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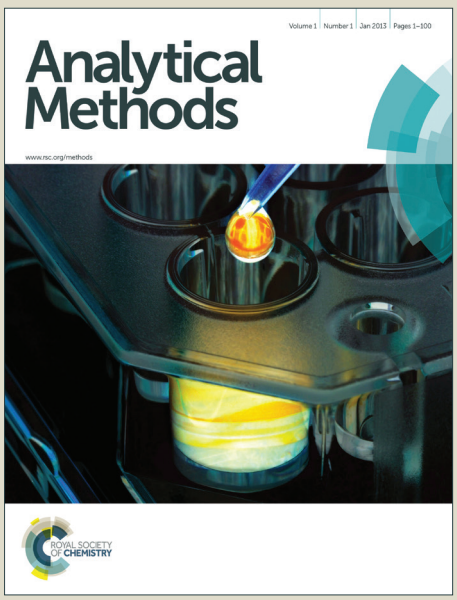

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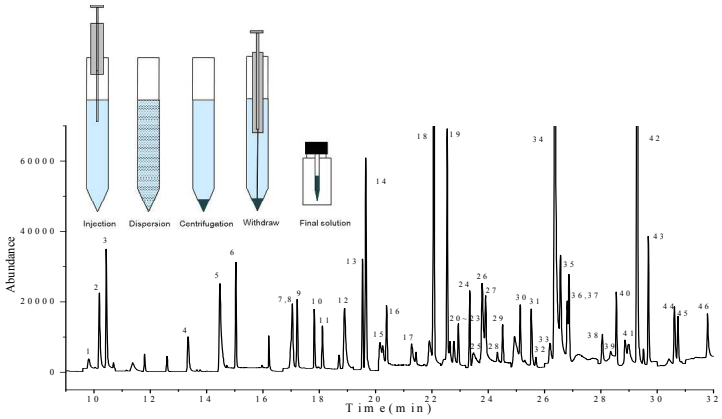

DLLME coupled with GC-MS was used to quantify and semi-quantify 304 pesticides and related organic pollutants in surface water.

Screening and quantification of 304 pesticides and related organic pollutants in surface water using dispersive liquid-liquid microextraction coupled with gas chromatography-mass spectrometry

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ABSTRACT

Dispersive liquid-liquid microextraction (DLLME) coupled with gas chromatography-mass spectrometry (GC-MS) was used to quantify and semi-quantify 304 pesticides and related organic pollutants in surface water. Extraction parameters including types and volumes of extraction solvent, disperser solvent, and amount of salt addition were optimized to obtained highest recoveries and lowest detection limits. A mixture of 35 μL carbon tetrachloride (extraction solvent) and 1 mL acetone (disperser solvent) was added into 5 mL of water sample. After agitation and centrifugation, 20 μL of the sedimented phase was mixed with 1 μL of the internal standard solution, and 1μL of the final solution was injected into GC-MS for separation and quantification. The enrichment factors ranging from 42- to 299-fold were obtained for all compounds. The limits of detection ranged from 0.001 to 1.125 μg/L, and the limits of quantification ranged from 0.003 to 3.75 μg/L. Of all 304 compounds, 90 compounds showed recoveries from 60% to 120% and RSDs lower than 20%. The proposed method is very low cost, rapid and convenient, and could be an effective method for monitoring of multi-pesticide in surface water.

Keywords: Pesticide; Surface water; dispersive liquid-liquid microextraction; gas chromatography-mass spectrometry

1. Introduction

Agricultural applications of pesticides lead to contamination of surface water, which has caused great concern with respect to the effects on environment and public health [1-3]. Many countries have begun to take legislative actions to protect the water supply from pesticides pollution. European regulations on drinking water quality have set a maximum concentration of 0.1 μg/L for a single active ingredient of pesticides and 0.5 μg/L for the total concentration (European Union Drinking Water Directive, 98/83/EC). In China, GB 5749-2006 sets a maximum residual level (MRL) for 19 pesticides in drinking water, with the MRLs ranged from 0.4 μg/L to 700 μg/L.

At present, over 9700 pesticides based on the 502 active ingredients have been registered in China and over 16,000 pesticide formulations based on the 1055 active ingredients are labeled for use in the whole world. Considering so many varieties of pesticides, as well as the low tolerable limits for most of the pesticides in water, the ultrasensitive analytical methods with the screening ability are mandatory, and gas chromatography-mass spectrometry (GC-MS) is still the most commonly used instrument for separating and identifying pesticide residues [4-6].

For determining pesticide residues and related chemical residues in water samples, sample preparation steps are usually required to clean-up and preconcentrate the analytes. Typical sample preparation methods employed for trace pesticide residues and related chemical residues in water are liquid-liquid extraction (LLE) [7] and solid phase extraction (SPE) [8-10]. Most of these methods were time consuming, labor-intensive, and required large volumes of water samples and organic solvents. In the past few

decades, several miniaturized methods including solid-phase microextraction (SPME) [11-13], single drop microextraction (SDME) [14-16], and hollow fiber liquid-phase microextraction ((HF-LPME) [17-19] were developed for extraction and concentration of trace pesticide residues. These microextraction methods are economical, environmental-friendly and effective. However, most of these methods need a long equilibrium time. To overcome this drawback, a more efficient and time-saving microextraction technique termed as dispersive liquid-liquid microextraction (DLLME) was developed [20].

DLLME is based on a ternary component solvent system, in which the extraction solvent and disperser solvent are rapidly injected into the aqueous sample, and form a cloudy solution. The large surface area between the extraction phase and water sample results in fast extraction and short equilibrium time. After extraction, the mixture was centrifuged, and the analytes in the settled phase are collect and analyzed by gas chromatography (GC) or high performance liquid chromatography (HPLC). The DLLME method have been reported for the extraction of pesticide residues in water including organochlorine [21-23], organophosphorus and azole group pesticides [24], triazole fungicides [25], polycyclic aromatic hydrocarbons [26] and multipesticides [27].

