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ENVIRONMENTAL CHEMICAL CONTAMINANTS

Experimental Design of Vortex Assisted Switchable Solvent Homogeneous Liquid-Liquid Microextraction for Simultaneous Determination of Four Pesticides in Wastewater

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Abstract

Background: Pesticides are chemicals used mainly to protect plant crops in order to increase their production efficiency and quality.
Objective: Switchable-solvent homogeneous liquid-liquid microextraction was optimized using a Box-Behnken experimental design and validated on a gas chromatography mass spectrometry system for the determination of analytes.
Method: The significance of independent variables (switchable solvent volume, sodium hydroxide volume, and vortex period) and their interactions were evaluated by analysis of variance at 95% confidence limits ($\alpha = 0.05$).
Results: The LOD and LOQ ranges of the analytes were found to be 0.42–1.90 μg/L and 1.36–6.33 μg/L, respectively. Percentage recovery results were found to be in the range of 87–113% in spiking experiments.
Conclusions: A simple, efficient, and accurate analytical method was developed for the simultaneous determination of the selected pesticides. *Highlights:* Matrix matching was used to enhance quantification accuracy for real samples.
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Pesticides are chemicals used mainly to protect plant crops in order to boost their production yields and quality. In addition to plant protection, pesticides are also used to protect humans and other animals from disease-transmitting insects (1). Despite these wide applications and benefits, several adverse effects of pesticides on the environment and living organisms have been reported. Pesticides are directly applied to plants and soils but only a low percentage reaches its intended target, with the greater percentage settling on non-target organisms and surroundings (2). One of the alarming effects of pesticides is accumulation in the environment and in living organisms over time (3). Surface water and groundwater are common environmental resources that are contaminated as a result of the widespread use of pesticides (4). Due to the ubiquitous nature of pesticides in the environment, it is prudent to develop systematic and rapid analytical procedures for their determination (5). There are diverse problems that are encountered in pesticide analysis, because pesticides are composed of active ingredients and chemicals with a wide variety of acidic and polarity properties (6). The complexity of environmental samples in which pesticides occur also hinders the accuracy of detection and quantification, especially when they occur at trace levels (7).

Extraction is a common analytical strategy used to isolate analytes of interest from complex sample matrices into suitable forms for instruments, and preconcentrate them for lower detection limits (8). The traditional liquid-liquid extraction (LLE)

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(9) and solid-phase extraction (SPE) (10) methods have been widely used as pretreatment methods for pesticide determinations (11, 12). Due to the high cost, time consumption, and use of large volumes of hazardous chemicals, microextraction methods, termed liquid phase microextraction (LPME) and solid phase microextraction (SPME), have been developed to replace the conventional LLE and SPE, respectively (13, 14). Some common microextraction methods employed for preconcentration of pesticides include hollow fiber (HF) LPME (15), deep eutectic solvent (DES) LPME (16, 17), dispersive liquid-liquid microextraction (DLLME) (18), solidified floating organic drop microextraction (SFODME) (19), single-drop microextraction (SDME) (20), and supramolecular solvent-based microextraction (SSME) (21).

Recent developments in green chemistry have led to the development of a variety of environmentally friendly materials from green sources. Green analytical chemistry is of great interest as it leads to a significant reduction in the use of toxic chemicals that subsequently produce toxic wastes (22). In 2005, switchable polarity solvent was first reported by Jessop et al., where they utilized CO_2 to trigger the switch of a non-polar amine into a water miscible form and subsequently reverted it back into its original non-polar state by flushing with an inert gas or sodium hydroxide addition (23, 24). The use of CO_2 for the triggering process stems from its non-toxicity, low cost, and ease of removal in the deprotonation step (25). Switchable solvents (SS) are efficient extractants and the analyte-rich amine phase obtained after the extraction process is compatible with most instrumental systems, although they might require further processing for compatibility. Homogenous liquid-liquid extraction/microextraction (HLLE/HLLME) refers to extraction methods that begin as a single phase and separate into a two-phase system with the addition of organic salts or other reagents (26). SS-based extractions fall into this category. Others include deep eutectic solvents (27), iso-propanol/sodium sulfate (28), and acetonitrile/sodium sulfate (26). For the separation of volatile organic compounds, GC-MS is greatly preferred as it utilizes the difference in vapor pressure and fragmentation patterns (*m/z*). The mass selective detector does not only identify compounds, but it is also capable of performing selective determination for a group of compounds (*m/z* scan range) or determination of a specific compound [selected ion monitoring (SIM)] (7).

