Determination of 23 Organophosphorous Pesticides in Surface Water Using SPME Followed by GC–MS

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Abstract

Determination of 23 organophosphorous pesticides (sulfotep, phorate, demeton, diazinon, disulfoton, kitazzin.P, chlorpyrifos-methyl, methyl-parathion, ronnel, fenitrothion, malathion, chlorpyrifos, fenthion, parathion, bromophos, isofenphos-methyl, phenthoate, quinalphos, ethion, triazophos, carbophenothion, pirimiphos-methyl, and pirimiphos-ethyl) in water using solid-phase microextraction (SPME) with gas chromatography–mass spectrometry detection (GC–MS) was investigated. The influence of various parameters on pesticides extraction efficiency by SPME was thoroughly studied. For quantitation in the selective ion monitoring (SIM) mode, the linear range of most compounds was found to be between 0.05–10 µg/L, and the detection limits were between 0.7–50 ng/L. To validate matrix effects for surface water, the recoveries were calculated between 71–104%. SPME in combination with GC–MS is a sensitive and effective method for the determination of organophosphorous pesticides (OPPs) in water samples.

Introduction

Organophosphorous pesticides (OPPs) are widely used in agriculture due to their relatively low cost, broad spectrum of activity, and high efficiency on insects. However, the utilization of this class of pesticides could cause extensive pollution of the environment and constitutes a potential risk for human health (1,2). OPPs have been found in drinking water in various concentrations, and therefore, there is an increasing environmental concern with regard to these compounds (3). Pollution caused by effluents discharged from plants with heavy organophosphorous contaminations has been a major problem in the world. Thus, the determination of OPPs residues in water samples is necessary for solving various environmental and biological problems.

The low concentration of OPPs and the complexity of the environmental water make it necessary to include pre-concentration and cleanup steps in the analysis procedure. Current methods used for extracting organophosphorous pesticides from aqueous samples involve solvent extraction techniques including liquid–liquid extraction (LLE), solid-phase extraction (SPE), and SPME procedures (4–8). However, in both LLE and SPE, more toxic organic solvents are used than SPME, multiple operation steps are needed, pre-concentration of the extract prior to analysis is required, and interferences are often introduced due to the extraction procedure. For example, the volume of organic solvents may be interfering with the determination of objective compounds in the LLE and SPE procedures. SPME is a novel solvent-free extraction technique, which integrates sampling, extraction, concentration, and sample introduction into a single step. Compared to the LLE and SPE methods, SPME is advantageous because of its speed, sensitivity, and operational ease. In recent years, SPME has received increasing attention and is now widely accepted as a reliable technique. It has been successfully applied in the analysis of a wide range of organic compounds in water samples (9–11) or from other sample matrices (12–15).

There are some reported methods for monitoring organophosphorous pesticides in water, soil, food, and biological samples (16–23). They are based on using different GC detectors such as GC–flame photometric detector (FPD) and GC–NPD. However, these technologies do not provide unequivocal confirmation of identity and are often subject to matrix interferences. But, the use of MS detection clearly increases detection capabilities giving spectral identification of separated compounds. Therefore, MS detection, usually in selected ion monitoring (SIM) mode, is the preferred method of choice for monitoring purposes as it is sensitive, selective, and provides mass separation. For example, phenthoate and quinalphos cannot be separated absolutely by GC–FPD or GC–NPD, so that they can not be accurately quantitated. But by using MS detection SIM mode, they can be quantified accurately by selecting different quantitation ions. Although, there are a few previous works using SPME-GC–MS for analyzing OPPs from

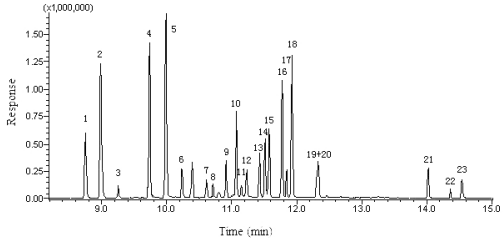

Figure 1. SPME-GC–MS (TIC) chromatogram of a distilled water sample spiked at 2 µg/L. For peaks assignments refer to Table I.

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water samples (24,25), only several OPPs were included. In this work, more OPPs (23 OPPs) can be analyzed simultaneously by the established method.

