



POLY(DIMETHYLSILOXANE)-POLY(VINYL ALCOHOL) COATED SOLID PHASE MICROEXTRACTION FIBER FOR CHLORPYRIFOS ANALYSIS

(Gentian Pengekstrakan Mikro Fasa Pepejal Tersalut Poli(Dimetilsiloksana)-Poli(Vinil Alkohol) untuk Analisis Klorpirifos)

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Received: 9 December 2014; Accepted: 16 October 2015

Abstract

Traditional liquid – liquid extraction of pesticides consumes large volumes of organic solvent which are hazardous to the operator and is not environment friendly. Solid phase microextraction (SPME) is a solvent less extraction method which is safer to the operator and is environmental friendly. A sol-gel hybrid fibre coating material, poly(dimethylsiloxane)-poly(vinyl alcohol) (PDMS-PVA) was synthesized and used in head space solid phase microextraction (HS-SPME) of chlorpyrifos. The thickness of the synthesised PDMS-PVA fiber coating was 13.5 μm and it is thermally stable up to 400 $^{\circ}\text{C}$. The PDMS-PVA sol-gel hybrid fiber was also stable to two organic solvents tested; acetonitrile and dichloromethane (1 hour dipping) and showed no significant changes in extraction performance for chlorpyrifos. Extracted chlorpyrifos was analysed using gas chromatography electron capture detector (GC-ECD). Optimum SPME parameters affecting the PDMS-PVA HS-SPME performance namely extraction time (15 min), extraction temperature (50 $^{\circ}\text{C}$), desorption time (5 min), desorption temperature (260 $^{\circ}\text{C}$) and stirring rate (120 rpm) were used for extraction. It was found that HSSPME using PDMS-PVA sol-gel fiber gave significantly better extraction performance of chlorpyrifos compared to commercial 100 μm PDMS fiber. The PDMS-PVA fiber showed excellent operational performances such as temperature stability (up to 380 $^{\circ}\text{C}$), coating lifetime (up to 170 times use) and organic solvent stability. The PDMS-PVA-HS-SPME method showed excellent recovery for chlorpyrifos from tomatoes (98.0 %, 5.9% RSD) at 0.01 $\mu\text{g/g}$ spiked level (5 times lower than maximum residue limit set by European Union).

Keywords: sol-gel hybrid, solid phase microextraction, chlorpyrifos, gas chromatography-electron capture detector

Abstrak

Pengekstrakan cecair – cecair tradisional bagi pestisid menggunakan isipadu pelarut organik yang banyak yang membahaya kepada operator dan tidak mesra alam. Pengekstrakan mikro fasa pepejal (SPME) adalah teknik pengekstrakan tanpa pelarut yang lebih selamat kepada operator dan mesra alam. Bahan gentian tersalut hibrid sol-gel poli(dimetilsiloksana)-poli(vinil alkohol) (PDMS-PVA) telah disintesis dan digunakan untuk pengekstrakan mikro fasa pepejal ruang kepala (HS-SPME) klorpirifos. Ketebalan PDMS-PVA gentian tersalut yang telah disintesis ialah 13.5 μm dan stabil terma sehingga 400 $^{\circ}\text{C}$. Gentian hibrid sol-gel PDMS-PVA juga stabil terhadap dua pelarut organik yang diuji, asetonitril dan diklorometana (1 jam celupan) dan tidak menunjukkan perbezaan ketara dalam prestasi pengekstrakan klorpirifos. Klorpirifos yang telah diekstrak dianalisis menggunakan kromatografi gas-pengesan penangkapan elektron (GC-ECD). Parameter optimum SPME yang mempengaruhi prestasi PDMS-PVA-HS-SPME iaitu masa pengekstrakan (15 min), suhu pengekstrakan (50 $^{\circ}\text{C}$), masa penyaherapan (5 min), suhu penyaherapan (260 $^{\circ}\text{C}$) dan kadar putaran (120 rpm) telah digunakan untuk pengekstrakan. HS-SPME menggunakan gentian sol-gel PDMS-PVA menunjukkan prestasi pengekstrakan yang jauh lebih signifikan untuk klorpirifos berbanding dengan gentian komersial 100 μm PDMS. Gentian PDMS-PVA telah menunjukkan prestasi operasi yang cemerlang seperti kestabilan

suhu (sehingga 380 °C), jangka hayat salutan (sehingga 170 kali penggunaan) dan kestabilan terhadap pelarut organik. Kaedah PDMS-PVA HS-SMPE menunjukkan perolehan semula yang cemerlang untuk klorpirifos daripada sampel tomato (98.0 %, 5.9% RSD) pada aras pakuan 0.01 µg/g (5 kali lebih rendah daripada had maksimum residu yang ditetapkan oleh Kesatuan Eropah).