In this study, a vortex assisted (VA)SS-HLLME method was optimized and validated for the determination of selected pesticides by GC-MS. A Box-Behnken experimental design was utilized to evaluate the effect of individual parameters and interaction of parameters on extraction efficiency.

METHOD

Chemicals and Reagents

Analytical grade chemicals and reagents were used in this study. Chlorpyrifos (CAS# 2921-88-2), endosulfan beta (CAS# 33213-65-9), acibenzolar s methyl (CAS# 135158-4-2), and propham (CAS# 122-42-9), having purities greater than 98%, were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solutions (1000 mg/L) of each standard were prepared by dissolving appropriate amounts in acetonitrile, and aliquots were taken from each to prepare mixed calibration and working standard solutions. Standard solutions for direct GC-MS analysis were prepared in acetonitrile, while aqueous standard solutions for method development were prepared daily in ultrapure deionized water obtained from a Milli-Q Reference Water Purification System. N, N-dimethylbenzylamine (DMBA), acetonitrile, and sodium chloride were all purchased from Merck, and dry ice (solid CO_2) was purchased from a local café in İstanbul, Turkey. The SS was prepared according to the procedure reported by Fırat et al. (29), and it is hereinafter referred to as protonated DMBA.

Samples

Two different domestic wastewater samples were taken from aeration pools at treatment facilities in Istanbul. Particulate matter in the wastewater samples were eliminated by successive filtrations through 11 μm filter papers and 0.45 μm filters. The samples were stored in a refrigerator (4.0 °C) when not in use. Prior to filtration, centrifugation was performed to settle particle matter and enable filtration without clogging of filter pores.

Instrumentation

A gas chromatograph (Agilent 6890) and mass spectrometry detector (Agilent 5973) from Agilent Technologies (USA) were used for qualitative and quantitative determination of the four analytes. Elution of the analytes through a 30 m capillary column (HP-5MS: 5.0% phenyl methyl siloxane) was achieved using the following temperature program: 70 °C initial temperature ramped to 180 °C (30 °C min^{-1}) and finally to 300 °C (40 °C min^{-1}). The flow rate of helium used as carrier gas was kept constant at 1.8 mL min^{-1}. The transfer line and front inlet temperatures were 250 °C and 280 °C, respectively. All injections were made in splitless mode and 1.0 μL was set as the sample/standard injection volume. Chlorpyrifos, endosulfan beta, acibenzolar s methyl, and propham were quantified/qualified with the *m/z* ions 97/197, 195/241, 182/135, and 43/93, respectively.

VA-SS-HLLME Procedure for the Determination of Pesticides

The optimized protonated DMBA volume of 1.1 mL was pipetted into a 15 mL centrifuge tube filled with 8.0 mL sample solution and shaken slightly. Then, 1.5 mL of 0.50 M sodium hydroxide solution was added for deprotonation, which was observed as a cloudy white solution. The solution was vortexed for 20 s followed by 120 s centrifugation at 6000 rpm. The separated amine phase settled above the aqueous solution and 40 μL was withdrawn into microliter glass vials for auto-injection into the GC-MS system.

Results and Discussion

The performance of the GC-MS system for the four analytes was determined prior to the method development experiments, which were performed with 0.10 mg/L aqueous standard solutions. Three replicates were performed for all variables and the highest mean peak area was selected as optimum value. The detection limit obtained for the optimized method was compared to the limit obtained by direct GC-MS analysis to calculate enhancement in detection power.

NaOH Concentration Optimization

The concentration and the volume of sodium hydroxide are two parameters that affect the outcome of the deprotonation process, but fitting the two parameters into the experimental design would produce redundant results. To elaborate, twice a

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concentration and half the volume of sodium hydroxide would give a similar effect. For this reason, the optimum concentration of sodium hydroxide was determined separately in order to fit its varying volumes in the experimental design. Here, 2.0 mL of 0.50, 1.0, 2.0, and 3.0 M sodium hydroxide solutions were added to four equivalent mixtures comprised of 8.0 mL standard solution (0.10 mg L^{-1}) and 1.0 mL protonated DMBA. As shown in Figure 1, the peak area values of all four analytes decreased with increasing concentration of sodium hydroxide due to dilution effect of the higher concentrations. The final volume of separated amine after separation was observed to increase proportionally to the concentration of sodium hydroxide, causing dilution of extracted analytes. This suggested that concentrations below 0.50 M would give higher peak area values. When the lower concentrations were tested, there was no clear separated amine phase collected for instrumental reading. Thus, 0.50 M sodium hydroxide was maintained as optimum concentration.

