

**SOL-GEL ORGANIC-INORGANIC HYBRID POLYDIMETHYLSILOXANE-3-  
AMINOPROPYLTRIMETHOXYSILANE AS SORBENT FOR STIR BAR  
SORPTIVE EXTRACTION OF ORGANOPHOSPHORUS PESTICIDES**

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AMINOPROPYLTRIMETHOXYSILANE AS SORBENT FOR STIR BAR  
SORPTIVE EXTRACTION OF ORGANOPHOSPHORUS PESTICIDES

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requirements for the award of the degree of  
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*Dedicated to my beloved father, mother, sisters and friends*

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## ABSTRACT

An organic-inorganic hybrid 3-aminopropyltrimethoxysilane (APTMS)-polydimethylsiloxane (PDMS) was produced using sol-gel method and used as coating on glass encased stir bar. The physico-chemical properties and extraction ability of the APTMS/PDMS hybrid coatings were manipulated by varying the molar ratio of APTMS to PDMS, amount of water and types of catalysts during sol synthesis. Fourier Transform Infrared Spectroscopy results showed successful hybridization between PDMS and amino moiety. Field Emission Scanning Electron Microscopy showed a homogenous surface image of the APTMS/PDMS hybrid coating while nitrogen adsorption indicated that the hybrid is a mesoporous material (pore size ~2.9 nm). The ability of the APTMS/PDMS hybrid coatings were investigated for stir bar sorptive extraction (SBSE) of two selected organophosphorus pesticides (OPPs) namely polar dicotophos and mid-polar malathion. Analysis was performed using HPLC with UV detector. Optimized SBSE parameters using APTMS/PDMS hybrid coating were 300 rpm stirring rate, 15 min extraction time, 1 mL methanol as ultrasonic assisted liquid desorption (UA-LD) solvent and 25 min desorption time. The optimized SBSE parameters using PDMS-coated *TWISTER* were also similar with the APTMS/PDMS hybrid coating except that the stirring rate used was 600 rpm. The limit of detection (LOD) ( $S/N=3$ ) of dicotophos is 0.108 mg L<sup>-1</sup> and 0.158 mg L<sup>-1</sup> for malathion using APTMS/PDMS hybrid coating. LOD ( $S/N=3$ ) of malathion is 0.31 mg L<sup>-1</sup> but dicotophos was not detected with the PDMS-coated *TWISTER*. The APTMS/PDMS sol-gel coating developed for SBSE was successfully applied for the determination of OPPs in grape and cucumber samples, and its performance was compared with commercial PDMS *TWISTER*. The recoveries of dicotophos and malathion from cucumber and grape samples using APTMS/PDMS hybrid coating was 71% and 98%, respectively with RSD 3.1%-3.6%. The recoveries of malathion in cucumber and grape using PDMS-coated *TWISTER* was 91% and 62% respectively, with acceptable RSD 7.46%. SBSE using APTMS/PDMS hybrid coating showed better selectivity for the polar dicotophos compared to commercial PDMS-coated *TWISTER*, which failed to extract the polar dicotophos.

## ABSTRAK

Hibrid organik-tak organik 3-aminopropiltrimetoksisilana (APTMS)-poli-dimetilsiloksana (PDMS) telah dihasilkan menggunakan kaedah sol-gel dan digunakan sebagai salutan pada bar berputar berbungkus kaca. Sifat fizik-kimia dan keupayaan pengekstrakan salutan hibrid APTMS/PDMS telah dimanipulasikan dengan mengubah nisbah molar APTMS terhadap PDMS, jumlah air dan jenis pemangkin semasa sintesis sol. Spektroskopi Inframerah Transformasi Fourier menunjukkan kejayaan penghibridan antara PDMS dan bahagian amino. Mikroskopi Imbasan Elektron Pancaran Medan menunjukkan imej permukaan salutan APTMS/PDMS hibrid adalah homogen manakala penjerapan nitrogen menunjukkan bahawa hibrid adalah suatu bahan mesoporous (saiz liang  $\sim 2.9$  nm). Keupayaan salutan hibrid APTMS/PDMS diuji bagi pengekstrakan jerapan bar berputar (SBSE) untuk dua pestisid organofosforus (OPPs) iaitu pestisid berketub dikrotofos dan pestisid separa berketub; malation. Analisis telah dijalankan menggunakan HPLC dengan pengesanan UV. Parameter optimum SBSE menggunakan salutan hibrid APTMS/PDMS adalah 300 rpm kelajuan putaran, 15 min masa pengekstrakan, 1 mL metanol sebagai pelarut penyahjerapan dengan bantuan ultrasonik (UA-LD), 25 min masa penyahjerapan. Parameter optimum SBSE menggunakan PDMS *TWISTER* adalah sama dengan salutan hibrid APTMS/PDMS kecuali kelajuan putarannya adalah 600 rpm. Had pengesanan ( $S/N=3$ ) (LOD) dikrotofos ialah  $0.108 \text{ mg L}^{-1}$  dan  $0.158 \text{ mg L}^{-1}$  untuk malation menggunakan salutan hibrid APTMS/PDMS. LOD ( $S/N=3$ ) untuk malation ialah  $0.31 \text{ mg L}^{-1}$  tetapi dikrotofos tidak dapat dikesan oleh salutan PDMS *TWISTER*. Salutan hibrid sol-gel APTMS/PDMS yang dihasilkan untuk SBSE telah berjaya diaplikasikan dalam mengesan OPPs dalam sampel timun dan anggur, dan perbandingan telah juga dilakukan dengan salutan PDMS *TWISTER* komersil. Perolehan semula dikrotofos dan malation dalam sampel timun dan anggur menggunakan salutan hibrid APTMS/PDMS adalah masing-masing 71% dan 98% dengan RSD 3.1%-3.6%. Perolehan semula malation dalam timun dan anggur menggunakan salutan PDMS *TWISTER* adalah masing-masing 91% and 62% dengan RSD yang sederhana iaitu 7.46%. SBSE menggunakan salutan hibrid APTMS/PDMS telah menunjukkan kepilahan yang lebih baik terhadap dikrotofos berketub berbanding PDMS *TWISTER* komersil yang gagal mengekstrak dikrotofos berketub.

