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Combination of vortex assisted binary solvent microextraction and QuEChERS for the determination of prothiofos, oxadiargyl, and gamma-cyhalothrin in water and pineapple samples by gas chromatography mass spectrometry

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Abstract An accurate and sensitive dispersive liquid-liquid microextraction method based on binary solvents was used to enrich prothiofos, oxadiargyl, and gamma-cyhalothrin for quantification by GC-MS. The combination of two extraction solvents (binary mixture) resulted in higher extraction efficiencies compared to the single solvent extraction systems. Parameters of the binary extraction method where optimized to enhance the extraction output of the analytes. The limits of detection calculated for the analytes ranged between 0.59 and 1.6 ng/mL. Linear calibration plots of the analytes covered wide concentration ranges with R^2 values greater than 0.9996 and percent relative standard deviation lower than 10%. Spiked recovery experiments were performed well and wastewater at two different concentrations and satisfactory results (89–104%) were obtained. The binary solvent microextraction method was combined with QuEChERS to quantify the analytes in pineapple matrix, using matrix matching method to enhance the accuracy of the method to almost 100%.

Keywords Pesticides · Binary solvent microextraction · GC-MS · Prothiofos · Oxadiargyl · Gamma-cyhalothrin

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Introduction

Pesticides are chemical compounds that are mainly used in agriculture to protect plants and animals from infections arising from molds, fungi, insects, and any other agents that affect the quality/yield of animals and crops (Poulsen et al. 2007; Farajzadeh and Mohebbi 2018). Pesticides are also used for non-agricultural protection purposes such as public lawns, sports fields, parks, pet shampoos, building materials, and the bottom part of boats from mollusk growth (Hoffman et al. 2000; Johnston 2001). Advantages derived from pesticide usage include prevention of diseases from vector bearing insects, improved food quantity and quality which provides healthy diets, and increased revenue for both farmers and exporters (Bokhart et al. 2015). Despite these advantages, there are several reports and studies that have been published on health defects in humans and other organisms, such as different types of cancers, diabetes, neurodegenerative disorders (Alzheimer and Parkinson), liver damage, birth defects, and reproductive disorders that arise from exposure to different types of pesticides (Rajendran 2016; Nicolopoulou-Stamati et al. 2016).

Gamma-cyhalothrin belongs to the pyrethroid chemical class of pesticides, which are synthetic versions of the natural pyrethrins found in some plants. It is a single insecticidal enantiomer of lambda-cyhalothrin and both are approved for usage by the European Commission (Richterová et al. 2014). Despite this approval, there are studies that have shown them to pose acute health

effects such as irritation of the eyes and skin, convulsions, and severe muscle twitching, as well as chronic effects such as cell damage, endocrine toxicity, and changes in organ weights (Elhalwagy et al. 2015). Prothiofos and oxadiargyl are two prohibited pesticides which belong to the chemical classes of organophosphate and oxidiazole, respectively (Dahshan et al. 2016; Velini et al. 2005). Prothiofos is used as an effective insecticide for the control of several insects on maize, tea, fruits, sugar cane, and tobacco fields (Abdel-Gawad et al. 2015). Oxadiargyl is a very effective herbicide used against persistent broad-leaf plants that compete with food crops such as rice. However, it could hinder the germination and growth of the plant of interest, leading to low crop yields (Deng et al. 2018). These pesticides were banned after showing endocrine disruptive effects and potential to cause other harms to both humans and other organisms (Manabe et al. 2006; Marx-Stoelting et al. 2014). Environmental and food samples require regular monitoring to ensure that prohibited pesticides are not being illegally used, and approved pesticides are being used within their stipulated limits.