Box-Behnken Design

The Design Expert 7.0.0 program was used to develop a Box-Behnken experimental design for three parameters of the SS-HLLME method including protonated DMBA volume, 0.50 M sodium hydroxide volume, and vortex period. Each parameter was varied at high, mean, and low levels, which are denoted as +1, 0, and −1, respectively. The actual high and low levels used in the design experiment were 1.0 and 2.5 mL for both protonated DMBA and sodium hydroxide volumes, while 15 and 45 s were used for vortex period. In the first optimization step (sodium hydroxide concentration), the final volume of amine phase after deprotonation was about 200 µL for 1.0 mL of protonated DMBA and 2.0 mL of 0.50 mL sodium hydroxide. Thus, the high and low levels were set as 2.5 and 1.0 mL to obtain sufficient final volumes for instrumental measurement. With five center points, three replicates performed for each of the 17 combinations of parameter variables produced a data pool. The average values of the respective runs for each analyte were inserted into the design program for evaluation using the analysis of variance tool. Evaluation was based on parameters significant to the design model as well as the significance of the interaction between any two parameters. Conformity of experimented results to values estimated by the design program was determined with the normal probability plot of both values and the coefficient of determination (R^2) value of the plot was 90%. With a *P*-value of 0.0526, the lack of fit of the model was found to be insignificant (*P*-value < 0.05) and certified that the model sufficiently interpreted the experimental data. The *P*-value of the design model on the other hand was <0.0001 and this confirmed the model to be statistically significant.

The effect of parameters on extraction output was characterized as positive main effect when high variables (+1) resulted in the highest outcomes and negative main effect when low variables (−1) produced the highest outcome. Both protonated DMBA and sodium hydroxide volumes showed negative main effects and according to the *P*-values, sodium hydroxide volume (*P*-value <0.0001) was the most significant parameter of the extraction method followed by protonated DMBA volume (*P*-value = 0.0003). The negative main effect of these parameters is linked to the final volume of amine extractant after the extraction process. Adding low volumes produces a correspondingly low amine phase with highly concentrated analytes. The different periods of vortex affected the outcome of extraction but the effect was not significant. The interaction effect between protonated DMBA and sodium hydroxide volumes, as shown in Figure 2, was significant to the model. The model predictor suggested the optimum parameter values as 1.10 mL of protonated DMBA, 1.48 mL of sodium hydroxide, and 19 s of mixing by vortex. As the optimum parameters, the volume of sodium hydroxide was adjusted to 1.5 mL due to the peculiar scale of the automatic pipette used, the mixing period was fixed at 20 s, and 1.10 mL of protonated DMBA was selected as the optimum value for further experiments. These conditions were applied to aqueous calibration standard solutions to determine the method's analytical figures of merit.

Analytical Figures of Merit

Mixed calibration standard solutions of the analytes were prepared between the range of 1.0 µg/L and 1.0 mg/L, and the lowest concentration of each analyte (signal-to-noise ratio >3) was run six times to obtain standard deviation (SD) values. The LOD, LOQ, and RSD, % were calculated from the obtained SD values while coefficient of determination (R^2) and linear dynamic range were obtained from the linear calibration plot. The LOD

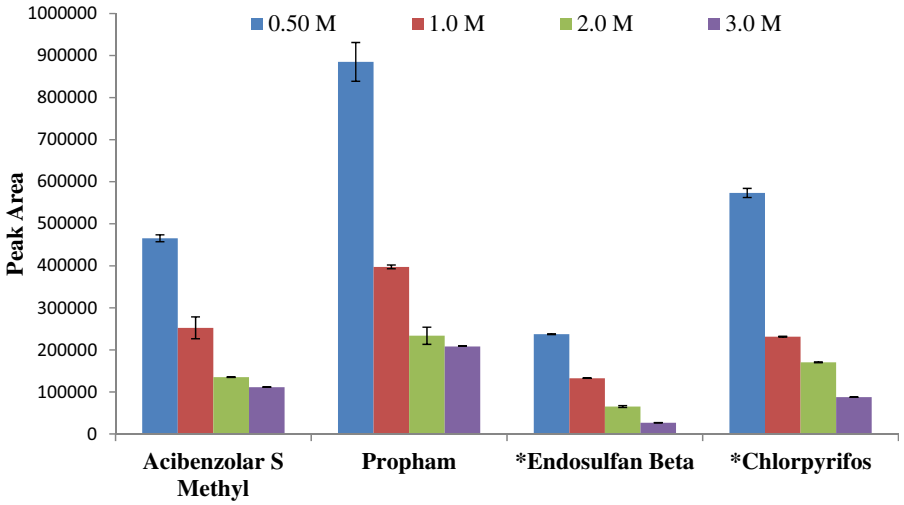


Figure 1. Optimization of sodium hydroxide concentration, $n = 3$ for error bars. *Peak area values of analytes scaled up 3 fold.