Multi-pesticide detection method has drawn more attention recently. In this research work, a DLLME sample preparation method was developed for preconcentration of 304 pesticides and related organic pollutants from surface water. Several parameters of the extraction procedure including type and volume of extraction solvent, type and volume of disperser solvent, and salinity were optimized, and the developed method was applied for real water analysis.

2. Experimental

83 *2.1. Chemicals and water samples*

84 All pesticides and related chemical residues used were purchased from Dr.
85 Ehrenstorfer (Germany). Individual pesticide stock solutions were prepared in toluene, *n*-
86 hexane, acetone, acetonitrile or mixture of toluene and acetone, according to its solubility
87 characteristic. A composite stock standard solution was prepared in acetone, and the
88 concentrations of all pesticides were 20,000 times higher than spiked level A. The
89 equivalent concentrations of spiked level A for pesticides in experiment were shown in
90 Supplementary Information. Additional spiked solutions were 5 times (level B) and 10
91 times (level C) of level A. Heptachlor-epoxide (35 mg/L in acetone) obtained from
92 Supelco was used as internal standard (I.S.) for calibrating the retention time fluctuation.
93 All the solutions were stored at -18 °C before use. The concentration of stock standard
94 solution and selection of I.S. were referred to the National Standard Method of China,
95 GB/T 19648-2006.
96 Carbon tetrachloride, chloroform, chlorobenzene, dichloroethylene and sodium
97 chloride (NaCl) were analytical grade (Kemiou, Tianjin, China). Disperser solvents
98 acetone, acetonitrile and methanol were HPLC grade obtained from Merck.
99 Surface water samples were collected from Pearl River (Guangdong, China) using
100 glass bottle, and stored at 4 °C before analysis. The water sample was filtered with a 0.45
101 μm nylon membrane (Xiboshi, Tianjin, China) before analysis.

102 *2.2. Instrument*

103 A gas chromatography (Agilent 7890) equipped with a split/splitless injector system
104 and a mass detector (Agilent 5973C) was used for separation and quantification. Agilent
105 Chemstation (MSD Chemstation E.02.00.493) was used for data collection/processing

and GC-MS control. Ultra pure helium (99.999 %, Shente Industrial gases Co., Shenzhen, China) made to pass through a molecular sieve trap and oxygen trap was used as the carrier gas. A volume of 1 μL extract was injected in splitless mode (purge time 0.5 min, purge flow 30 mL/min). The injection port was held at 300 °C. Separation was carried out on a DB-1701 (30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed as follows: initial 40 °C and held for 1min, then increased to 130 °C at the rate of 30 °C/min, ramped to 250 °C at the rate of 5 °C/min, finally ramped to 280 °C at the rate of 10 °C/min and held for 8 min. The MS spectrometric parameters were set as follows: electron impact ionization with 70 eV energy; ion source temperature, 230 °C and MS quadrupole temperature, 150 °C. The MS system was routinely set in selective ion monitoring (SIM) mode with a solvent delay of 5 min. 304 pesticides and related chemical residues were divided into 6 groups (A-F) for GC-MS analysis according to the national standard method (GB/T 19648-2006). The grouping principle was to separate the compounds with close retention time and/or similar fragment ions into different groups. The GC conditions were kept the same for the 6 injections while the MS SIM parameters were varied. Complete SIM parameters and retention times of each analyte are shown in Table S1. Compounds were qualified according to the retention time and the selected fragment ions, while quantitative analysis was conducted based on the retention time, fragment ions as well as the recoveries.

2.3. Dispersive liquid-liquid microextraction procedure

The DLLME procedure was shown in Fig. 1. An aliquot of 5 mL water was placed to a 15 mL glass tube with conical bottom. A mixture of acetone (1000 μL) and carbon tetrachloride (35 μL) was rapidly injected into the sample tube and shaken gently by hand

for 30 seconds. After centrifuging at 4700 rpm for 5 min, 25 μL sedimented phase was obtained, and 20 μL was transferred to a 200 μL glass insert in a 2 mL vial. 1 μL heptachlor epoxide (35 mg/L) was added into the glass insert and mixed by vortex. Then, 1 μL of the extract was injected into GC-MS system for analysis.

3. Results and discussion

3.1. Optimization of extraction procedure

There are some factors that affect the extraction process, including extraction solvent type and volume, disperser solvent type and volume, salinity and extraction time. Since 304 compounds with different polarities were studied, it is impossible to optimize a DLLME method fit for all compounds. According to the grouping principle, Group A to group F all cover compounds with polarities from strong to weak. Therefore, group A （Table 1）were selected as representative of all compounds to optimize the extraction parameters for all the compounds.

3.1.1. Selection of extraction solvent

Three factors should be taken into consideration for the selection of extraction solvent: higher density than water, excellent extraction capability to the interested compounds, and good gas chromatography behavior. Four extraction solvents, including chloroform, tetrachloride, dichloroethylene and chlorobenzene, were tested and compared. Results show that all the solvents except chlorobenzene provided good chromatography behavior. Therefore, further investigation of the extraction recoveries was done with the chloroform, tetrachloride and dichloroethylene. One milliliter of acetone as disperser solvent was spiked into the 5 mL sample solution. Different volume of the extraction solvents were

optimized to obtain 20 μL of sedimented phase, and finally 43, 30, and 24 μL of chloroform, tetrachloride and dichloroethylene were selected, respectively. After sampling, 1μL of each extracted solvent was injected into the GC-MS for quantification. The average recoveries and standard deviations (SD) obtained from different extraction solvents were shown in Fig. 2. Tetrachloride observed the highest average extraction recovery (79.8%) for most compounds in group A compared to dichloroethylene (63.7 %) and chloroform (61.6%). Therefore, tetrachloride was selected as the extraction solvent.