Simultaneous determination of multiple pesticides requires proper extraction/separation methods for easy detection and quantification by detectors. Chromatographic techniques such as liquid chromatography (LC) (Wu et al. 2010; Millán et al. 2003) and gas chromatography (GC) (Pinheiro et al. 2011; Farajzadeh et al. 2016) with different detection systems offer efficient separation of organic compounds based on different polarities and vapor pressures, respectively. Gas chromatography mass spectrometry (GC-MS) is a compelling combination that allows separation, identification, and quantification of a wide range of organic compounds. However, for most organic compounds, GC-MS does not exhibit high sensitivity for trace level determinations but this limitation can be mitigated using extraction methods that isolate analytes from the matrix and concentrate them into measurable amounts (Tan and Abdulra'uf 2012). Dispersive liquid-liquid microextraction (DLLME) is simple and rapid extraction technique used to concentrate analytes from aqueous sample solutions for measurement by different instrumentations. The use of dispersive solvents significantly increases the surface area between extractant and sample/standard solution, leading to high mass transfer, and extraction output (Fortes et al. 2013). In as much as dispersive solvents increase extraction surface area, extraction efficiency greatly relies on the extractants solubility for the analyte of interest. Simultaneous determinations could be limited by the selectivity of extractant for only a few analytes and, thus, result in poor efficiencies for the other analytes. To alleviate this problem, binary solvent microextraction, which involves a combination of two extraction solvents is used to improve the overall extraction efficiency of the analyte(s) (Estevão et al. 2018). The quick, easy, cheap, effective, rugged, and safe (QuEChERS) method is a very practical sample pre-treatment method used to eliminate complex matrices by employing peculiar sorbents for analyte extraction. Matric components such as steroids, pigments, polar organic acids, and sugars are conveniently removed by sorbents such as graphitized carbon black (GCB) and primary secondary amine (PSA) (Wilkowska and Biziuk 2011).

The aim of this study was to utilize the advantage of vortex assisted binary solvents in dispersive liquid-liquid microextraction (VA-BS-DLLME) for the determination of selected pesticides in aqueous samples and pineapple matrix at trace levels by gas chromatography mass spectrometry. In addition, VA-BS-DLLME was combined with QuEChERS in the quantitative determination of analytes.

Materials and methods

Chemicals and reagents

Standards of the analytes prothiofos (CAS# 34643–46-4), oxadiargyl (CAS# 39807–15-3), and gamma-cyhalothrin (CAS# 76703–62-3) were purchased from Dr. Ehrenstorfer (Augsberg, Germany) with percent purities greater than 98%. All three standards were dissolved in acetonitrile to prepare 1000 μg/mL stock solutions, from which aliquots were taken to prepare mixed calibration standards and aqueous working standard solutions. Aqueous solutions were prepared with ultrapure deionized water obtained from a Milli-Q water purification system and all glassware were cleaned with deionized water. Solvents used in the optimization process included dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), carbon tetrachloride (CCl4), chloroform (CHL), acetonitrile, methanol, ethanol, and 2-propanol, all purchased from Merck (Darmstadt – Germany).

Instruments

Chromatographic separation of analytes was achieved using a 30 m long HP-5MS capillary column fitted inside an Agilent 6890 gas chromatograph and connected to the inlet of an Agilent 5973 mass spectrometry (MS) detector. The MS transfer line temperature was 280 °C, the MS source temperature was 230 °C, and the MS quad temperature was set to 150 °C. All injections were performed in the splitless mode with 1.0 μL injection volume and an injection port temperature of 250 °C. The oven temperature program was started at 70 °C after which it was ramped at 60 °C/min, 4.0 °C/min, and 40 °C/min to 180 °C, 210 °C, and 280 °C, respectively. The oven was held at the final temperature (280 °C) for 2.5 min. Helium was used as carrier gas for the analytes at a constant flow rate of 1.8 mL/min. The mass-to-charge ratio (m/z) of ions used to quantify/qualify prothiofos, oxadiargyl, and gamma-cyhalothrin were 309/43, 340/150 and 181/197, respectively.

Procedure

The binary solvent (100 μL chloroform +100 μL 1,2-dichloroethane) and dispersive solvent (2.0 mL ethanol) mixture was prepared in a clean tube, withdrawn into 5.0 mL plastic syringe and injected into another tube containing 8.0 mL of standard/sample solution. The cloudy solution that resulted from the injection was vortexed for 15 s before centrifuging for 120 s min at 6000 rpm. The extractant settled to the bottom of the tube and was collected into insert vials for GC-MS auto injections.