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and LOQ were respectively calculated using the expressions 3.SD/slope and 10.SD/slope. Analytical figures of merit calculated for the analytes using the optimized method are summarized in Table 1 and compared to other methods reported in the literature. It is clear in this table that LOD values (below 2.0 μg L^{-1}) found in this study are lower than those in the literature. The repeatability of the instrumental reading/extraction procedure was checked using SDs of the lowest concentrations in the calibration plots and the RSD, % values obtained below 7.0% established good repeatability and high precision for replicate extractions.

By comparing the LOD values of the developed method to direct GC-MS analysis, enhancement in detection power values of 245, 264, 261, and 203 fold were respectively recorded for chlorpyrifos, endosulfan beta, acibenzolar s methyl, and propham. The method optimized is simple, rapid, and has high enhancement in detection power.

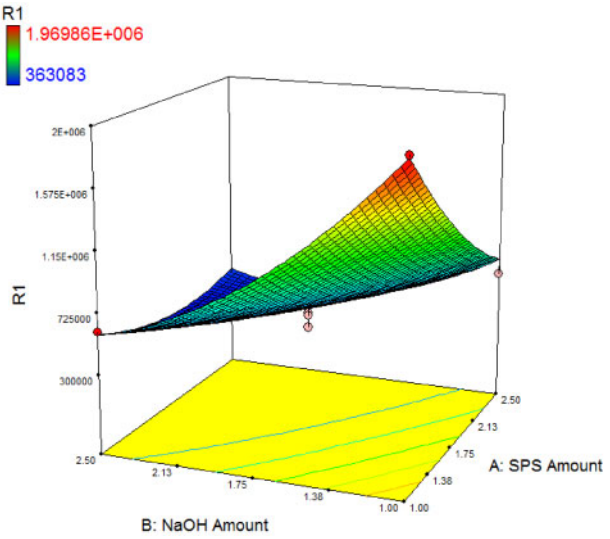


Figure 2. Response surface depicting the effects of (A) protonated DMBA/SPS and (B) sodium hydroxide volumes on response (vortex held constant at 30 s).

Analysis of Samples and Recovery study

The optimized method was applied to water sampled from an irrigation canal, two lakes, and two municipal wastewater treatment sites. The analytes were not detected in all five samples, and the two municipal wastewater samples were selected to ascertain the method's compatibility to real samples and accuracy of quantification. Prior to spiked recovery studies, blank analyses including extractions and measurements were performed to ascertain the presence or absence of the analytes in the samples. No signals were recorded at the retention times of the analytes, indicating their absence or amounts below the LOD. The samples were then spiked using very low amounts of appropriate standard solutions to avoid dilution of the matrix. Overlay chromatogram of wastewater sample, wastewater sample spiked at 100 μg/L and 100 μg/L aqueous standard solution can be seen in Figure 3. Calibration standards were prepared in deionized water and used to quantify the analytes in the samples, but the results obtained were higher than 110% (110–175%). Since the analytes were not determined in the sample blanks, it was assumed that the sample matrix enhanced extraction output. Matrix matched calibration standards were therefore employed with the aim of correcting the excess analyte concentration recorded with respect to aqueous calibration standards. A different wastewater sample was analyzed under the optimum conditions and it was established that the analytes were absent. Then, low volumes of stock standard solutions were diluted with the wastewater to prepare the matrix matching standards. The percentage recovery results of the analytes determined by matrix matching at three different spike concentrations are given in Table 2. As seen in Table 2, recovery results in three different spiked concentrations were in the range of 94.5–107.6, 87.0–113.8, 95.2–104.7, 95.5–103.8% for chlorpyrifos, acibenzolar s methyl, propham, and endosulfan beta, respectively. It is clear that a matrix matching strategy can overcome the interference problem caused by matrix components, and high recovery results validated the applicability/accuracy of the developed method to complex matrices such as wastewater samples.