3.1.2. Selection of disperser solvent

The disperser solvent should be miscible with both water and extraction solvent. According to this principle, acetone, acetonitrile and methanol were selected and compared. One milliliter of each disperser solvent together with 30 μL of tetrachloride was injected into 5 mL of spiked water samples. The average recoveries of all pesticides using different disperser solvents were showed in Fig. 3. Acetone was selected because of the obtained highest average recovery (82.4%) compared to the ones obtained from methanol (75.3%) and acetonitrile (66.5%). Additionally, acetone is less toxic than the other two solvents.

3.1.3. Effect of disperser solvent volume and extraction solvent volume

The disperser solvent volume directly affects the formation of cloudy solution. Larger amount of disperser solvent improves the dispersion effect of the extraction solvent in water. However, higher volume of disperser solvent may also reduce the recoveries of compounds, because it may increase the solubility of compounds in water solution. Since the effect of disperser solvent on the extraction efficiencies of 304 pesticides may be

different and complex, 1 mL of the disperser solvent from the previous studies [20,28] was utilized in this experiment without further optimization.

Lower volume of extraction solvent usually results in higher enrichment factor, and lower detection limit [20]. Additionally, the volume of extracted solvent needed for GC/MS analysis should be considered. In this experiment, 304 pesticides were divided to 6 groups and measured in 6 runs, which mean more extraction solvent was required. Therefore, 25, 30, 35, 40, 45, 50 μL of tetrachloride were investigated, and the results illustrated in Fig. 4 show that the recoveries of all pesticides were gradually increased with the volume of tetrachloride increased from 25 to 35 μL, but the difference of the average recoveries is insignificant when the extraction solvent was more than 35 μL. As a result, 35 μL of tetrachloride was selected as the optimum volume of extraction solvent, because higher enrichment factors could be obtained, and the final obtained volume of the extracted solvent (~25 μL) is enough for 6 runs in GC/MS.

3.1.4. Effect of salt addition

The solubility of the target analytes and organic extraction solvent in aqueous phase are usually decreased with the increase of ionic strength, which is favorable for reaching high recovery. However, the volume of the sedimented phase may also be increased, which may decrease the enrichment factor. In this experiment, 35 μL tetrachloride was used as extraction solvent, and 1 mL acetone was used as disperser solvent, extractions were performed with the adding of different amounts of NaCl (ranging from 0 % to 5 % (w/v)) into water samples. With the increase of salt addition, the average recoveries of 15 compounds increased from 77.6% to 81.5%. However, the sedimented phase increased from 25 μL to 30 μL, which decreased the enrichment factors. Fig. 5 illustrated that for

196 most compounds the enrichment factor decreased with the salinity changing from 0% to
197 5%. Therefore, no salt was added in the following experiments.

198 *3.2. Evaluation of the method performance*

199 Fig. 6 shows a typical GC-MS chromatogram of group F extracted with DLLME
200 from a spiked surface water sample at concentration level C (Table S2). The calibration
201 curve was obtained by analyzing standard solutions with five concentration levels. Good
202 linearity of GC-MS response was found for all pesticides at concentrations within the test
203 intervals, with linear regression coefficients (r^2) higher than 0.990 (Table S2). The
204 average recoveries and repeatability of the proposed method were evaluated by extracting
205 six consecutive aqueous samples spiked at three different levels. For all 304 compounds,
206 the average recoveries for pesticides spiked at three different levels ranged from 20.8 to
207 149.3 %. The enrichment factors ranged from 42- to 299-fold for all compounds. Among
208 these 304 compounds, 90 compounds with good recoveries and intra-day repeatability
209 (recoveries from 60~120%, RSDs < 20%) were listed in Table 1.

210 The limits of detection (LODs) were established by considering a value of three times
211 of the background noise in a blank sample at the retention time of each pesticide, and the
212 limits of quantification (LOQs) were calculated by considering a value of ten times of
213 that background noise. Table S2 shows the LODs and LOQs obtained for each pesticide.
214 The LODs obtained for all the pesticides ranged from 0.001 to 1.125 μg/L, the LOQs
215 ranged from 0.003 to 3.75 μg/L.

216 *3.3. Real sample analysis*

217 The established method was applied to analyze pesticides in 32 surface water samples
218 from Pearl River (Guangdong, China). Results show that, of all 304 pesticides, 3

pesticides (pirimiphos-methyl, beta-HCH, chlorpyrifos-methyl) were found in 3 samples. The concentrations of pirimiphos-methyl and beta-HCH were below LOQs, and the concentrations of chlorpyrifos-methyl were 0.12 μg/L and 0.021 μg/L in 2 collected samples.

4. Conclusion

In the present study, a new powerful sample preparation method coupled with GC-MS was developed to screen and quantify up to 304 pesticide residues and related chemicals residues in surface water. The optimized conditions for DLLME sampling of pesticides in water were investigated, and of all 304 compounds, 90 compounds showed good recoveries and repeatability. Besides, the method only needs very small amount of solvent and can be finished within few minutes. Thus, the DLLME method should be an attractive alternative sample preparation method for pesticides in water sample, and could be an effective method for monitoring of multi-pesticide in surface water.

Acknowledgment

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Figure Captions

Figure 1. Dispersive liquid-liquid microextraction procedure

Figure 2. The effect of different extracting solvent on the recoveries of pesticides obtained from DLLME.