Kata kunci: hibrid sol-gel, pengekstrakan mikro fasa pepejal, klorpirifos, kromatografi gas pengesanan penangkapan elektron

Introduction

The social concern about the levels of pesticides in the environment and the constant trend observed in current legislations to reduce their maximum residue levels allowed in a variety of matrices is increasing the number of samples to be analyzed well as the need for their accurate determination at very low levels. The help from the advance and improving technology especially in extraction and detection makes the study on pesticides more significant.

In recent years, separation and extraction sciences faced important developments. Starting with solid-phase extraction (SPE) in the 1980s, other modern methods, such as supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC), solid-phase microextraction (SPME) and capillary electro-chromatography (CEC) have been introduced. Among the extraction methods available, SPME is more favorable due to its simplicity, solvent free application, rapid and versatility. Therefore to expand the potential of SPME as an extraction method is a very interesting challenge in improving separation science.

Commercial SPME fibers have generally good extraction properties compared to other conventional extraction method. However there are some drawbacks and certain aspects of their performance that can be improved. For instance, incomplete desorption that causes carry-over problems and a reduction of the lifetime of the fibers due to direct extraction of higher salt content samples and complex matrices, have been reported in the literature [1]. Furthermore, the low thermal stability, generally bleeding at high temperature (> 250 °C) and solvent stability can lower the extraction and desorption process. Recently, some new types of fibers, such as non polar silica particles bonded with C₈, C₁₈ [2], pencil lead [3], graphite [4], nafion perfluorinated resin [5], polypyrrole [6], anodized aluminum wire [7], and molecularly imprinted polymer-coated fiber [8] have been prepared. However, almost all of these fibers coated with polymer are generally prepared by mere physical deposition, high temperature epoxy immobilization or partial crosslink of the polymer coating on the surface of the fused-silica fibers. The lack of proper chemical bonding between the polymer coating and fused-silica fiber surface may be responsible for the low thermal and chemical stability. The fiber coating lifetime is also limited, usually from 40 to 100 extractions [1]. In addition, the price of commercially available fibers is high due to their preparation process requiring expensive equipment.

Apparently the introduction of sol-gel technology has a promising alternative to overcome those problems. Sol-gel coating technology offers important advantages compared with conventional coating technique; strong adhesion between the coating and the bare fused-silica surface, the porous silica surface structure of sol-gel coating which can provide high surface areas and allow for high extraction efficiency and relative ease to change the composition of the coating which therefore will have different selectivity. This technology has been widely used to prepare SPME fiber because it can effectively create chemically bonded, porous and highly crossed coating on the fused silica fiber surface [9 – 12]. The simplicity of the sol-gel coating procedure provides excellent batch-to-batch reproducibility of the home-made fibers. A work done by Cajlakovic et al. [13] using poly(vinyl alcohol) (PVA) copolymer as optical pH sensing material offers a promising option for PVA to become as coating material in SPME fiber. This work successfully demonstrated that PVA with cross-linked produced a homogenous and crack-free membrane, making it more suitable for SPME fiber coating by sol-gel technology process.

In the current study, a simple and economical methodology for the determination of chlorpyrifos using headspace solid phase microextraction (HS-SPME) with an in-house silica-based sol-gel hybrid, polydimethylsiloxane-poly(vinyl alcohol) (PDMS-PVA) fiber coupled to gas chromatography equipped with an electron capture detector is presented and its use assessed in terms of thermal stability, solvent stability, reusability and application to real sample analysis of chlorpyrifos from water and tomato samples.

Materials and Methods

Reagents

Methyltrimethoxysilane (MTMOS), hydroxyl-terminated polydimethylsiloxane (OH-TPDMS), poly(vinyl alcohol) (PVA), trimethylmethoxysilane (TMMS), poly(methylhydroxysilane) (PMHS), and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (USA). Sulfuric acid was obtained from Merck (Darmstadt, Germany). Hydrochloric acid and sodium hydroxide were purchased from Fluka Chemika (Switzerland). Chlorpyrifos was purchased from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade methanol was obtained from Merck (Schuchardt, Germany). Double-distilled deionized water of at least 18 M Ω was purified by Nano ultra pure water system (Barnstead, USA). Stock solution of 1000 ppm of chlorpyrifos was prepared in methanol. Working standard solutions were prepared by diluting the stock solutions with HPLC grade methanol. The stock solution and working standard were stored at 4 °C when not in use.

Preparation of fused silica fiber and PDMS-PVA sol-gel hybrid coating

Pieces of fused silica fiber were soaked in concentrated sulfuric acid for 3 h to remove original polyimide layer and to expose the fused silica core for sol-gel coating process. The fused silica fibers were then rinsed with distilled water and dipped into 1 M NaOH solution. The basic solution was removed and the fibers were exposed to 0.1 M HCl solution for 30 min to neutralize the excess NaOH. The activated fused silica fibers were then rinsed with distilled water, dried at 120 °C and stored for 12 h in a desiccator before use.