This paper will focus on the optimization and performance of an SPME-GC–MS procedure for the determination of 23 organophosphorous pesticides in water samples. The effect of various parameters on the extraction efficiency by SPME will be discussed in detail. GC parameters were optimized for baseline resolution between targeted pesticides themselves. SIM parameters were optimized for highest sensitivities. The method was performed in linearity, reliability, recovery, and limits of detection (LOD). Finally, the method was applied for analyzing real surface water samples, which were collected from Zhujiang River in China. The SPME-GC–MS is simple and useful for analyzing organophosphorous pesticides in water samples.

Experimental

Chemicals and Materials

The tested insecticides sulfotep, phorate, demeton, diazinon, disulfoton, kitazzin.P, chlorpyrifos-methyl, methyl-parathion, ronnel, fenitrothion, malathion, chlorpyrifos, fenthion, parathion, bromophos, isofenphos-methyl, phenthoate, quinalphos, ethion, triazophos, carbophenothion, pirimiphos-methyl, and pirimiphos-ethyl were purchased from Dr. Ehrenstorfer (Augsburg, Germany). All pesticide standards were of 98–99% purity. Stock solutions of each compound were prepared at the 200 mg/L level in HPLC-grade methanol. Working standards solutions were prepared by diluting the stock solutions to appropriate concentrations in methanol. The stock and working standards were stored at 4°C. Aqueous solutions were prepared by spiking the water with an appropriate amount of working solution.

HPLC-grade methanol was obtained from Merck (Darmstadt, Germany). Water was double distilled. Analytical-grade sodium chloride was used after purification by heating at 300°C overnight.

The SPME holder for manual was obtained from Supelco (Bellefonte, PA). Four different types of fibers, polyacrylate (PA, 85 µm), polydimethylsiloxane (PDMS, 100 µm), polydimethylsiloxane (PDMS, 30 µm), and polydimethylsiloxane/divinylbenzene (PDMS/DVB, 65 µm), were also obtained from Supelco. The coated fibers were conditioned according to the manufacturer's recommendations for the removal of possible contaminants prior to use. The stirrer used was a Corning PC-420D stirrer (Lowell, MA).

SPME procedure

Extraction of water samples was carried out by direct immersion of the PDMS/DVB fiber in the 4 mL sample contained in a 5-mL clear glass vial under magnetic stirring for 45 min at 60°C. Sample agitation was done 1150 rpm by a magnetic stirrer. Then the fiber was removed from the sample solution and immediately inserted into the GC injector for GC–MS analysis. SPME fibers were desorbed in the splitless mode for 5 min at 250°C.

GC–FPD analysis

A Hewlett Packard 6890 GC equipped with a split-splitless injector, a FPD, and operated by HP Chemstation Software was used for the experiments to optimize SPME conditions. The

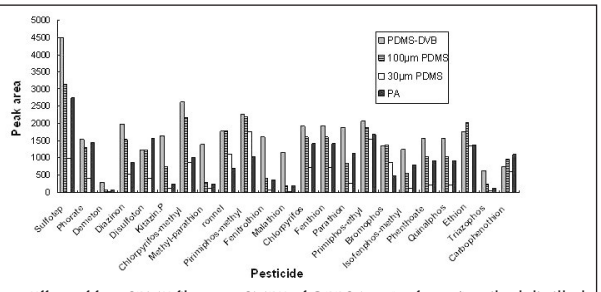

Figure 2. Effect of four SPME fibers on SMPE of OPPS (4 mL of 2 µg/L spiked distilled water stirred at 700 rpm and extracted 40 min at ambient temperature) (n = 3).

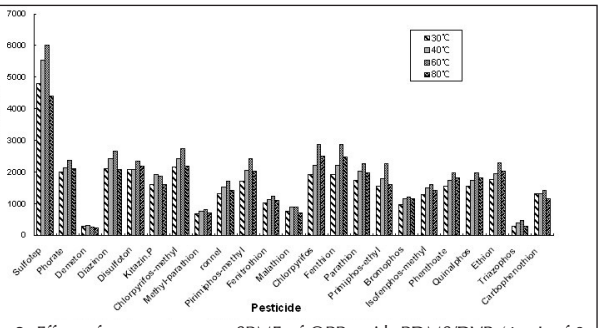

Figure 3. Effect of temperature on SPME of OPPs with PDMS/DVB (4 mL of 2 µg/L spiked distilled water stirred at 700 rpm and extracted 40 min at ambient temperature) (n = 3).