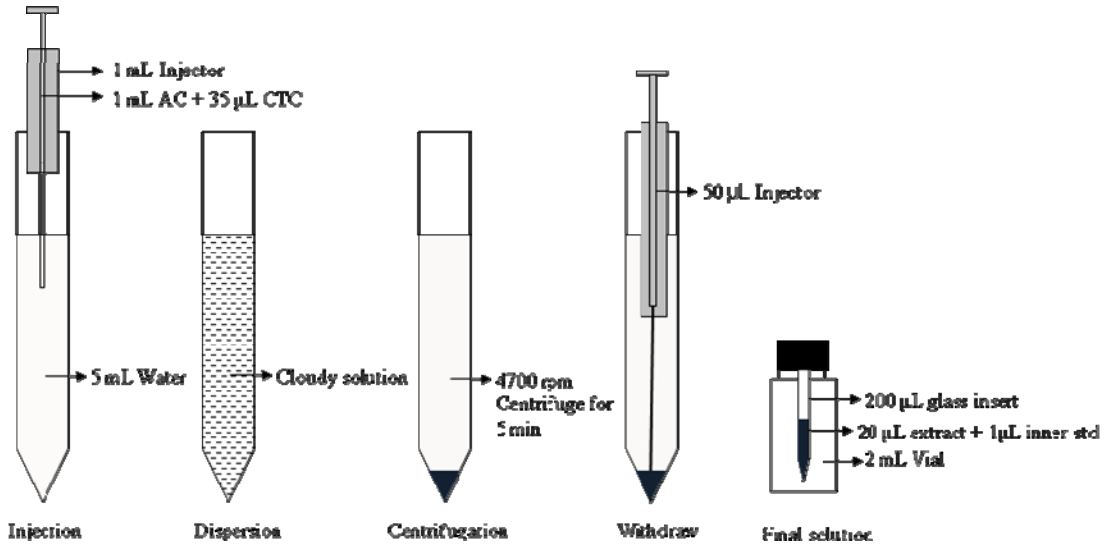
Figure 3. The effect of different disperser solvent on the recoveries of pesticides obtained from DLLME.

Figure 4. Comparison of the recoveries of pesticides obtained from DLLME using different volume of extraction solvent.

Figure 5. Comparison of enrichment factors using different amounts of salt addition.

Figure 6. Chromatogram of spiked blank water sample obtained by the optimized DLLME-GC-MS method (Group F, level C). Peak numbers correspond to: (1)fenobucarb, (2)phorate, (3) alpha-HCH, (4)Quintozene, (5)hexaflumuron, (6) gamma-HCH, (7) beta-HCH, (8)heptachlor, (9)phosphamidon, (10)aldrin, (11)chlorpyrifos-methyl, (12)pirimiphos-methyl, (13) epsilon-HCH, (14)chlorpyrifos, (15)methyl-parathion, (16) delta-HCH, (17)fenthion, (18)malathion, (19)fenitrothion, (20)heptachlor-epoxide(I.S.), (21)parathion, (22)quinalphos, (23)2-4'-DDE, (24)captan, (25)methidathion, (26)2,4'-DDD, (27)4,4'-DDD, (28)4,4'-DDT, (29)bifenthrin, (30)triazophos, (31)fenpropathrin, (32)cis-permethrin, (33)lambda-cyhalothrin, (34)trans-permethrin, (35)fenvalerate, (36)deltamethrin.

307 Figure 1.



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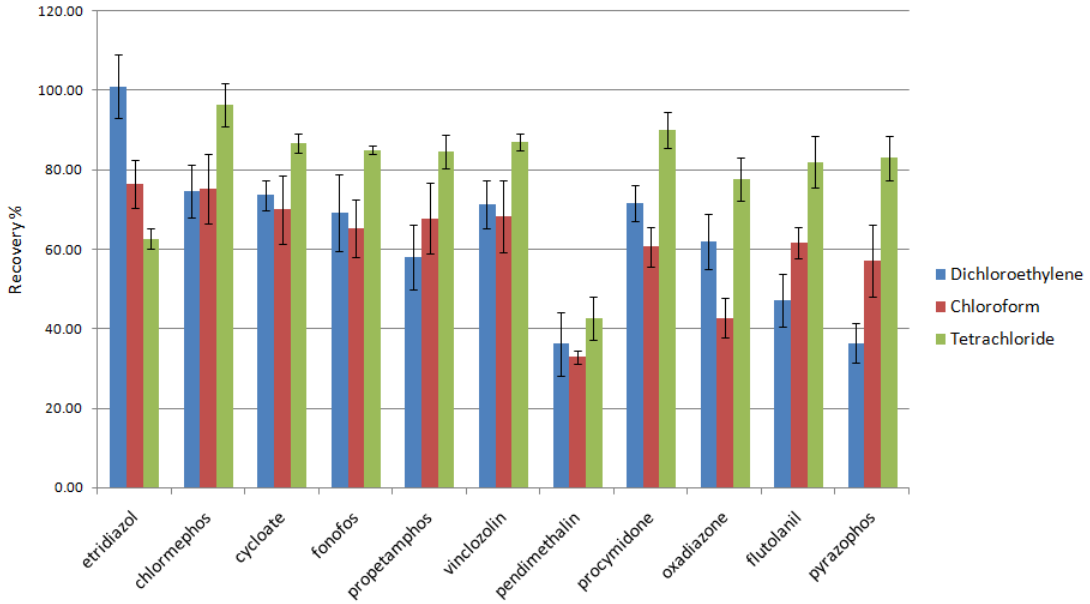

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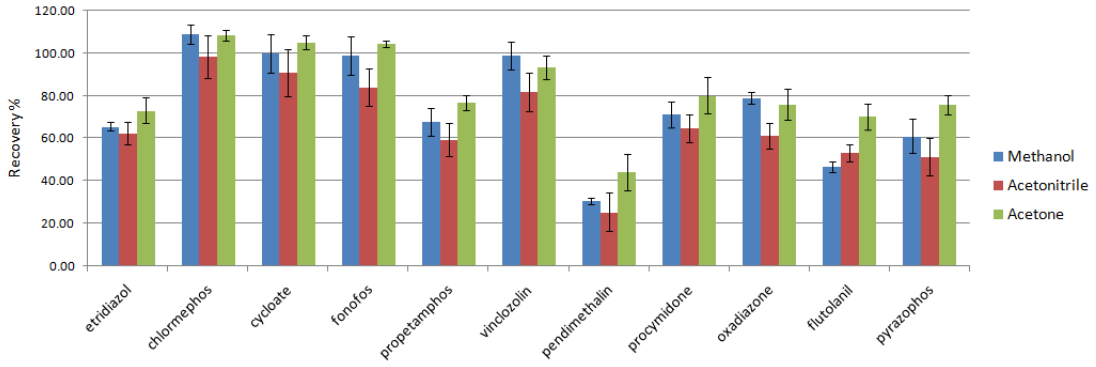