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**LIST OF ABBREVIATIONS**

AAPTS	-	N-(2-aminoethyl)-3-aminopropyl trimethoxysilane
ACN	-	Acetonitrile
AMPTMOS	-	Aminopropyltrimethoxysilane
CE	-	Capillary electrophoresis
CNPrTEOS	-	Cyanopropyltriethoxysilane
CW	-	Carbowax
DAD	-	Photodiode array detection
DLLE	-	Dispersive Liquid-liquid extraction
DM- $\beta$ -CD	-	Heptakis (2,6-di-O-methyl)- $\beta$ -CD
DVB	-	Divinylbenzene
EA	-	Ethyl acetate
EtOH	-	Ethanol
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transformed infrared spectroscopy
GC	-	Gas chromatography
GMPTMOS	-	Glycidoxypropyltrimethoxysiloxane
HPLC	-	High performance liquid chromatography
IUPAC	-	International Union of Pure and Applied Chemistry
KH-560	-	3-(2-cyclooxypropoxyl) propyltrimethoxysilane
LD		Liquid desorption
LOD	-	Limit of detection
LOQ	-	Limit of quantitation
LPME	-	Liquid phase microextraction
MeOH	-	Methanol
MS	-	Mass spectrometric detection

MTMOS	-	Methyltrimethoxysilane
NA	-	Not available
NSAIDs	-	Non steroidal anti-inflammatory drugs
OH-PDMS	-	Hydroxy-terminated polydimethylsiloxane
OH-TSO	-	Hydroxy terminated silicone oil
PA	-	Polyacrylate
PDMS	-	Polydimethylsiloxane
PEG	-	Polyethylene glycol
PMHS	-	Polymethylhydrosilane
PVA	-	Polyvinyl alcohol
rpm	-	Rotation per minute
SBSE	-	Stir bar sorptive extraction
SDME	-	Single drop microextraction
SPE	-	Solid phase extraction
SPME	-	Solid phase micro extraction
TD	-	Thermal desorption
TEOS	-	Tetraethylethoxysilane
TFA	-	Trifluoroacetic acid
TMOS	-	Tetramethylsilane
UA-LD	-	Ultrasonic-assisted liquid desorption
UV	-	Ultraviolet
$\beta$ -CD	-	$\beta$ -cyclodextrin
2OHMe18C6	-	2-hydroxymethyl-18-crown-6

**LIST OF SYMBOLS**

$\mu\text{L}$	-	microliter
nL	-	nanoliter
cm	-	centimeter
$\mu\text{A}$	-	microampere
$\mu\text{m}$	-	micrometer
$k$	-	retention factor
$N$	-	peak efficiency
$K_{O/W}$	-	octanol/water partition coefficient
$\text{Log } K_{O/W}$	-	log octanol/water partition coefficient
$R_s$	-	peak resolution
T	-	temperature ( $^{\circ}\text{C}$ )
$t_M$	-	migration time
$w_{50}$	-	peak width at half height
$pK_a$	-	acid ionization constant
$R^2$	-	correlation coefficient
$\text{mg L}^{-1}$	-	milligram per liter
$\text{ng L}^{-1}$	-	nanogram per liter

## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

Pesticide residues are widely present in our environment, water, soils, agricultural products and food. Despite their benefits, pesticides if used in excess may produce many toxic side effects and pose potential hazard to the environment as well as our body. In the past sixty years, development on synthetic organic chemistry for fertilizer has been rapid due to the progressive agriculture sector. Many types of pesticides have been developed. Some are named after their commercial label, the type of pest they control and according to chemical pesticides or derived from a common source or production method (Consumer's Association of Penang, 1985). Classes of chemically related pesticides are organophosphorus pesticides (OPPs), carbamate pesticides, triazine pesticides, pyrethroid pesticides and organochlorine pesticides (OCPs). Only recently there have been a few changes in the pesticides usage. Increasing awareness on environment and health issues has open people eyes on the benefits in optimizing the use of sustainable resources such as recycling of waste products by animals for food production and protection for the environment.