Table I. Retention time (t_R), Quantitation Ions, Confirmation Ion 1, and Ion 2 (Relative Abundance %) of 23 Organophosphorous Pesticides

Peak No.	Pesticide	t_R ± SD (min)	Quantitation ion (m/z)	Relative abundance %	
				Conf. Ion 2	Conf. Ion 2
1	Sulfotep	8.73 ± 0.02	322	202 (85%)	97 (50%)
2	Phorate	8.96 ± 0.01	75	121 (32%)	47 (19%)
3	Demeton	9.22 ± 0.02	88	60 (52%)	89 (38%)
4	Diazinon	9.72 ± 0.03	179	137 (98%)	152 (87%)
5	Disulfoton	9.96 ± 0.01	88	89 (39%)	61 (24%)
6	Kitazin.P	10.21 ± 0.02	91	204 (45%)	123 (15%)
7	Chlorpyrifos-methyl	10.59 ± 0.03	286	288 (71%)	125 (65%)
8	Methyl-parathion	10.71 ± 0.01	109	125 (75%)	263 (55%)
9	Ronnel	10.90 ± 0.01	285	287 (71%)	125 (47%)
10	Primiphos-methyl	11.05 ± 0.03	290	276 (82%)	305 (47%)
11	Fenitrothion	11.13 ± 0.02	125	109 (92%)	277 (84%)
12	Malathion	11.26 ± 0.02	127	173 (82%)	158 (31%)
13	Chlorpyrifos	11.41 ± 0.01	97	197 (95%)	199 (89%)
14	Fenthion	11.49 ± 0.01	278	125 (35%)	109 (32%)
15	Parathion	11.55 ± 0.03	97	109 (95%)	291 (75%)
16	Primiphos-ethyl	11.75 ± 0.02	333	318 (88%)	168 (78%)
17	Bromophos	11.83 ± 0.01	331	329 (68%)	125 (42%)
18	Isofenphos-methyl	11.90 ± 0.02	58	121 (83%)	199 (99%)
19	Phenthoate	12.29 ± 0.01	274	121 (64%)	93 (46%)
20	Quinalphos	12.32 ± 0.03	146	157 (65%)	118 (41%)
21	Ethion	14.01 ± 0.01	231	97 (71%)	121 (40%)
22	Triazophos	14.37 ± 0.03	161	162 (71%)	172 (50%)
23	Carbophenothion	14.52 ± 0.01	157	153 (45%)	121 (38%)

injector was used in splitless mode (5 min) and held at 250°C. The column used for analysis was a fused silica capillary Agilent HP-5 (30 m × 0.25 mm, 0.25 µm) (Santa Clara, CA). The oven temperature was programmed as follow: initial temperature 100°C (hold 2 min), 20°C/min to 180°C, and 10°C/min to 250°C (hold 2 min). The FPD system was maintained at 280°C. Nitrogen was used as carrier gas and make up gas (99.999% purity) at a constant flow rate of 1 and 60 mL/min, respectively. The pressure of detector gases, hydrogen and air, was set at 150 and 110 mL/min, respectively.

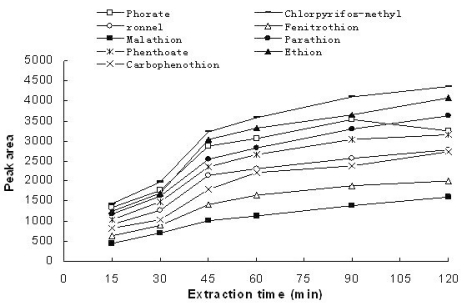

Figure 4. Effect of extraction time on SPME of OPPs with PDMS/DVB (4 mL of 2 µg/L spiked distilled water stirred at 700 rpm and set temperature at 60°C) (n = 3).

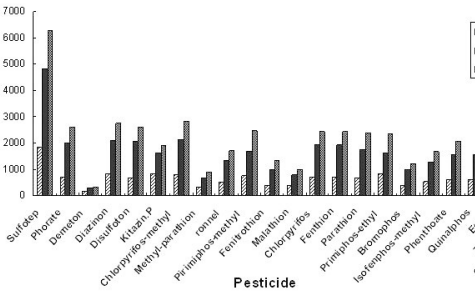

Figure 5. Effect of stirring rate on SPME of OPPs with PDMS/DVB (4 mL of 2 µg/L spiked distilled water stirred at 700 rpm and extracted 45 min at 60°C) (n = 3).

