cypermethrin, deltamethrin, tefluthrin, and dimefluthrin from water samples. These compounds were selected because of their frequent occurrence in the surface water of agricultural watersheds in Germany. Results were compared with a traditional liquid–liquid extraction (LLE) method.

2 Materials and methods

2.1 Chemicals

λ -Cyhalothrin, α -cypermethrin, deltamethrin, tefluthrin, and dimefluthrin were obtained from Sigma-Aldrich Chemie GmbH (Schnelldorf, Germany). Some properties of them are summarized in Table 1. All other reagents were of analytical grade and were purchased from the

Table 1: Octanol–water partition coefficients, retention times, and selected SIM ions for pesticides studied

Analyte	Sigma-Aldrich Cat. No.	log $k_{o/w}$ (ref)	Retention time (min)	SIM ions
λ -Cyhalothrin	91465086	6.85 [26]	7.64	204.5/240.5
α -Cypermethrin	67375308	6.38 [26]	8.22	206.4/208.4
Tefluthrin	79538322	6.40 [31]	5.80	204.5/240.5
Dimefluthrin	271241146	5.40 [25]	6.44	167.6/166.6
Deltamethrin*	52918635	6.18 [26]	8.83	78.8/296.6

* Internal standard.

same company. 5 mg L⁻¹ stock solution of each pesticide was prepared in acetone and stored in a refrigerator at 4°C. A mixed standard containing 0.05 mg mL⁻¹ of all pesticides was also prepared in acetone for simultaneous measurements.

2.2 Instrumentation

An Agilent 7890A gas chromatograph with 7000C triple quadrupole MS (Agilent technologies, Walsbronn, Germany) was employed for performing chromatographic analysis and mass detection. The system was equipped with a commercial TDU, which was connected to a large volume injector, model CIS-4 injector (GERSTEL). The TDU unit was equipped with a GERSTEL MPS auto-sampler, which can sequentially introduce 98 samples into the TDU. The glass tubes containing the stir bars were placed in a tray that was assembled in MPS. Stir bars coated with 0.5 mm (10 mm × 0.5 mm thickness) and 1 mm (10 mm × 1 mm thickness) PDMS were also purchased from GERSTEL. River water was taken from a local river in Schmallingenberg (Germany). Splitless thermal desorption was performed by TDU programming from 30°C (0.25 min) to 250°C (10 min) at a rate of 360°C min⁻¹ with a helium flow rate of 1.2 mL min⁻¹. The analytes were cryo-focused in a cooled injection system (CIS-4) inlet at -50°C using liquid nitrogen. Splitless injection was then performed by ramping the CIS-4 from -50°C (0.1 min) to 250°C (5 min) at a rate of 12°C min⁻¹. Chromatographic analysis was performed on a DB-5MS ultra inert capillary column of 30 m × 0.25 mm I.D. and a phase thickness of 0.25 μ m (Agilent technologies). GC oven was programmed from 100°C (2 min) to 320°C (3.5 min) at a rate of 40°C min⁻¹. The transfer line, ion source, and mass analyzer temperatures were set at 280, 150, and 150°C, respectively, with the solvent delay of 5 min. Negative chemical ionization (NCI) mass spectra were recorded with an ionization current of 34.6 μ A. Two characteristic ions of each compound, target and qualifier ions, in the selected ion monitoring (SIM)

mode are listed in Table 1. The dwell time was 50 ms. Data acquisition, instrument control, and data analysis were performed by Agilent mass hunter quantitative analysis software.

2.3 SBSE extraction procedure

Twister stir bars were preconditioned before use by heating them in TDU at 300°C for 30 minutes with a helium stream of 100 mL min⁻¹. Water sample or standard was poured in a glass vial containing 20 mL of water adjusted at pH 7. The stir bar was placed in vial, and the extraction was performed for 180 min with a stirring speed of 700 rpm at 40°C. In all extractions, deltamethrin was used as an internal standard. After extraction, the stir bars were taken out of the vials, washed with deionized water, and dried under nitrogen stream for 1 min. The stir bars were then put into autosampler tubes and sealed and then were placed into the autosampler tray for CGC/MS analysis.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Optimization of extraction conditions