The PDMS-PVA sol phase was prepared by mixing 600 μ L MTMOS, 300 mg OH-TPDMS, 80 mg PVA, 50 μ L PMHS, and 400 μ L of 95 % aqueous TFA in a glass tube. The mixture was vortexed for 2 min before being centrifuged at 12 000 rpm for 5 min. The top sol solution was used for fiber coating (1 cm length). After the treated fiber was dipped vertically into the sol solution for 20 min, a sol-gel coating was formed on the bare outer surface of the fiber end. For each fiber, this coating process was repeated three times with a freshly prepared PDMS-PVA sol phase. The coated fibers were then end-capped in a 20 % (v/v) methanolic solution of TMMS for 1 min. The in-house coated fibers were then mounted on used, discarded commercial SPME assemblies, after careful removal of the original fiber. Prior to use, the new PDMS-PVA fibers were conditioned in the GC injection port at 100°C for 2 h and then for 6 h at 280°C under 1 mL min⁻¹ of Helium flow. The remaining sol from the fiber coating process was allowed to gel at room temperature for 2 h, ground, washed with distilled water and methanol, and conditioned under the same conditions as the fibers. It was used to run field emission-scanning electron microscopy (FE-SEM) and Fourier transform infrared spectroscopy (FTIR).

Characterization of sol-gel hybrid PDMS-PVA

The sol-gel PDMS-PVA composite was characterized using a 1600 series PE spectrophotometer (MA, USA) FTIR using KBR method in the range of 400 – 400 cm⁻¹. Thermal gravimetric analysis (TGA) was conducted using a Mettler Toledo TG-50 thermal analyser (Greifensee, Switzerland) within a temperature range 50 –800 °C. The thickness and surface morphology of the sol-gel hybrid PDMS-PVA was determined using a JEOL JSM-6710F FE-SEM (Tokyo, Japan).

Head space-solid phase microextraction

The fiber was conditioned by inserting it into the GC injection port at 250°C for a period of 30 min to 1 h. Then the fiber was repeatedly injected into the GC-ECD system until interfering peaks disappeared from the chromatogram monitored and satisfying baseline was obtained. Injection was performed under the same temperature programming for analysis. For HS-SPME mode, 2 mL of sample solution was placed in a 5 mL sample vial containing a magnetic stir bar and the vial was sealed with a PTFE septum. The vial was placed on a magnetic hot plate. Then the fiber was carefully introduced directly into the head space above the aqueous phase and stirred at a rate of 120 rpm for 15 min (temperature set to 20 °C). After the preset extraction time, the fiber was retrieved and introduced for a period of 5 min into the GC injection port for chlorpyrifos analysis.

Gas chromatography-electron capture detector conditions

The OPPs extracted by the SPME fiber were analyzed using an XL Perkin Elmer gas chromatography-electron capture detection (GC-ECD) system (CA, USA). For desorption of the analytes inside the GC injection port was set

at 280 °C. The column was kept at 180 °C for 2 min, then ramped at 4 °C min⁻¹ to 200 °C, hold for 1 min and finally ramped at 10 °C min⁻¹ to 290 °C, and hold for 1 min. The detector temperature was set at 300 °C. Helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹ and nitrogen as a make-up gas was used at a flow rate of 32.4 mL min⁻¹. The pressure of the carrier gas was 10.0 psi. Peak areas of the ECD chromatogram signals were used to demonstrate the effect of parameters on the extraction efficiency of chlorpyrifos.

Real sample analysis

For real sample analysis, tomato (*Solanum lycopersicum*) was chosen as the sample as the matrix contains high colorant pigment due to the presence of carotenoid to assess matrix effect in PDMS-PVA-HS-SPME. The tomato was purchased from one of the local markets in Skudai, and stored in refrigerator to keep them fresh before analysis. The tomato was cut into small pieces and finely homogenized by using a chopper. Analytical portions of the tomato samples (10.0 g) were weighed in a 50 mL centrifuge tube and 20 mL deionized water was added. Then the sample was left to be extracted for 30 min on an ultrasonic bath. After the ultrasonication process, it was filtered through a filter paper. For analysis purpose, an aliquot of the sample (2 mL) was taken by micro-pipette to a SPME vial and followed by PDMS-PVA-HS-SPME procedure. For the accuracy test (recovery), the samples were fortified with chlorpyrifos at three different concentrations (0.005, 0.008 and 0.01 µg/g) and stored in refrigerator for one night to allow interactions between the chlorpyrifos and sample matrix. The chlorpyrifos concentration used is well below the MRL (5 – 100 times lower than the MRL) set by European Union for chlorpyrifos in tomato (0.5 mg/kg).