Table II. Linearity Data, Limit of Detection, Limit of Quantification, Repeatability, and Reproducibility of the Pesticides Analyzed by SPME-GC–MS method

Pesticide	Linearity range (µg/L)	Regression equation	Correlation coefficient (r^2)	LOD (ng/L)	LOQ (ng/L)	Precision (%) (n = 6)	
						Intra-day	Inter-day
Sulfotep	10–0.05	$y = 143758x + 12238$	0.9862	1.0	4.2	7.9	9.5
Phorate	10–0.05	$y = 497887x - 64009$	0.9966	2.1	7.1	9.6	8.9
Demeton	25–0.1	$y = 3003x - 179$	0.9912	27.6	93.4	16.2	17.4
Diazinon	10–0.05	$y = 186822x + 11173$	0.9906	1.9	6.3	12.4	14.2
Disulfoton	10–0.05	$y = 451994x - 45593$	0.9914	0.9	3.1	7.0	9.1
Kitazin.P	10–0.05	$y = 51196x - 4413$	0.9984	6.2	21.2	4.9	6.7
Chlorpyrifos-methyl	10–0.05	$y = 14064x - 2231$	0.9992	6.1	20.1	7.7	9.1
Methyl-parathion	25–0.1	$y = 3205x - 1796$	0.9946	32.2	106.2	6.8	8.2
Ronnel	10–0.05	$y = 36684x - 6197$	0.9992	1.9	6.3	14.2	16.8
Primiphos-methyl	10–0.05	$y = 81229x - 4587$	0.9972	0.7	2.3	10.0	13.4
Fenitrothion	10–0.05	$y = 10629x - 5970$	0.9952	19.4	64.1	18.6	19.1
Malathion	25–0.1	$y = 234x + 360$	0.9972	41.0	135.3	7.5	8.9
Chlorpyrifos	10–0.05	$y = 39590x - 3492$	0.9994	8.8	29.1	17.0	18.7
Fenthion	10–0.05	$y = 82587x - 2924$	0.9996	3.0	10.2	7.4	9.7
Parathion	10–0.05	$y = 45880x - 13144$	0.9920	11.1	36.7	12.1	14.8
Primiphos-ethyl	10–0.05	$y = 135030x + 11310$	0.9823	14.4	47.6	5.5	7.2
Bromophos	10–0.05	$y = 8043x - 2857$	0.9936	1.3	4.3	8.0	9.1
Isofenphos-methyl	10–0.05	$y = 316247x - 7894$	0.9956	1.3	4.3	6.6	8.0
Phenthoate	10–0.05	$y = 14983x - 4356$	0.9966	5.6	18.5	6.6	8.5
Quinalphos	10–0.05	$y = 38526x - 12045$	0.9958	3.2	10.6	8.1	10.1
Ethion	10–0.05	$y = 21278x - 9695$	0.9809	1.9	6.3	13.3	14.1
Triazophos	25–0.1	$y = 577x - 85$	0.9843	50	165.1	8.7	11.5
Carbophenothion	10–0.05	$y = 22713x - 19694$	0.9948	10.6	35	11.3	14.3

GC–MS analysis

GC–MS was performed with a Shimadzu QP2010 equipped with a split-splitless injector and connected to a quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). Data handling and system operations were controlled by the GC–MS Solution software. Separation was carried out using a DB-5 MS capillary column (30 m × 0.25 mm, 0.25 µm, contained 5% phenyl-methylpolysiloxane) (J&W Scientific, Santa Clara, CA). For the chromatographic determination, helium (99.999%) was used as the carrier gas at a constant flow rate of 1 mL/min. Injector temperature was kept at 250ºC in splitless mode (5 min), and oven temperature was programmed as follows: initial temperature 100°C (hold 2 min), 20°C/min to 180°C, and 10°C/min to 250°C (hold 2 min). The total SPME-GC–MS analysis time is 60 min.

The MS ionization was carried out in the electron ionization mode. The spectra were obtained at 70 eV. The GC–MS interface and the ion source temperature were set at 250 and 200ºC, respectively. OPP standards and samples were analyzed in the selected ion monitoring (SIM) mode. For each analyte, the most abundant and characteristic mass fragment ion was chosen for quantification and two others were for confirmation. The quantification ions and relative abundances of confirmation ions were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio (m/z) ranging from m/z 50 to 500. Table I lists the pesticides along with their retention times, the quantification and confirmation ions, and their confirmation to quantification abundance ratios. Pesticides were confirmed by their retention times, the identification of quantification and confirmation ions, and the determination of confirmation to quantification ratios. Retention times had to be within ± 0.1 min of the expected time, and confirmation to quantification ratios had to be within a 10% range for positive confirmation. A typical GC–MS chromat-ogram for distilled water spiked at 2 µg/L extracted with SPME is shown in Figure 1.