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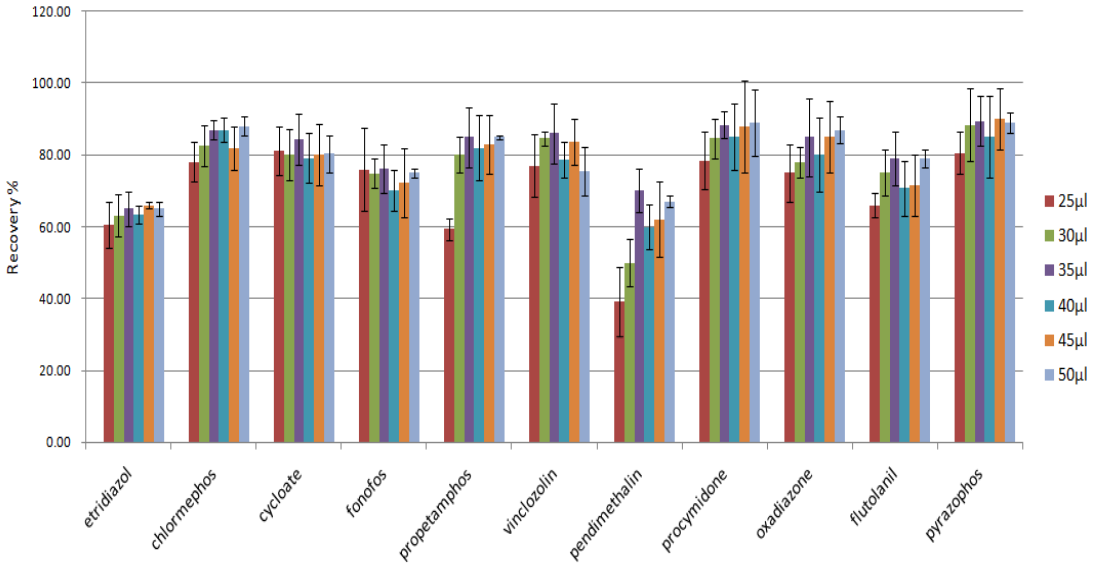

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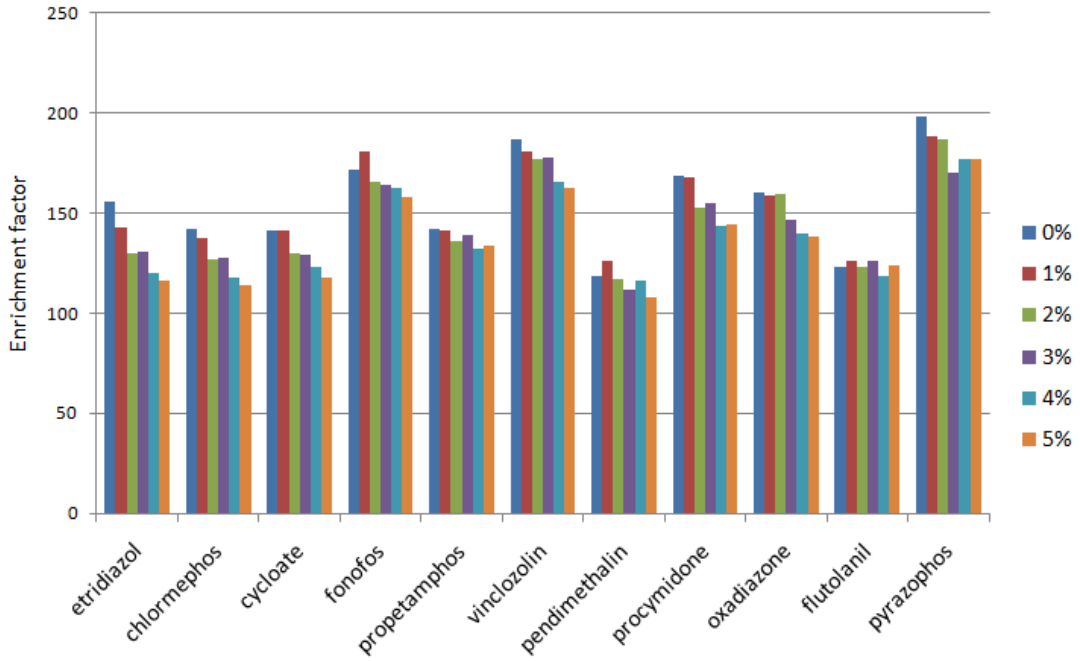
327 Figure 5.