Results and Discussion

Preparation of sol-gel hybrid PDMS-PVA coating

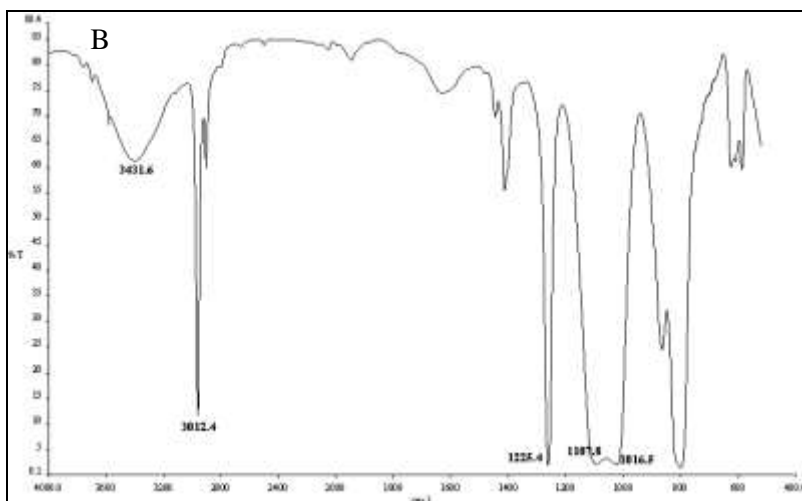
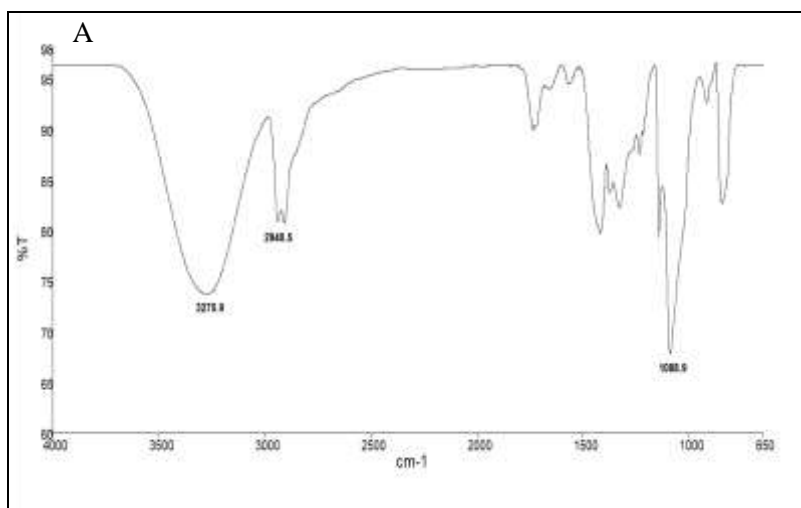
In this study, the sol-gel process was carried out using four principal ingredients which are, precursor, coating materials, deactivation reagent and acid catalyst. MTMOS was selected as precursor as it can avoid cracking and shrinkage of the coating during the gel-drying process. The sol-gel network originating from an alkyl derivative of precursor possesses a more open structure and can more effectively relieve stresses during drying, minimizing the cracking tendency [14]. PDMS is well known as a good non-polar stationary phase [15], but the addition of PVA is likely to improve the selectivity of fiber towards relatively polar or lower molecular weight compounds. As studied by Li et al. [16] who used terminated silicone oil as one of his coating material, it was not only to lengthen the silica network, leading to increase surface area of the fiber but also to spread the stationary phase of the fiber uniformly. In addition Cajlakovic et al. [13] proved PVA can be incorporated in sol-gel networks by the usual polycondensation processes and acts as a strong cross-linking agent. Another important ingredient used in the sol-gel coating process is PMHS, a well-known surface deactivation reagent in gas chromatography [10, 17]. Molecules of PMHS contain reactive hydrogen atoms capable of derivatizing silanol groups at elevated temperatures. Molecules of this ingredient get physically incorporated in the coating during the coating process. Post-coating thermal conditioning step leads to the deactivation of the fiber surface. The chemical structure of PMHS is very similar to that of PDMS, so it would not be a problem with PMHS as a deactivation reagent since its incorporation into the coating structure should have little effect on the sol-gel SPME fiber characteristic. Trifluoroacetic acid (TFA) was chosen as an acid catalyst to be added in the sol solution mixture. The reason for this is because during the sol-gel reaction, if the hydrolysis and polycondensation reaction rate is too fast, the coating stationary phase can hardly bond because of the space resistance of the three-dimensional network existed. Therefore, TFA is used to decrease the water reaction content in the sol, resulting in a slower hydrolysis reaction.