Results and Discussion

SPME optimization

Twenty-three organophosphorous with various chemical structures were selected for this study. SPME conditions were optimized using a GC–FPD. Extraction efficiencies were optimized in spiked distilled water by

evaluating the following parameters: fiber type, temperature, extraction time, agitation, and salting out effect.

The choice of an appropriate coating is essential for the SPME method. Four commercially SPME fibers (70 or 100 µm PDMS, PDMS/DVB, PA) were evaluated for the extraction of 23 OPPs. A sample volume of 4 mL and 40 min extraction time with constant agitation at ambient temperature were used. Desorption of the fibre was carried out at 250°C for 5 min. Figure 2 illustrates the extraction efficiencies of the studied compounds using various SPME fibers. The results clearly showed that the PDMS/DVB fiber had the better extraction efficency for the majority of target analytes. Thus, PDMS/DVB fiber was the most suitable for the extraction of OPPs and was used for further investigation.

Extraction temperature plays an important role in the extraction process by controlling the diffusion rate of analytes onto the coating. The effect of temperature on the amount of analytes extracted by SPME with PDMS/DVB fiber was investigated at 30, 40, 60, 80°C with a constant extraction time of 40 min. Responses obtained were plotted versus temperature for each analyte are shown in Figure 3. From Figure 3, it is clear that the peak areas of most OPPs increased when the temperature was increased from 30 to 60°C. However, at higher temperature of 80°C the ability of SPME fiber to adsorb the tested insecticides begins to decrease. Evaluation of temperature effect showed that when the temperature was 60°C, the majority OPPs had the best sensitivity achieved. Thus, the optimum extraction efficiency was achieved at 60°C, and this temperature was selected.

The effect of extraction time on the adsorption was investigated by plotting the profile of the GC peak area versus the extraction time. All of the experiments were carried out under the same conditions: the extraction temperature was 60°C, 4 mL of water was added, and the adsorption time was 5 min. The results are shown in Figure 4. From Figure 4, it is clear that the responses to the OPPs greatly increase with increasing extraction time, but only gradually increase when the extraction time increases beyond 45 min. The optimum time was found to be 45 min; this was a compromise between the time spent and the amount of analytes extracted.

For SPME, stirring should be vigorous and has to be maintained constant in all experiments. The influence of agitation on extraction efficiency was investigated. The optimum stirring rate was determined by analyzing samples at different stirring rates between 200–1150 rpm. The results are shown in Figure 5. It was concluded that for agitation at 200 rpm a poor extraction level was achieved, and the extraction efficiency increased with increasing the stirring rate. The maximum speed (1150 rpm), at which larger areas were achieved for the studied compounds, was chosen for the subsequent analyses.

The effect of ionic strength on extraction efficiency was evaluated by analyzing the amount of OPPs extracted by PDMS/DVB fiber in water sample containing 5, 10, and 20% (W/V) of sodium chloride. Figure 6 shows the profile of the effect of salt addition on the extraction efficiency. The results revealed that sodium chloride improved the extraction efficiency only for some organophosphorous pesticides such as demeton, parathion, and quinalphos. But the majority of compounds did not show a significant increase and even showed a decrease in extraction yield with the addition of sodium chloride. Thus, the salt addition was not recommended.

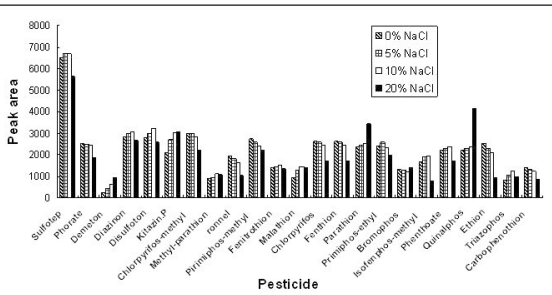

Figure 6. Effect of sodium chloride addition on SPME of OPPs with PDMS/DVB (4 mL of 2 µg/L spiked distilled water stirred at 1150 rpm and extracted 45 min at 60°C) (n = 3).

Method performance

The optimized SPME procedures were evaluated referring to validation guide lines by International Conference on Harmonization (ICH).