Samples

The municipal wastewater used in this study was sampled from an open-air pool of a biological wastewater treatment plant. Solid particulate matter was eliminated by successive filtrations through 11 μm filter paper and 0.45 μm PTFE syringe filter. Well water was taken from a borehole into polypropylene plastic bottles and filtered through 125 mm filter paper. Fresh pineapple sample (imported from abroad) purchased from a supermarket in Europe part of İstanbul was cut into small pieces, blended homogeneously, and 15 g sample was weighed into a 50 mL polypropylene plastic tube. This was followed by successive additions of 15 mL acetonitrile with 1.0% acetic acid, 1.5 g sodium acetate, and 6.0 g magnesium sulfate. After shaking vigorously for 60 s, the liquid phase was separated from the solid by cold (4.0 °C) centrifugation at 4000 rpm for 300 s. A 15 mL polypropylene plastic tube containing 1.1998 g magnesium sulfate, 0.4001 g C18EC, and 0.4001 g PSA was filled with the acetonitrile supernatant, shaken for 60 s and centrifuged at the same temperature for 180 s. The liquid layer was filtered through a syringe filter (0.45 μm) for analysis.

Results and discussions

Analytical performance of direct GC-MS analysis for the three analytes was determined using mixed calibration standards prepared between 0.20 and 100 mg/L. The limit of detection was then compared to the developed method's detection limit to determine the enhancement in detection power. The method was developed in a stepwise manner by changing variables of one parameter at a time while keeping the other parameters at fixed values. After an initial extraction was performed on aqueous standard solutions between 20 and 200 μg/L, 50 μg/L was selected and used for all optimization tests.

Type of extraction solvent

The first parameter optimized in this study was the type of extraction solvent. This was considered very important because an ideal extraction solvent should have high solubility for the analyte(s) of interest to ensure significant mass transfer from the sample solution (Erarpat et al. 2017). High density solvents were used in this study to avoid the possibility of upper phase solvent evaporation, which could affect the accuracy and repeatability of results and enrichment factor. The solvents tested were 1,2-dichloroethane, chloroform, carbon tetrachloride, and dichloromethane. Here, 300 μL of extractor solvent was mixed with 3.0 mL of dispersive solvent (ethanol) in the extraction. Chloroform gave the highest result for oxadiargyl and 1,2-dichloroethane was optimum for the other analytes. The settled phase for dichloromethane was extremely low and could not be taken for analysis. Binary mixtures of the solvents were also tested and compared to the mono solvents (Fig. 1). The binary solvents produced peak area values higher than the mono solvents, and this could be due to the mixture's modified polarity and percent solubility in water. The peak area values of the

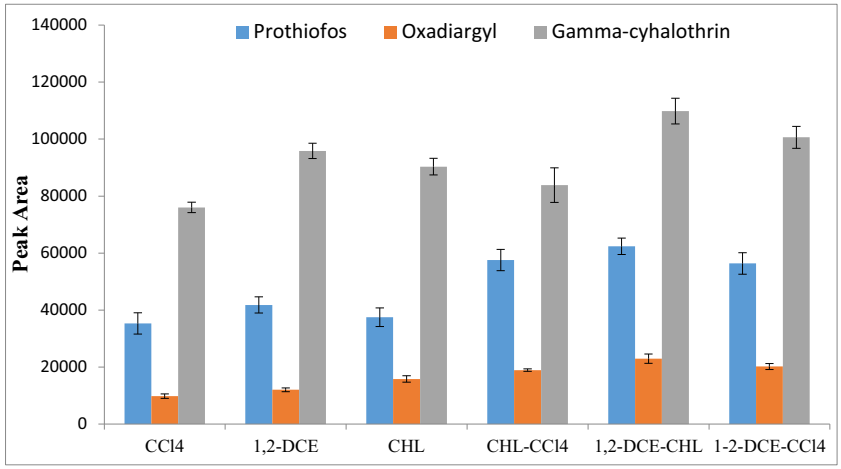


Fig. 1 A chart of extraction solvent types against average peak values, $n = 3$ error bars

chloroform/1,2-dichloroethane binary mixture was the highest for all analytes among the tested solvents and was, therefore, selected for subsequent experiments.