Characterization of sol-gel hybrid PDMS-PVA

Characterizations of the sol-gel hybrid PDMS-PVA were carried out on the in-house sol-gel PDMS-PVA fiber in order to verify whether the fiber was successfully synthesized. The physical characterizations included Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and field emission-scanning electron microscopy (FE-SEM).

The FTIR spectra obtained from the sol-gel OH-TPDMS and PDMS-PVA composite were evaluated and subsequently compared. The spectrum of PDMS-PVA with the corresponding spectrum of the conventional PDMS from pure OH-TPDMS and PVA is also shown for comparison purposes (Figure 1). The position and characteristic of OH-TPDMS bands observed were in good agreement with those reported in the previous studies [18, 19]. The broad absorption band at 3436.7 cm⁻¹ for sol-gel PDMS-PVA matches to the axial stretching of O-H bonds, and is

attributed to residual hydroxyl groups not eliminated after the end-capping treatment. However the intensity absorption present is small as the percentage transmittance is only 2 %. The decrease in hydroxy group peak in PDMS-PVA shows that it has been chemically bonded with other components. This band is also present in the OH-TPDMS with major intensity at 3431.6 cm^{-1} . Other absorption peaks match both those of sol gel PDMS-PVA and OH-TPDMS: 2965.0 cm^{-1} corresponds to the stretching of C-H bonds on methyl groups and 1022.3 , 1096.1 and 1262.2 cm^{-1} corresponds to the stretching of Si-O bonds. However peaks at 2168.1 and 900.8 cm^{-1} present in sol-gel PDMS-PVA but not found in OH-TPDMS spectrum are attributed to Si-H bonds from PMHS, used as a surface deactivation reagent. The broad absorption peak around 1622.4 cm^{-1} found on PDMS-PVA can be attributed to the stretching of alkenic and vinylic C=C bonds, possibly formed by loss of water from poly(vinyl alcohol) (PVA) chains incorporated in the polymer framework. However, the presence of the hydroxyl absorption band suggests that the dehydration of the PVA chains have not been completed under the conditions used. This did not happen in PDMS-PVA fiber because the conditioning temperature for the fiber was up to 300°C compared to that the composite in example around 120°C for the maximum temperature.



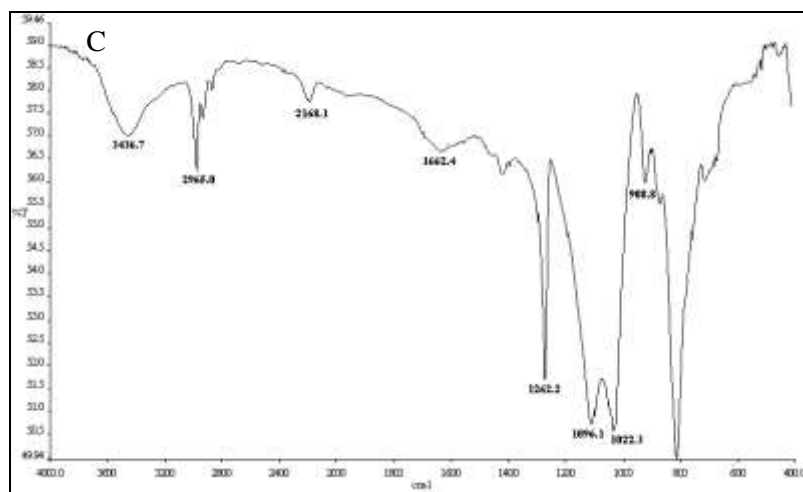


Figure 1. Infrared absorption spectra of: (A) PVA, (B) OH-TPDMS and (C) sol-gel PDMS-PVA

Thermal stability of the sol-gel PDMS-PVA fiber was studied using TGA in order to determine the limit of the operating temperature for the fiber and also helpful to enhance its coating lifetime. The TGA was performed under nitrogen gas and over the range temperature of 50-800°C at heating rate of 10°C min⁻¹. TGA curves (Figure 2) shows that the thermal degradation of the sol-gel PDMS-PVA composite occurs in three main stages. The first mass loss corresponds to slight degradation of PDMS-PVA which occurs at 240 °C. Between 240 °C and 330 °C, only 2 % of the total mass is lost for the sol-gel PDMS-PVA. The main mass loss step happens between 400 °C and 630 °C, corresponding to a loss 50 % of the initial mass with no other thermal series visible after this temperature. The last event was considered as characteristic of the thermal degradation of the sol-gel PDMS-PVA and can be assigned as its maximum practicable temperature. For the commercial PDMS SPME fiber, the maximum recommended operating temperature is only 280 °C; otherwise the fiber will deteriorate and affect analysis result negatively.