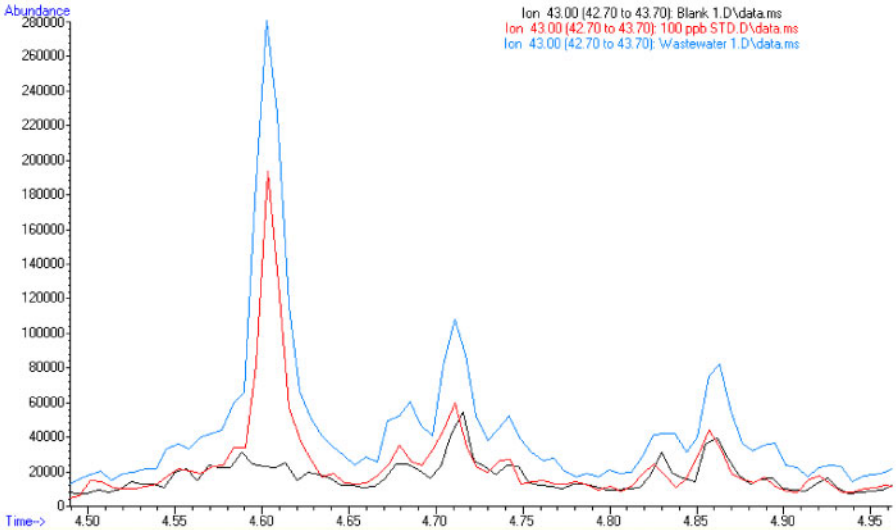


Figure 3. Overlay chromatogram of wastewater sample 1 blank (black), wastewater sample 1 spiked at 100 μg/L (blue), and 100 μg/L aqueous standard solution (red) of propham (4.6 min).

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Table 1. Analytical figures of merit of the VA-SS-HLLME method for the analytes

Chemical	LOD	LOQ	RSD, %	R^2	Method	References
Acibenzolar s methyl	0.42 μg/L	1.4 μg/L	4.4	0.9997	VA-SS-LPME-GC-MS	This study
	5.0 μg/kg	—	8.0	0.9990	QuEChERS -LC-MS/MS[a]	(30)
Chlorpyrifos	0.70 μg/L	2.4 μg/L	6.0	0.9998	VA-SS-LPME-GC-MS	This study
	9.1 μg/kg	30 μg/kg	6.8	0.994	MSPD-GC-FPD[b]	(31)
Endosulfan beta	1.9 μg/L	6.3 μg/L	6.8	0.9991	VA-SS-LPME-GC-MS	This study
	2.1 μg/L	6.9 μg/L	9.2	0.9992	DLLME-GC-MS[c]	(32)
Propham	0.42 μg/L	1.4 μg/L	3.4	0.9994	VA-SS-LPME-GC-MS	This study
	50 μg/kg	200 μg/kg	—	—	MSPD-(LC–APCI–MS)[d]	(33)

[a] QuEChERS -LC-MS/MS = Modified QuEChERS liquid chromatography tandem mass spectrometry.
[b] MSPD-GC-FPD = Matrix solid phase dispersion gas chromatography flame photometric detector.
[c] DLLME-GC-MS = Dispersive liquid-liquid microextraction gas chromatography mass spectrometry.
[d] MSPD-(LC–APCI–MS) = Matrix solid phase dispersion liquid chromatography–atmospheric pressure chemical ionization–mass spectrometry.

Table 2. Percentage recovery results obtained for spiked wastewater samples

	Wastewater 1, %			Wastewater 2, %		
Analyte	50 μg/L	100 μg/L	200 μg/L	50 μg/L	100 μg/L	200 μg/L
Chlorpyrifos	107.6 ± 9.7	99.4 ±2.1	94.7 ± 2.1	95.3 ± 1.1	105.4 ± 6.5	94.5 ± 1.0
Acibenzolar S Methyl	90.0 ± 1.5	113.8 ± 4.9	87.0 ± 6.3	90.9 ± 8.6	109.5 ± 7.5	94.3 ± 1.9
Propham	95.4 ± 2.4	104.7 ± 2.1	95.2 ± 4.6	102.0 ± 5.9	101.5± 5.1	102.3 ± 1.5
Endosulfan Beta	95.5 ± 4.7	97.6 ± 9.6	103.8 ± 4.9	103.0 ± 13	95.5 ± 4.7	97.6 ± 9.6

Conclusions

In this study, variable parameters of the VA-SS-HLLME method were optimized with a Box-Behnken design and experimented results were compatible with the design model. Optimum conditions obtained from the model predictor were used to validate the developed method. The LOD and LOQ ranges calculated for the four analytes were 0.13–2.3 μg/L and 0.45–7.5 μg/L, respectively. The optimum method was applied to two municipal wastewater samples but the analytes were not detected. The samples were spiked at three different concentrations and a matrix matching calibration method was used to improve the recovery results to almost 100%. This confirmed the accuracy of the method, and good repeatability for multiple extractions established the method's precision. This study presents a simple and green microextraction method that is highly efficient for preconcentration of the analytes from wastewater matrices.

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Conflict of Interest

Authors have no interests to declare.

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