Amount of binary solvent

The binary solvent was kept at a 1:1 ratio throughout the study and its optimum amount was determined by testing different volumes. The amount of extraction solvent is crucial for preconcentration studies because it directly affects the level of analyte enhancement or concentration. An inverse relation exists between solvent amount and enhancement, where low volumes result in high enhancement factors, and vice versa. However, the solvent can only be reduced to a minimum volume, below which adequate amounts of the analyte cannot be collected, or the solvent completely dissolves in the sample medium thereby not producing a separate phase. For these reasons, binary solvent amounts between 100 and 500 μL (100 μL intervals) were tested for their extraction efficiencies. No distinct or separate phase was observed for the 100 μL volume but the other amounts produced phases that increased proportionally to the volumes added. On the other hand, the peak area values obtained decreased linearly (Fig. 2) with increasing binary solvent volume as a result of the extra volume diluting extracted analytes. Further experiments were, therefore, performed with 200 μL volume of the binary solvent.

Type of dispersive solvent and amount

Dispersive solvents play a vital role in the extraction of analytes in DLLME and selecting an appropriate dispersant enables the most efficient distribution of extraction solvent throughout sample solution. The basic requirement for a dispersive solvent is for it to be miscible with both aqueous sample and extraction solvent (Erarpat et al. 2017). For binary solvent extraction, the dispersive solvent has to be miscible with the three solvent system, in or other to obtain the true effect of dispersion. Low-molecular-weight alcohols including methanol, ethanol, and isopropyl alcohol have mid-polarity values that make them miscible with most solvents. Acetonitrile also has good miscibility with water and most organic solvents, and was, therefore, run alongside the three alcohols to determine the most efficient dispersive solvent for the binary mixture. Two milliliter of each solvent was added to 200 μL of the binary mixture and injected into similar aqueous standard solutions. Ethanol recorded the highest peak area values for all three analytes. The optimum amount of ethanol was investigated by performing extractions with 0.50, 1.0, 2.0, and 3.0 mL volumes. The peak area values obtained increased sharply with increasing ethanol volume, where the average value of the 3.0 mL volume was about 2.3, 4.0, and 5.7-fold higher than 0.50, 1.0, and 2.0 mL, respectively. It became apparent that dispersion and extraction efficiency increased with increasing dispersant volume, but when volumes higher than 3.0 mL were tested, the extraction solvent became totally soluble in the aqueous medium due to over dispersion. Thus, 3.0 mL ethanol was selected as optimum dispersive solvent volume for subsequent experiments.

Effect of mixing period

Vortex is a very common mixing apparatus found in most laboratories due to its simplicity and practical

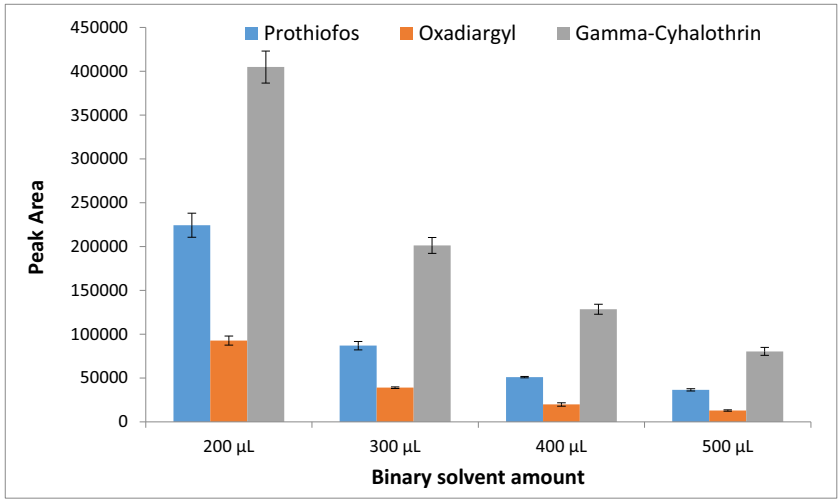


Fig. 2 A chart of binary solvent volumes against average peak values, $n = 3$ error bars