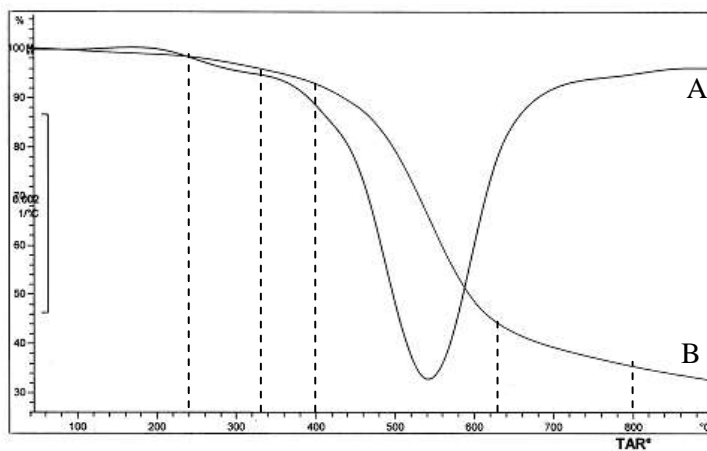


Figure 2. (A) TGA curve and (B) its first derivative of TGA curve for the sol-gel hybrid PDMS-PVA composite

The morphology of the sol-gel PDMS-PVA fiber surface was analyzed using FE-SEM. The average thickness of the sol-gel PDMS-PVA layer was estimated as being $\sim 13 \mu\text{m}$. This thickness is 6.5-8 times considerably thinner than most conventional coating thickness on commercial SPME fibers ($100 \mu\text{m}$ for PDMS and $85 \mu\text{m}$ for polyacrylate). From this point of view, sol-gel coatings might seem inconvenient for SPME. However, the surface of the PDMS-PVA coating seems to be compact and smooth and also shows a high density of small particles with apparent rugged surface. Therefore increased in the availability of the surface area on the fiber thus enhanced the extraction performance.

Optimization of HS-SPME process

In order to optimize the HS-SPME technique, factors affecting the extraction efficiency such as extraction time, extraction temperature, stirring rate, desorption time, and desorption temperature were studied. Extraction time is determined by the length of time required for the analyte to reach equilibrium between the concentrations of analyte in the sample and the fiber stationary phase. Six different extraction times ranging from 5 to 40 min of HS-SPME with stirring rate fixed at 120 rpm have been studied. According to the literature [20 – 22], the extraction time can be shortened by working in the non-equilibrium area. Indeed, full equilibrium is not necessary as long as other parameters such as stirring rate and sampling time are kept constant and the result allowed a good and reproducible extraction response for chlorpyrifos. The optimum extraction time selected for the sol-gel PDMS-PVA fiber is 15 min (Figure 3). The rugged structure believed to be possessed by the PDMS-PVA fiber provided high surface area, allowing fast and effective extraction.

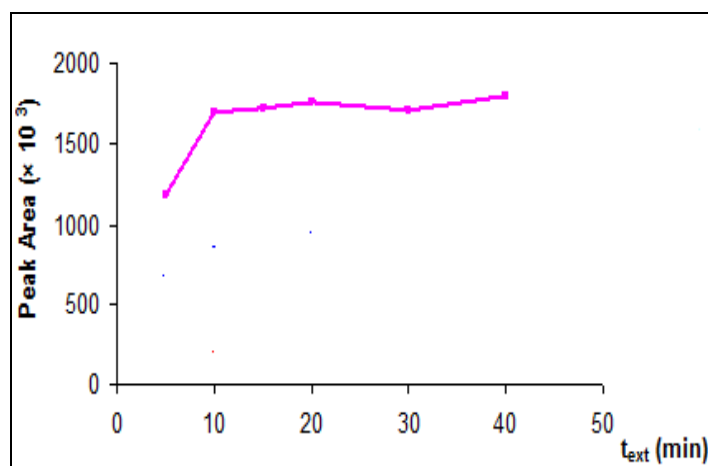


Figure 3. Extraction time profile for chlorpyrifos using PDMS-PVA fiber. HS-SPME conditions: $t_{\text{ext}} 50 \text{ }^\circ\text{C}$, $t_{\text{des}} 5 \text{ min}$, $T_{\text{des}} 250 \text{ }^\circ\text{C}$, and stirring rate 120 rpm

The effects of extraction temperature ranging from 25 to $80 \text{ }^\circ\text{C}$ have been studied. In general with increasing temperature, the extraction ability of the fiber increased, this is because increasing temperature can significantly increase analyte evaporation rates (distribution constant) and mass transfer at the solution-gas interface (distribution velocity), which enhances the analytes to enter the gas phase and fiber coating. The extraction temperature profile for chlorpyrifos is shown in Figure 4. The figure shows that the equilibrium was established at extraction temperature of $50 \text{ }^\circ\text{C}$. Consequently, $50 \text{ }^\circ\text{C}$ was selected as the optimum extraction temperature for PDMS-PVA fiber. The rate of diffusion of analytes through the static layer at the fiber solution interface increase with increasing temperature, so that more analytes are extracted at high temperature if equilibrium has not been reached [23].