In the SBSE (PDMS) theory [5], the extraction efficiency of an analyte is related to the partitioning between the PDMS phase of the stir bar and the water sample, which shows a performance close to the octanol–water partition coefficients distribution during static equilibrium. Therefore, to achieve the best efficiency of SBSE extraction, parameters that could have an effect on the partitioning of sample between water and PDMS extracting phase were studied and optimized, including extraction time, stirring speed, sample volume, extraction temperature, ionic

strength of sample solution, and pH value. Twenty milliliters of freshly prepared individual solution of 100 ng L^{-1} of each pesticide were used for all optimization. Initial tests showed that the signal of a Twister with a coating layer of 1 mm is about two times higher than that of 0.5 mm thickness; so, for all experiments, a Twister with 1 mm thickness was employed.

3.1.1 Effect of extraction time

Extraction with SBSE can be regarded as an equilibrium process rather than exhaustive. In most SBSE applications, the efficiency of extraction increases with the extraction time [32]. The extraction of the target analytes into SBSE was carried out in a range of time between 60 and 180 min. It was observed that the peak areas of all compounds were increased up to 120 min sharply and to 175 min, and this increase is not rapid and then achieved an equilibrium state. Longer contact times had no effect on improving extraction efficiency. To be sure of giving enough time to the system to reach equilibrium in various media (such as viscous or very dilute samples), 180 min was chosen as extraction time for all pesticides (Figure 1).

3.1.2 Effect of stirring speed

Increasing the stirring rate has a positive effect on the amount of extraction because equilibrium will be reached faster at a higher stirring speed. Consequently, at a preset time, increasing the speed will result in extraction increment [33]. The experimental results showed that the extraction efficiency increases by increasing the stirring rate up to 600–700 rpm and then stays constant. After extraction

Figure 2: Effect of stirring speed on the extraction efficiency (extraction conditions: $100 \mu\text{L}$ of 100 ng L^{-1} of each analyte; extraction time: 180 min; sample volume: 20 mL; temperature: 40°C ; pH: 7).

reaches to its equilibrium, further increase in the stirring speed has no effect on the amount of the analytes uptake, and so the signal will remain constant; however, to be sure of reaching a maximum extraction recovery, 700 rpm was selected as the best stirring speed (Figure 2). Increasing the stirring speed even further can be considered since no additional costs or time is required.

3.1.3 Effect of sample volume

Sample volumes tested in this work were 10, 20, 40, and 60 mL. The total amount of each target compound was 100 ng L^{-1} . According to the data in Figure 3, increasing the sample volume causes increasing chromatographic peak areas for all pesticides up to a certain volume and then decreases. For cyhalothrin's curve, this volume is 40 mL, and for three other compounds, this maximum was observed at 20 mL. Since signal improvement for cyhalothrin volume from 20 to 40 mL is only about 6.5%,

Figure 1: Effect of time on the efficiency of extraction (extraction conditions: $100 \mu\text{L}$ of 100 ng L^{-1} of each analyte; stirring speed: 700 rpm; sample volume: 20 mL; temperature: 40°C ; pH: 7).

Figure 3: Effect of sample volume on the efficiency of extraction (extraction conditions: $100 \mu\text{L}$ of 100 ng L^{-1} of each analyte; extraction time: 180 min; stirring speed: 700 rpm; temperature: 40°C ; pH: 7).

20 mL sample volume was chosen for further experiments. As can be observed, changing the volume of sample has no significant effect on the extraction recovery. This can be considered as a positive aspect of this method because one can start eventually with a different sample volume and still is not far from the optimum point.

3.1.4 Effect of temperature

Effect of the temperature on extraction efficiency of the analytes were also studied, and it was found that the area of chromatographic peaks was increased with an increase in temperature up to 40°C and decreases after then (Figure 4). This is because increasing the temperature increases the mobility of molecules of samples, so they can adsorb on the stir bar faster during a preset time. Temperatures higher than 40°C result in even more mobility of molecules of the analytes, which prevents them to absorb properly on Twister's coating.