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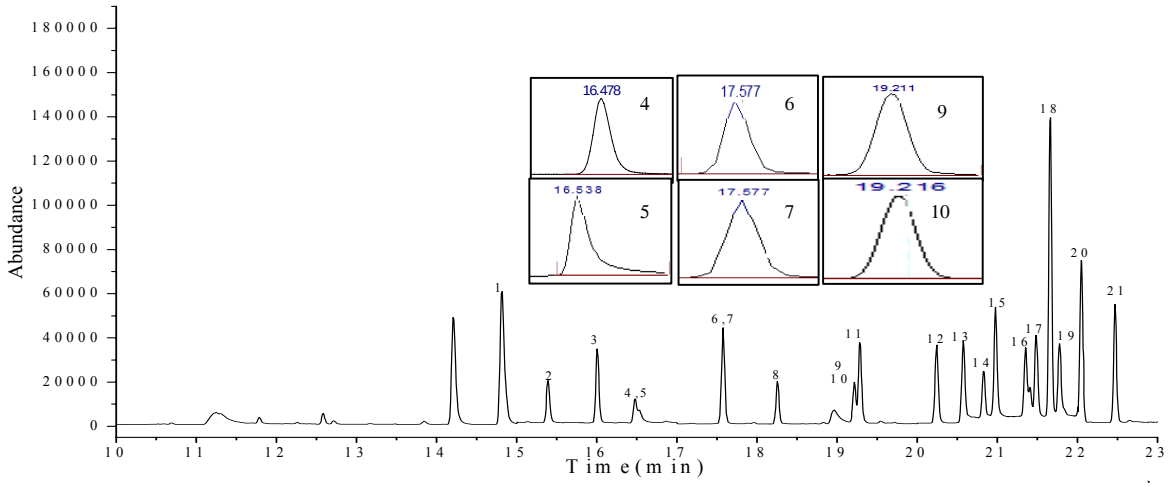

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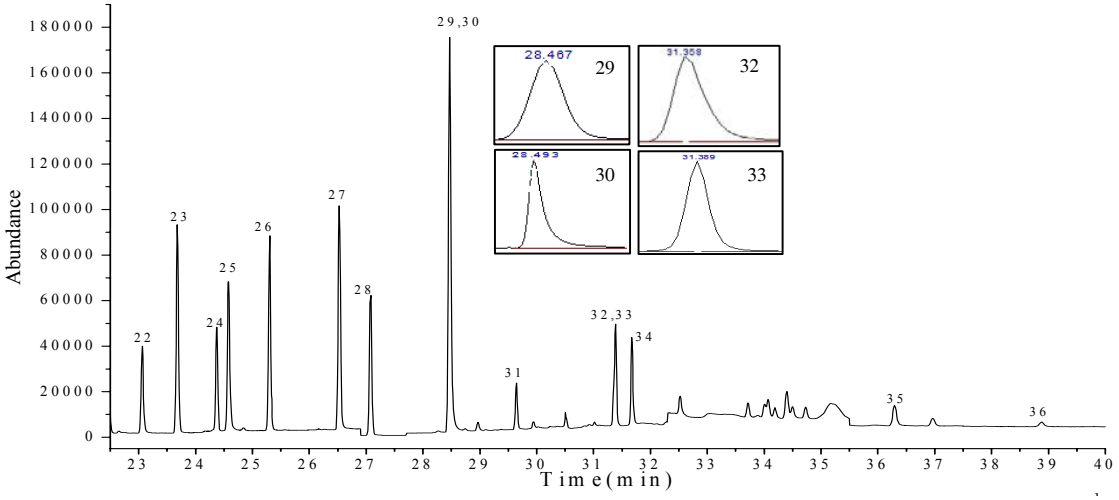

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336 **Table 1.** Linearity, average recovery, intra-day repeatability, enrichment factor (EF), LODs and LOQs obtained with the DLLME
337 method in spiked surface water (90 compounds with recovery from 60-120% and RSDs < 20%). The concentrations of spiked levels B
338 and C are 5 and 10 times of level A.

Pesticides	Linearity (r^2, neari	Spiked level A				Spiked level B			Spiked level C			LOD (μg/L)	LOQ (μg/L)
		Spiked concentration (μg/L)	Recovery	Intra-day RSD	EF	Recovery	Intra-day RSD	EF	Recovery	Intra-day RSD	EF		
					A								
etridiazol	0.9998(0.075-3.75)	0.375	70.2	15.5	140	85.6	8.7	171	72.4	9.2	145	0.025	0.085
chlormephos	0.9997(0.05-2.5)	0.25	71.7	14.9	143	80.9	9.4	162	80.3	7.5	161	0.016	0.052
cycloate	0.9994(0.0625-1.25)	0.125	77.8	19.3	156	94.6	9.5	189	87.8	8.1	176	0.003	0.008
fonofos	0.9961(0.025-1.25)	0.125	91.6	17.9	183	84.8	11.2	170	98.4	8.7	197	0.007	0.023
propetamphos	0.9965(0.025-1.25)	0.125	81.6	14.2	163	74	18.9	148	105.2	10.1	210	0.007	0.022
vinclozolin	0.9999(0.025-1.25)	0.125	87.3	18.2	175	101	4.7	202	86.5	8	173	0.008	0.025
pendimethalin	0.9925(0.1-5)	0.5	72.6	18.2	145	72.1	12.6	144	86.2	8.6	172	0.018	0.060
procymidone	0.9995(0.025-1.25)	0.125	95	16.7	190	102.8	4.9	206	77.5	7.5	155	0.011	0.038
oxadiazone	0.9999(0.025-1.25)	0.125	76.9	19.7	154	104.7	5.1	209	85.2	6.3	170	0.005	0.017
flutolanil	0.9982(0.025-1.25)	0.125	67.4	14.9	135	91	18.3	182	84.8	9.7	170	0.007	0.024
pyrazophos	0.9929(0.05-2.5)	0.25	111.9	11.9	224	109.5	14.1	219	90.7	16	181	0.011	0.038
					B								
EPTC	0.9957(0.075-3.75)	0.375	61.3	15.3	123	69.7	11	139	67.3	8.3	135	0.018	0.060
butylate	0.9962(0.075-3.75)	0.375	61.6	19.6	123	71.3	9.8	143	73.3	8.8	147	0.012	0.040
pebulate	0.9951(0.075-3.75)	0.375	63	18.8	126	71.2	9.6	142	71.7	9.4	143	0.016	0.053
ethofumesate	0.9993(0.05-2.5)	0.25	79.1	4.8	158	62.2	5.1	124	64.6	12	129	0.006	0.020
					C								
molinate	0.9975(0.025-1.25)	0.125	98.6	8.6	197	75.4	9.6	151	67.4	9.1	135	0.01	0.033
triallate	0.9988(0.05-2.5)	0.25	107.2	11.1	214	101.1	8.4	202	93.6	7.1	187	0.007	0.024
isazofos	0.9955(0.25-2.5)	0.25	113.7	5.2	227	100	12.3	200	107.8	10.8	216	0.027	0.091
fluchloralin	0.9978(0.1-5)	0.5	118.4	13.5	237	109.3	10.4	219	107.4	5.9	215	0.008	0.028
propisochlor	0.9987(0.025-1.25)	0.125	116.2	5	232	98.2	10.2	196	82.6	6.6	165	0.001	0.003