Desorption time of the analyte from the fiber was studied to ensure complete desorption of the chlorpyrifos into the GC column. Six different desorption time varying from 1 to 10 min were studied. It was observed that desorption efficiency increase with an increase in desorption time from 1 to 5 min. After 5 min, there was no significant

increase in the peak area observed. Therefore 5 min of desorption time was selected as the optimum desorption time as it gave the highest amount of the analyte extracted (based on peak area).

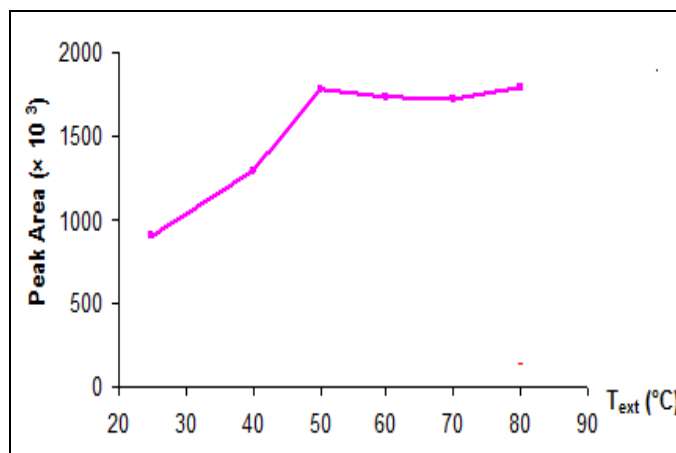


Figure 4. Extraction temperature profile for chlorpyrifos using PDMS-PVA fiber. HS- SPME conditions: t_{ext} 20 min, t_{des} 5 min, T_{des} 250 °C, and stirring rate 120 rpm

Desorption temperature of HS-SPME is measured from the GC injection port temperature indicator. In the current study, the effects of desorption temperatures ranging from 230 °C to 280 °C have been studied. Desorption temperature is important to guarantee complete desorption of the analyte studied to avoid carryover at the fiber. The result shows that there are no significant differences in peak area obtained at different temperature. Even though high temperature enhanced the desorption process but it can also degrade the analytes, worst it can damage the fiber and shorten its lifetime. Therefore, 260 °C was selected as the optimum desorption temperature since complete desorption the analyte studied were obtained from the coating. Furthermore, the PDMS-PVA fiber reveals that it can maintain the OPP peak area value obtained at different desorption temperature, which was almost the same.

Sample agitation or stirring was applied to enhance extraction and reduce extraction time, especially for higher molecular weight analytes with high diffusion coefficients. For practical purposes magnetic stirring bar was used in this study. It allows the control of the stirring rate and cyclic change in stirring direction. The effects of stirring rate ranging from 0 rpm to 600 rpm have been studied in the current work. The result obtained shows that the extraction efficiency increases as the stirring rate increased up to 120 rpm and decreases when the stirring rate further increased to 600 rpm. This agrees with the fact that SPME is a method based on equilibrium and that good diffusion through the phases is essential to reach equilibrium faster. Therefore a constant 120 rpm stirring rate was selected as the optimum stirring rate for HS-SPME of the chlorpyrifos.

Method validation

The optimized conditions for the HS-SPME extraction of chlorpyrifos using PDMS-PVA fiber are as follows; 15 min extraction time, 50 °C extraction temperature, 5 min desorption time, 260 °C desorption temperature and 120 rpm stirring rate. Under the optimum conditions, the PDMS-PVA-HS-SPME method was developed and validated for the extraction of spiked chlorpyrifos from water samples in terms of linearity, precision, limits of detection (LOD) and limits of quantification (LOQ). Good coefficient of determination was obtained ($r^2 = 0.9972$) within linearity range 0.001-0.1 ppm. The LOD at S/N = 3 obtained was 0.0076 ppm which is 5 –10 times lower than the maximum residue limit (MRL) set by the European Union (EU) [24].