3.1.5 Effect of ionic strength

Salting-out effect is in wide use in liquid–liquid extraction because it lowers the solubility of the analytes in the aqueous phase; so, more analytes can be entered into the extracting phase. Here, the influence of this parameter was studied with the addition of different amounts of sodium chloride, ranging from 0.0 to 0.4 g mL⁻¹, on the under-experiment solutions. Figure 5 shows that salt addition decreases the peak area because of increasing the viscosity of solution that leads to a decrease in the speed of stir bar rotation. Also there is a strong correlation between octanol–water partitioning coefficient and SBSE

Figure 4: Effect of temperature on the efficiency of extraction (extraction conditions: 100 μ L of 100 ng L⁻¹ of each analyte; extraction time: 180 min; stirring speed: 700 rpm; sample volume: 20 mL; pH: 7).

Figure 5: Effect of ionic strength on the efficiency of extraction (extraction conditions: 100 μ L of 100 ng L⁻¹ of each analyte; extraction time: 180 min; stirring speed: 700 rpm; sample volume: 20 mL; temperature: 40°C; pH: 7).

efficiency. Since our desired analytes have high octanol–water partitioning coefficient, adding sodium chloride and increasing the ionic strength cannot affect recovery. Hence, further experiments were performed in the absence of sodium chloride [34].

3.1.6 Effect of pH

The effect of sample pH on the extraction efficiency of four pesticides was also investigated. Dropwise addition of either 0.1 M HCl or 0.1 M NaOH was used for pH adjustment between 2.0 and 9.0. The highest extraction for cyhalothrin, tefluthrin, and dimefluthrin was observed at pH of 6, whereas for cypermethrin, this point was achieved at pH 8 (Figure 6). This can be described according to the molecular

Figure 6: Effect of pH of solution on the efficiency of extraction (extraction conditions: 100 μ L of 100 ng L⁻¹ of each analyte; extraction time: 180 min; stirring speed: 700 rpm; sample volume: 20 mL; temperature: 40°C; pH: 7).

structure of target pesticides. The presence of halogens in organic molecules causes molecule to have a lower pK_a [35] and analytes with pK_a values more than 4.5, showing an increase in extraction efficiencies with a decrease in pH

[36]. In the subsequent studies, pH of solutions was adjusted to 7.0, in which extraction of all analytes are close to their maximum value. Moreover, by working at this pH, there is no need for pH adjustment.

Table 2: Analytical figures of merit for determination of four target pesticides by SBSE-TD-CGC-MS and LLE and comparison with other methods proposed for their analysis in water samples