use. It was used in this study for sample agitation to further enhance the interaction between extractant and analyte solution for effective mass transfer of analytes. DLLME does not greatly rely on sample agitation for mass transfer but the repeatability of replicate extractions can be significantly improved by using mixing methods such as vortex. For this purpose, and to determine the effect of mixing on extraction output, mixing periods between 0.0–60 s were tested at 15 s intervals. The 0.0 s period refers to an extraction experiment performed without vortexing, but directly centrifuged for phase separation. The highest extraction output was recorded by the 15 s vortexing period and it also recorded very low standard deviation values.

Analytical performance of systems under optimum conditions

Optimum parameters obtained from the univariate optimization of VA-BS-DLLME are given in Table 1. These parameters were applied to aqueous standard solutions of the mix analytes prepared from 1.0 µg/L to 1.0 mg/L. Each analyte's linear dynamic range (LDR) was determined from their respective calibration curves and the linear expression of the calibration plots were used to calculate limits of detection (LOD) and quantification (LOQ). The calibration plots of the analytes all exhibited coefficient of determination (R^2) values greater than 0.9996. The method developed in this study was validated using LOD, LOQ, LDR, R^2, and percent relative standard deviation (%RSD). The analytical figures of merit are summarized in Table 2 and the detection limits have also been compared with other studies reported in literature for the analytes using other methods. By comparing to direct GC-MS analysis, the developed method recorded about 237, 273, and 400-fold increase in detection power for prothiofos, oxadiargyl, and gamma-cyhalothrin, respectively.

Recovery tests

In the method development process, the analytes were easily extracted for GC-MS determination because the deionized water used for aqueous standard preparation was void of matrix interference. This is contrary to environmental and food samples that contain various matrix components that could suppress or boost the extraction of an analyte, leading to inaccurate

Table 1 Optimum parameters of the VA-BS-DLLME-GC-MS method

Parameter	Value
Solvent A	Chloroform
Solvent B	1,2-dichloroethane
Binary solvent amount	200 µL (100 µL 1,2-DCE+ 100 µL CHL)
Dispersive solvent type	Ethanol
Dispersive solvent amount	3.0 mL
Mixing type	Vortex
Mixing period	15

Table 2 Analytical performance of the VA-BS-DLLME-GC-MS and comparing of detection limits to other methods

Analyte	LOD, μg/L	LOQ, μg/L	LDR, μg/L	%RSD	R^2
Prothiofos	0.59 (0.6[1])	2.0 (2.0[1])	2.0–200	9.0	0.9998
Oxadiargyl	1.5 (6.0[2])	4.9 (20[2])	5.0–200	2.2	0.9997
Gamma-cyhalothrin	1.6 (1.0[3])	5.4 (3.0[3])	5.0–500	7.5	0.9997

[1] Liquid-liquid extraction combined with dispersive solid phase extraction GC-MS (Fang et al. 2017)

[2] Modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample preparation method coupled with high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) (Deng et al. 2018)

[3] Multi-walled carbon nanotubes as reversed-dispersive solid-phase extraction materials GC-MS/MS (Han et al. 2016)

quantification. Thus, suitability of the developed method for environmental samples was tested on wastewater and well water samples. Three replicates of each sample were analyzed under optimum conditions but none of the three analytes were detected. Spiked recovery tests were performed to mimic the presence of analytes in the sample to ascertain the effects the matrices would have on their extraction. The spiking experiment was performed using low volumes from high concentration standard solutions to prevent dilution of the sample matrices. A five point calibration plot of aqueous standard solutions was developed for each analyte and used to quantify the spiked analytes. The percent recoveries calculated for the analytes spiked at 50 and 100 μg/L ranged between 89 and 104% as detailed in Table 3. The results obtained for wastewater was relatively lower than the results of well water and this was anticipated due to the complex nature of wastewater, which contains a variety of organic and inorganic components. However, the results show that the analytes can be quantified with appreciable accuracy and precision in both matrices.