The precisions of the method were evaluated by inter-day and intra-day analysis, which were determined with spiked distilled water samples. The intra-day precision and inter-day precision carried out six independent extractions of the studied compounds at 2 µg/L under the optimized conditions in one day and on six different days, respectively. The results of intra-day and inter-day precision experiments were expressed as relative standard deviation (RSD%) and given in Table II. The intra-day

Table III. Recovery of the Studied Pesticides in Spiked Surface Water Samples at Three Concentration Levels

Pesticide	Analytical recovery (%) ± SD (n = 5)		
	0.1 µg/L	2 µg/L	10 µg/L
Sulfotep	85 ± 4	86 ± 7	88 ± 10
Phorate	93 ± 9	103 ± 6	104 ± 12
Demeton	94 ± 8	93 ± 8	95 ± 6
Diazinon	95 ± 7	96 ± 7	92 ± 8
Disulfoton	90 ± 10	103 ± 11	102 ± 9
Kitazin.P	87 ± 9	94 ± 5	90 ± 10
Chlorpyrifos-methyl	78 ± 13	82 ± 10	77 ± 9
Methyl-parathion	74 ± 11	77 ± 5	75 ± 12
Ronnel	79 ± 9	83 ± 12	85 ± 9
Primiphos-methyl	82 ± 13	84 ± 10	83 ± 10
Fenitrothion	90 ± 10	90 ± 15	88 ± 11
Malathion	76 ± 8	79 ± 8	86 ± 9
Chlorpyrifos	81 ± 9	87 ± 13	80 ± 7
Fenthion	71 ± 13	72 ± 14	83 ± 8
Parathion	82 ± 19	85± 18	79 ± 16
Isocarbophos	87 ± 10	96 ± 12	90 ± 15
Primiphos-ethyl	84 ± 8	89 ± 10	92 ± 6
Bromophos	75 ± 14	80 ± 12	85 ± 9
Isofenphos-methyl	72 ± 16	79 ± 8	76 ± 12
Phenthoate	77 ± 8	78 ± 9	73 ± 13
Quinalphos	82 ± 9	87 ± 12	90 ± 7
Ethion	80 ± 15	75 ± 16	75 ± 10
Triazophos	72 ± 16	77 ± 8	79 ± 13
Carbophenothion	84 ± 5	87 ± 9	92 ± 11

precision and the inter-day precision ranged from 4.9% to 18.6% and 6.7% to 19.1%, respectively.

To evaluate the linearity of the SPME method, a calibration study was performed by spiking deionized water with studied analytes in tested concentration ranges from 0.05 to 25 µg/L. Each calibration level was analyzed in two replicates. The determination coefficients in linear range of each analyte are presented in Table II. In summary, the (r^2) coefficients varied between 0.9809–0.9996.

The limits of detection (LOD) and the limits of quantification (LOQ) for each compound were also calculated for the optimized methods. The LOD and LOQ were calculated as the concentration of OPPs with signal-to-noise (S/N) ratios of about 3:1 and 10:1, respectively. The results are also shown in Table II. The LODs of SPME-GC–MS were lower than 20 ng/L except for demeton, methyl-parathion, malathion, and triazophos. The LOQ ranged from 2.3 to 165.1 ng/L.

Application to Real Samples

The SPME analysis of ten real surface water samples were collected from different stations and time of Zhujiang River in China, transported in pre-cleaned glass bottles, stored at 4°C, and were analyzed within 24 h of collection. No studied OPPs were detected in these real samples. Therefore, to assess matrix effects, the tested OPPs were spiked to real surface samples at three concentration levels (0.1, 2, 10 µg/L). Relative recoveries, defined as the ratio of MS quantitation ions areas of water extracts to spiked ultrapure water extract, were calculated to evaluate the effect of the matrices. The experiments were repeated five times. Results of all of the experiments are shown in Table III. For OPPs in this study at three concentration levels, the recovery values (%) were between 71% and 104%.

Conclusions

A highly satisfactory method for the simultaneous analysis of 23 organophosphorus pesticides from water was developed. The method is simple, sensitive, and very useful in routine laboratories. The PDMS/DVB fibre coating proved to be efficient in the extraction of 23 OPPs. The results obtained in the validation of SPME-GC–MS in SIM mode showed adequate sensitivity (LOD < 50 ng/L), good linearity, and accuracy. In addition, the combination of SPME with GC–MS further enhances the method's potential, enabling positive analytes identification.

Acknowledgements

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