kresoxim-methyl	0.9959(0.025-1.25)	0.125	94.5	13.3	189	111.4	12.1	223	108.3	16.3	217	0.008	0.025
fludioxonil	0.9994(0.05-1.25)	0.125	79.3	16.5	158.6 D	99.4	14.2	199	85.3	12.3	171	0.057	0.189
pentachlorobenzene	0.9958(0.025-1.25)	0.125	80.9	17.5	162	88.6	6	177	105.3	11.6	211	0.004	0.013
chlorfenprop-methyl	0.9981(0.025-1.25)	0.125	87.5	14	175	107.2	9.6	214	104.2	13.4	208	0.006	0.02
2,3,5,6-tetrachloroaniline	0.9968(0.025-1.25)	0.125	84.6	11.8	169	108.2	9.4	216	108.6	11.2	217	0.003	0.01
pentachloroanisole	0.9951(0.025-1.25)	0.125	81.3	14.4	163	104.6	10.1	209	118.4	10.8	237	0.002	0.007
tebutam	0.9996(0.05-2.5)	0.25	79.5	9.8	159	85	10.7	170	87.3	15.2	175	0.006	0.021
dioxabenzofos	0.9995(0.25-12.5)	1.25	71	13.9	142	83.1	12.3	166	87.6	15	175	0.012	0.040
trietazine	0.999(0.025-1.25)	0.125	70	11.2	140	74.7	13.1	149	80	14.2	160	0.003	0.011
DE-PCB 28	0.9981(0.025-1.25)	0.125	76.9	16	154	95.6	4.8	191	82.1	8.7	164	0.005	0.016
DE-PCB 31	0.9981(0.025-1.25)	0.125	76.9	16	154	95.6	4.8	191	82.1	8.7	164	0.002	0.007
musk ambrette	0.9983(0.025-1.25)	0.125	87.5	12.7	175	103.9	13.8	208	119.7	9.7	239	0.011	0.038
musk xylene	0.9991(0.025-1.25)	0.125	81	12	162	95.2	12.2	190	110.7	9.7	221	0.013	0.042
pentachloroaniline	0.9996(0.025-1.25)	0.125	85.9	12	172	108.2	7.8	216	106	10.7	212	0.005	0.017
DE-PCB 52	0.9978(0.025-1.25)	0.125	74.7	16.6	149	92.2	4.2	184	101.8	8.3	204	0.002	0.006
prosulfocarb	0.9971(0.025-1.25)	0.125	103.4	11.8	207	107.8	9.7	216	108.8	11.7	218	0.005	0.016
dimethenamid	0.9997(0.025-1.25)	0.125	67.8	9.8	136	69.2	12.3	138	66.9	15.7	134	0.006	0.018
monalide	0.9997(0.05-2.5)	0.25	90.3	10.4	181	99.8	10	200	92.1	13.9	184	0.023	0.077
isobenzan	0.9996(0.025-1.25)	0.125	78.9	13.9	158	90.9	6.5	182	110.4	9	221	0.011	0.037
isomethiozin	0.9917(0.05-2.5)	0.25	97.8	14.6	196	98.8	16.6	198	103.3	13.3	207	0.01	0.032
dacthal	0.9988(0.025-1.25)	0.125	92.6	13.5	185	115.3	6.3	231	118.1	10.7	236	0.002	0.006
4,4-dichlorobenzophenone	0.9998(0.025-1.25)	0.125	99.6	11.7	199	112.1	7.3	224	83.6	11.5	167	0.011	0.038
nitrothal-isopropyl	0.9964(0.05-2.5)	0.25	95.8	18.9	192	95.9	15.1	192	101.4	10.6	203	0.015	0.049
musk ketone	0.9968(0.025-1.25)	0.125	95.6	12.2	191	106.5	10.6	213	111.1	10.9	222	0.003	0.009