Real sample analysis

The method developed for HS-SPME-PDMS-PVA for water samples was extended to tomato samples. Since no chlorpyrifos was detected in the tomato samples analysed, it was spiked with three different concentrations of

chlorpyrifos in order to determine the accuracy and precision of the PDMS-PVA HS-SPME method developed. It was found that at 0.01 and 0.008 $\mu\text{g/g}$ spiking level, the accuracy of the PDMS-PVA-HS-SPME method developed was comparable with the commercial 100 μm PDMS-SPME. Sample matrix from the tomato samples was found not to significantly affect the accuracy of the PDMS-PVA-HS-SPME method. The precision of the PDMS-PVA-HS-SPME was better than the commercial 100 μm PDMS SPME. However, the accuracy of the commercial 100 μm PDMS SPME was better for samples spiked at the lowest level, 0.005 $\mu\text{g/g}$. The lower recovery obtained using the PDMS-PVA HS-SPME is probably due to the sample matrix effect which is more pronounced in the in-house SPME fibre. Comparable precision was obtained for samples spiked at 0.005 $\mu\text{g/g}$ for both the SPME fibres (Table 1). Figure 5 shows the chromatogram of a spiked tomato sample analysis using the HS-SPME-PDMS-PVA.

Table 1. Percentage recovery and RSD of different concentrations of spiked chlorpyrifos from tomato sample using optimum HS-SPME conditions

Spiked concentration ($\mu\text{g/g}$)	% Recovery (% RSD, $n = 3$)	
	13 μm PDMS-PVA	Commercial 100 μm PDMS
0.005	62.64 (5.35)	76.86 (5.68)
0.008	85.65 (8.24)	85.62 (6.81)
0.01	98.01 (5.91)	91.70 (7.02)

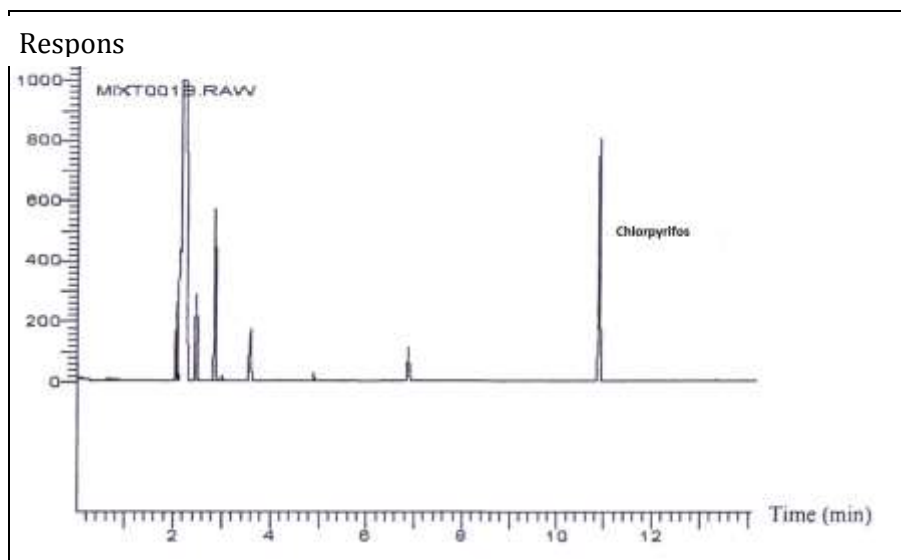


Figure 5. Chromatogram of spiked chlorpyrifos from tomato samples using the in house PDMS-PVA fibre. GC conditions: HP-5 column (30 m \times 0.32 mm ID and 0.25 μm film thickness). Carrier gas: He at 1.0 mL min^{-1} . Detector: ECD. Injection port temperature: 280 $^{\circ}\text{C}$, Detector temperature: 300 $^{\circ}\text{C}$. Temperature programming: 180 – 290 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C min}^{-1}$ to 200 $^{\circ}\text{C}$ (hold 1 min) and 10 $^{\circ}\text{C min}^{-1}$ to 290 $^{\circ}\text{C}$ (hold 2 min).

Conclusion

Sol-gel hybrid PDMS-PVA coating was successfully synthesized and applied as a SPME fiber coating for analysis of chlorpyrifos. The new sol-gel hybrid PDMS-PVA coating has high temperature stability up to 380 $^{\circ}\text{C}$ and showed comparable extraction performances to commercial 100 μm PDMS fiber in the extraction of chlorpyrifos

from tomato samples spiked at 0.01 and 0.008 µg/g. Matrix effect from the tomato samples did not significantly affect the extraction of chlorpyrifos spiked at these two levels (0.008 – 0.1 µg/g which is 5 – 60 times lower) below the MRL set by EU. The lower recovery of chlorpyrifos from tomato at a spiking level of 0.005 ppm (100 times lower than MRL) using the PDMS-PVA-HS-SPME could be due to matrix effect from the tomato samples. The sol-gel hybrid PDMS-PVA offers an alternative SPME coating of chlorpyrifos from water and vegetable samples such as tomato.

Acknowledgement

The authors would like to thank the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) for financial supports through IRPA Program Vote No. 74255 and 79085 and Department of Chemistry, Faculty of Science, UTM for facilitations.

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