Analytical feature	Extraction technique					
	SPME	SPE	UA-DLLME ^g	SALLE ^h	SBSE-TD-CGC-MS	LLE
Cyhalothrin						
Linear range	2.5–1,500 $\mu\text{g L}^{-1}$	NM	NM	NM	1–200 ng L^{-1}	10–6,000 $\mu\text{g L}^{-1}$
R^{2a}	0.9984	0.9992	0.9989	0.9996	0.998	0.9997
LOD ^b	0.3 $\mu\text{g L}^{-1}$	3.00 $\mu\text{g L}^{-1}$	0.30 $\mu\text{g L}^{-1}$	1.70 $\mu\text{g L}^{-1}$	0.32 ng L^{-1}	0.64 $\mu\text{g L}^{-1}$
LOQ ^c	0.7 $\mu\text{g L}^{-1}$	NM	1.00 $\mu\text{g L}^{-1}$	5.00 $\mu\text{g L}^{-1}$	1.07 ng L^{-1}	7.48 $\mu\text{g L}^{-1}$
RSD, ^d %	7.80	4.00	8.00	11.00	7.49	1.23
Enrichment factor ^e	NM ^f	NM	NM	NM	179	2
Detecting instrument	HPLC/FD	GC/MS	LC/MS	LC/MS	CGC/MS	CGC/MS
Extraction technique	SPME	SPE	DLLME	SALLE	SBSE	LLE
Reference	[38]	[39]	[41]	[41]	This work	This work
Cypermethrin						
Linear range	20–2,000 $\mu\text{g L}^{-1}$	NM	NM	NM	10–800 ng L^{-1}	10–6,000 $\mu\text{g L}^{-1}$
R^2	0.998	0.997	0.9990	0.9932	0.998	0.9973
LOD	NM	4.00 $\mu\text{g L}^{-1}$	0.800 $\mu\text{g L}^{-1}$	4.00 $\mu\text{g kg}^{-1}$	3.41 ng L^{-1}	3.63 $\mu\text{g L}^{-1}$
LOQ	13.3 $\mu\text{g L}^{-1}$	NM	2.50 $\mu\text{g L}^{-1}$	12.50 $\mu\text{g L}^{-1}$	11.39 ng L^{-1}	12.10 $\mu\text{g L}^{-1}$
RSD, %	11.3	9.40	8.00	12.00	4.44	2.87
Enrichment factor	NM	NM	NM	NM	7	2
Detecting instrument	GC/MS	GC/MS	LC/MS	LC/MS	CGC/MS	CGC/MS
Extraction technique	DI-SPME	SPE	DLLME	SALLE	SBSE	LLE
Reference	[40]	[38]	[41]	[41]	This work	This work
Tefluthrin						
Linear range	NM	NM	NM	NM	1–200 ng L^{-1}	30–5,000 $\mu\text{g L}^{-1}$
R^2	NM	NM	0.9986	0.9988	0.9988	0.9989
LOD	NM	NM	1.70 $\mu\text{g kg}^{-1}$	8.00 $\mu\text{g kg}^{-1}$	0.36 ng L^{-1}	4.67 $\mu\text{g L}^{-1}$
LOQ	NM	NM	5.00 $\mu\text{g kg}^{-1}$	25.00 $\mu\text{g kg}^{-1}$	1.22 ng L^{-1}	15.57 $\mu\text{g L}^{-1}$
RSD, %	NM	NM	13.00	16.00	6.95	6.10
Enrichment factor	NM	NM	NM	NM	162	2
Detecting instrument	NM	NM	LC/MS	LC/MS	CGC/MS	CGC/MS
Extraction technique	NM	NM	DLLME	SALLE	SBSE	LLE
Reference	NM	NM	[41]	[41]	This work	This work
Dimefluthrin						
Linear range	NM	NM	NM	NM	1–200 ng L^{-1}	30–5000 $\mu\text{g L}^{-1}$
R^2	NM	NM	NM	NM	0.9992	0.9997
LOD	NM	NM	NM	NM	0.69 ng L^{-1}	5.11 $\mu\text{g L}^{-1}$
LOQ	NM	NM	NM	NM	2.31 ng L^{-1}	17.03 $\mu\text{g L}^{-1}$
RSD, %	NM	NM	NM	NM	7.20	4.32
Enrichment factor	NM	NM	NM	NM	166	6
Detecting instrument	NM	NM	NM	NM	CGC/MS	CGC/MS
Extraction technique	NM	NM	NM	NM	SBSE	LLE
Reference	NM	NM	NM	NM	This work	This work

^a R^2 , coefficient of determination. ^b LOD, was based on $3S_b/m$ criterion for 10 blank measurements. ^c LOQ, was based on $10S_b/m$ criterion for 10 blank measurements. ^d RSD, relative standard deviation, for 3 replicate measurements. ^e Enrichment factors were obtained by dividing the concentrations equivalent to the peak area of the analytes after extraction to the concentration of them without extraction, which generates the same peak height when 1.0 μL of the sample was injected. Thereby, it was possible to compare the enrichment of the developed procedure with the output of normal CGC/MS injection [37]. ^f Not mentioned. ^g Ultrasound-assisted dispersive liquid–liquid microextraction. ^h Salting-out assisted liquid–liquid extraction.

Figure 7: Chromatograms of spiked river water sample obtained by (a) direct injection, (b) LLE, and (c) SBSE.