rabenzazole	0.9972(0.025-1.25)	0.125	92.8	13.5	186	93	13.9	186	94.5	10.6	189	0.008	0.025
cyprodinil	0.9975(0.025-1.25)	0.125	104.2	13.6	208	106.2	14.5	212	85.1	14.3	170	0.007	0.023
dicapthon	0.998(0.125-6.25)	0.625	90.9	13	182	106.2	16.3	212	81.5	11.3	163	0.008	0.026
DEP-PCB 101	0.9983(0.025-1.25)	0.125	70.9	19.3	142	88.4	5.9	177	92.9	8.1	186	0.002	0.005
MCPA-butoxyethyl ester	0.9929(0.025-1.25)	0.125	116.8	11.2	234	110.9	10.7	222	85	11.1	170	0.006	0.02
chlorfenethol	0.9965(0.025-1.25)	0.125	108.4	9.6	217	108.9	13	218	102.8	12.8	206	0.006	0.021
ditalimfos	0.9985(0.025-1.25)	0.125	99.9	13.8	200	105.6	16.1	211	83.3	12.7	167	0.007	0.022
nitralin	0.9992(0.25-12.5)	1.25	86.4	13.5	173	87.7	19.9	175	71.1	12.7	142	0.034	0.114
dibutyl succinate	0.9964(0.05-2.5)	0.25	80.8	10.3	162	94.2	7.8	188	79.6	9.2	159	0.005	0.015
chlorethoxyfos	0.9988(0.05-2.5)	0.25	63	13.1	126	79.1	8.9	158	83.2	4.5	166	0.015	0.049
cadusafos	0.9993(0.1-5)	0.5	86	10.6	172	79.9	11.3	160	84	14.6	168	0.043	0.143
tebupirimfos	0.9974(0.05-2.5)	0.25	77.7	9.2	155	71.2	17.7	142	92.7	4.9	185	0.003	0.01
propyzamide	0.9995(0.05-2.5)	0.25	67.8	9	136	64.5	15.4	129	65.3	8.5	131	0.008	0.028
benoxacor	0.9992(0.05-2.5)	0.25	68.5	9.7	137	70.4	12.3	141	68.3	6	137	0.009	0.032
acetochlor	0.9981(0.05-2.5)	0.25	81.9	11.2	164	84.4	11.6	169	72.7	6.7	145	0.011	0.035
tridiphane	0.999(0.1-5)	0.5	81.4	13.1	163	84.9	12.6	170	84.7	3.4	169	0.015	0.05
terbucarb	0.9979(0.05-2.5)	0.25	85.6	10.5	171	90.9	9.3	182	87.6	6.2	175	0.004	0.013
esprocarb	0.9986(0.05-2.5)	0.25	87.2	11.8	174	90.4	10.4	181	85.4	4.4	171	0.006	0.020
benfuresate	0.9964(0.05-2.5)	0.25	71.9	10.2	144	74.5	11.2	149	66.4	4	133	0.006	0.019
dithiopyr	0.9978(0.025-1.25)	0.125	80.6	12.5	161	75.2	8.4	150	86.6	7.5	173	0.002	0.007
chlorthal-dimethyl	0.9964(0.05-2.5)	0.25	87	11.5	174	97.4	9.6	195	83.6	7.3	167	0.004	0.013
thiazopyr	0.9996(0.05-2.5)	0.25	83.7	12.4	167	93.7	6.6	187	86.4	5.3	173	0.007	0.022
butralin	0.9982(0.1-5)	0.5	77.6	9	155	65.1	13.9	130	84.5	6.8	169	0.006	0.020
methothrin-2	0.9979(0.05-2.5)	0.25	85.2	18.3	170	62.5	15.5	125	85	8.3	170	0.004	0.015
picoxystrobin	0.9999(0.05-2.5)	0.25	106.1	9.2	212	85.9	10.3	172	87	6.4	174	0.005	0.016
butamifos	0.9978(0.025-1.25)	0.125	84.6	12.5	169	82.8	11	166	91.2	5.7	182	0.013	0.042
diofenolan	0.9998(0.05-2.5)	0.25	107.1	12.6	214	111.7	14.3	223	81.1	3.1	162	0.016	0.054
chlrofenapyr	0.9995(0.2-10)	1	71.8	13.4	144	76	8.4	152	85.5	16.1	171	0.1	0.333

trifloxystroibin	0.9966(0.1-5)	0.5	80.1	11.2	160	67.7	17.2	135	78.2	5.6	156	0.006	0.022
iprodione	0.9997(0.1-5)	0.5	78.4	18.7	157	84.7	12.4	169	81.7	4.3	163	0.045	0.152
dialifos	0.9911(2-40)	4	102.4	9.1	205	79.8	19.2	160	83.7	11.2	167	0.151	0.503
butafenacil	0.9947(0.025-1.25)	0.125	104.3	15.3	209	76.9	18.4	154	87.2	4.9	174	0.005	0.017
cyflufenamid	0.9998(0.4-20)	2	76.8	10.8	154	78.2	11.9	156	84.2	5.7	168	0.026	0.086
fipronil	0.9975(0.2-10)	1	75.8	9.6	152	60.1	14.5	120	75.6	5.9	151	0.018	0.060
					F								
phorate	0.9992(0.0625-1.25)	0.125	97.6	12.6	195	93.2	8.6	186	109.1	6.1	218	0.013	0.042
Alpha-HCH	0.9976(0.025-1.25)	0.125	71.3	10.6	143	84.9	5.6	170	70.4	4.7	141	0.004	0.014
Quintozene	0.997(0.05-2.5)	0.25	71.3	9.1	143	86.6	7.9	173	85.5	5.9	171	0.022	0.074
gamma-HCH	0.9901(0.05-2.5)	0.25	72.4	10.3	145	82.5	5.5	165	70.9	4.9	142	0.023	0.076
chlorpyrifos-methyl	0.9985(0.025-1.25)	0.125	88	8.8	176	87.6	9.2	175	83.3	6.1	167	0.002	0.007
pirimiphos-methyl	0.9991(0.025-1.25)	0.125	88.8	10.7	178	91	12.4	182	88.5	7.1	177	0.002	0.007
Beta-HCH	0.9949(0.025-1.25)	0.125	67.6	9.1	135	81	6.7	162	73.4	10.1	147	0.003	0.009
epsilon-HCH	0.9973(0.05-2.5)	0.25	72.1	14.5	144	79.1	9.1	158	67.8	8.8	136	0.019	0.062
chlorpyrifos	0.9982(0.0625-1.25)	0.125	76.3	17.4	153	88.7	9.2	177	82.1	6.4	164	0.003	0.011
Delta-HCH	0.9911(0.05-2.5)	0.25	75.8	11.4	152	79.3	7.4	159	64.9	4.3	130	0.025	0.084
fenthion	0.9996(0.025-1.25)	0.125	95.7	9.3	191	81.2	17.8	162	78.2	5.3	156	0.004	0.014
2,4'-DDD	0.9911(0.025-1.25)	0.125	66.3	12.7	133	66.2	14.8	132	62.6	11.1	125	0.003	0.009

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