QuEChERS-VA-BS-DLLME

Direct application of the binary DLLME method to the pineapple matrix extracted by QuEChERS was not possible due to total miscibility of the binary solvents and acetonitrile. The use of 15 mL solvent to extract 15 g of sample in the QuEChERS procedure given in section 2.4 did not result in dilution and this allowed the matrix to be diluted with deionized water to allow application of the binary microextraction. Four times dilution of the pineapple matrix was tested under optimum extraction conditions and a very low organic solvent phase was observed at the bottom of the tube. The dilution was increased to eight times and the organic solvent phase recorded after extraction was suitable for collection into insert vials. The method detection limit, therefore, increased by eight folds for all three analytes. The pineapple matrix was spiked at 20, 50, 100, and 200 μg/L. The samples were extracted under optimum conditions and percent recoveries calculated against aqueous calibration standards. The final volume after extraction for the spiked pineapple matrix was relatively lower than the aqueous standard solutions and this led to higher peak area values and percent recovery values above 120%. The low volume after extraction was due to acetonitrile in the pineapple extract which caused a dispersive medium prior to injection. In order to overcome this problem, blank QuEChERS pineapple extract was used to prepare calibration standards for

Table 3 Percent recovery results for spiked wastewater and well water

Analyte	Well Water		Wastewater	
	50 μg/L (%)	100 μg/L (%)	50 μg/L (%)	100 μg/L (%)
Prothiofos	101.6 ± 3.6	102.8 ± 7.8	86.1 ± 8.3	88.3 ± 5.7
Oxadiargyl	103.1 ± 5.8	91.5 ± 4.1	95.6 ± 2.1	89.6 ± 3.8
Gamma-cyhalothrin	95.8 ± 7.8	90.6 ± 7.2	89.2 ± 6.1	91.7 ± 8.0

Table 4 Matrix matched percent recovery results for pineapple using QuEChERS/VA-BS-DLLME-GC-MS

Analyte	20 μg/L (%)	50 μg/L (%)	100 μg/L (%)	200 μg/L (%)
Prothiofos	99.1 ± 7.0	100.1 ± 8.4	102.4 ± 6.2	97.2 ± 2.8
Oxadiargyl	96.4 ± 8.4	103.9 ± 6.1	101.7 ± 5.5	97.1 ± 7.2
Gamma-cyhalothrin	100.2 ± 4.7	103.9 ± 7.2	98.1 ± 3.2	101.6 ± 4.5

the calculation of percent recovery. Table 4 summarizes the percent recovery results calculated for the analytes at the four spiked concentrations and the closeness of the results to 100% validate the method's accuracy and applicability for quantifying the analytes in pineapple matrix.

Conclusions

This study took advantage of the benefits of binary solvent microextraction for the preconcentration of prothiofos, oxadiargyl, and gamma-cyhalothrin from well water, wastewater, and pineapple samples for the determination by GC-MS. Parameters of the extraction/preconcentration method that influence extraction efficiency were univariately optimized to obtain optimum conditions. Under these conditions, the limits of detection calculated for the analytes yielded 237, 273, and 400-fold enhancement in detection power for prothiofos, oxadiargyl, and gamma-cyhalothrin, respectively, in comparison to the limits obtained by direct GC-MS analysis. The analytes were not detected in the samples analyzed, but spiked recovery experiments were applied to validate the method's accuracy and suitability to real samples. Appreciable recovery results were obtained for well water and wastewater spike at two concentrations. The binary microextraction method was combined with QuEChERS to quantify the analytes in pineapple matrix and the recovery results obtained using matrix matching calibration method was close to 100% for all analytes at four different spiked concentrations. The method presented in this study is straightforward, rapid, accurate, precise, and high yielding for routine analysis.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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