3.2 Analytical performance of SBSE-TD-CGC/MS

Under the optimum conditions, linear range, coefficient of determination (R^2), limit of detection (LOD), limit of quantification (LOQ), and repeatability (expressed as relative standard deviation percent, RSD%) of the suggested stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry (SBSE-TD-CGC-MS) method were obtained and summarized in Table 2. This table also comprises a comparison of the suggested method with the previously published articles for the analysis of water samples using ME procedures. No data were found for the analysis of tefluthrin and dimefluthrin using SPME or solid-phase extraction (SPE). The developed

method has the highest preconcentration and sensitivity among similar MEs.

3.3 Analysis of real water samples

The proposed method was applied for extraction and determination of cyhalothrin, cypermethrin, tefluthrin, and dimefluthrin in river and tap water samples. No pesticides were detected in samples; therefore, to validate the method's accuracy, water samples were spiked with these pesticides at three concentration levels. Figure 7 depicts example chromatograms of spiked river water sample obtained by direct injection, liquid-liquid

Table 3: Results for the analysis of cyhalothrin, cypermethrin, tefluthrin, and dimefluthrin in spiked real samples with SBSE-TD-CGC-MS and LLE.

River water						
Insecticide	SBSE-TD-CGC-MS			LLE		
	Added (ng L^{-1})	Recovery (%)	RSD% ($n = 3$)	Added ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD% ($n = 3$)
Cyhalothrin	2.5	110.41	7.49	500	94.65	0.87
	25	94.68	3.95	1,000	96.16	0.46
	200	97.58	1.29	4,000	99.02	0.3
Cypermethrin	25	87.83	2.49	500	99.29	2.55
	100	114.78	4.16	1,000	99.09	0.63
	400	100.35	2.77	4,000	103.89	0.44
Tefluthrin	2.5	102.50	1.78	30	102.37	0.79
	25	112.30	1.41	300	99.28	6.10
	200	99.63	4.58	3,000	93.11	5.30
Dimefluthrin	2.5	109.35	7.20	30	93.23	3.90
	25	114.09	5.97	300	93.57	4.17
	200	107.31	5.47	3,000	95.68	3.73
Tap water						
	SBSE-TD-CGC-MS			LLE		
	Added (ng L^{-1})	Recovery (%)	RSD% ($n = 3$)	Added ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD% ($n = 3$)
Cyhalothrin	2.5	89.16	6.07	500	96.43	1.23
	25	104.44	7.26	1,000	102.52	0.93
	200	114.45	2.21	4,000	98.23	1.16
Cypermethrin	25	110.52	0.55	500	101.34	2.87
	100	113.37	2.47	1,000	105.65	0.94
	400	95.43	4.44	4,000	97.16	1.62
Tefluthrin	2.5	112.75	1.66	30	97.24	3.13
	25	109.64	6.95	300	99.51	2.76
	200	106.29	6.78	3,000	98.45	1.25
Dimefluthrin	2.5	106.93	1.94	30	95.76	2.43
	25	109.33	5.24	300	99.43	4.32
	200	112.11	5.95	3,000	98.12	2.61

extraction (LLE), and SBSE-TD-CGC/MS. The trueness of the method was evaluated by analyzing the same samples using the standard LLE method. Results are summarized in Table 3. *F*-test and paired *t*-test at 95% confidence level showed no difference between LLE and our suggested method.

4 Conclusion

A solventless stir bar sorptive extraction-thermal desorption large volume injection coupled to capillary gas chromatography-mass spectrometry (SBSE-TD-CGC/MS) was developed to determine ultra-trace amounts of λ -cyhalothrin, α -cypermethrin, tefluthrin, and dimefluthrin in river and tap water samples. Our proposed method showed high sensitivity, good repeatability, and linearity besides easy operation and being solvent free. In comparison to liquid-liquid extraction, in which a large amount of poisonous solvents must be used, stir bar sorptive extraction provides better extraction without requiring any solvents. So, it can be considered as a green method for the analysis of these pesticides. Using the most advanced instruments in the market enabled us to achieve lower LODs and LOQs in comparison to the similar researches previously performed on the same analytes with SBSE. Results also indicated better stability of both the instrument and the extraction system with good repeatability. The method was compared with other methods of determining the same pesticides, which showed that SBSE-TD-CGC/MS has higher sensitivity than others. However, the main disadvantage of the developed method is its slowness in extraction, which makes this method time consuming.

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