Ensuring a good agricultural practice and the health of people, maximum residue limits (MRL) for pesticides in food has been established by many countries and international organizations (Shulinget *al*, 2005). In response to this, the studies of multi-residue analysis methods are receiving a lot of attention.

In food analysis, traditional methods for sample preparation are labor-intensive, time consuming and usually requires large amounts of solvents, which are expensive, generate considerable waste, and contaminate the sample (Buldini *et al*, 2002). As a result, modern sample preparation procedures have been developed or improved to overcome the drawbacks of the traditional approaches. Methods that are fast, accurate, precise, solventless, and inexpensive are to be considered. Several methods have been developed to accomplish this often difficult task, including predominant analytical techniques such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), supercritical fluid extraction (SFE), solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE). SBSE offer an alternative method of extraction which is solvent free, rapid, easy, sensitive, and environmentally friendly.

## 1.2 Research Background

Over the years, analytical methods for sample preparations have increasingly been developed. The most important step in sample analysis is the pre-concentration step or the extraction of the sample before analysis because it influences the reliability and accuracy of the analysis. Therefore when used in regulatory situations, the analytical procedures have to be very robust, precise and sensitive.

Solid phase microextraction (SPME), a sample preparation technique was introduced by Arthur and Pawliszyn (1990). This technique is based on equilibrium of target analytes between fused silica fiber coated with a thin film of sorbent and the sample matrix. In SPME, the outer surface of a solid fused silica fiber is coated with a selective stationary phase. The preferred coating is polydimethylsiloxane (PDMS). SPME offers solvent free extraction and has been applied to pesticides analysis including organophosphorus pesticides (Wan Ibrahim *et al.*,2010), organochlorine pesticides, triazine, and many more. Although SPME is a simple and rapid technique, but according to Baltussen *et al.* (1999) the applicability of SPME is limited by the small amount of PDMS on the needle (typically less than 0.5  $\mu$ L)

which results in low extraction efficiencies. This demands the use of very sensitive and selective detectors.

One possibility to overcome the relatively low extraction capacity of SPME is the use of Stir Bar Sorptive Extraction (SBSE). SBSE is a new sample preparation method for the extraction and enrichment of organic compounds from aqueous matrices. There are numerous publications on SBSE but there are many more areas to explore especially related to SBSE coatings. The technique utilizes glass bar with a magnetic core and coated with a coating phase to extract organic compounds from liquid samples. The type of coating phase is important as it will determine the efficiency of analytes extraction. According to Huang and Yuan (2007) the amount of coating phase on the stir bar is 50-250 times higher than that on SPME fiber. This resulted in a significant increase in the recovery and extraction capacity. In the past few years, SBSE has been developed rapidly and successfully applied to the trace analysis of various target analytes in environmental and biological samples with extremely low detection limits. Compared to conventional methods (liquid-liquid extraction and solid phase extraction (SPE)), Liu *et al* (2005) reported that the limit of detection when using SBSE can reach sub- $\mu\text{g L}^{-1}$  or even  $\text{ng L}^{-1}$  level.

However, one of the disadvantages of SBSE is that the available SBSE coatings are limited. The only coating available commercially is polydimethylsiloxane (PDMS) and researches on preparation method of stir bar are still in preliminary stage. This limits the selectivity and applicability of SBSE as a sample preparation technique to only non-polar compounds and fails in the extraction of many polar compounds unless they have been previously derivatised. Furthermore, derivatisation of polar analytes to produce more hydrophobic species is not always possible. Therefore, extraction of strong polar compounds is still difficult with PDMS coated stir bars. Hence, further developments of SBSE especially the preparation method of stir bar is necessary. New material for SBSE is much needed especially coating materials with dual properties *i.e.* polar and non-polar for the simultaneous extraction of non-polar and polar compounds.

Recently, a stir bar coated with molecular imprinted polymers (MIP) based on nylon-6 polymer for selective extraction of polar monocrotophos has been reported by Zhu *et al.* (2006). In addition, a stir bar was prepared by physically coating alkyl-diol silica (ADS) restricted access material (RAM) on glass by a binding agent (Lambert *et al.*, 2005). The RAM-SBSE bar was able to directly extract caffeine and its metabolite from biological sample. Soon after that, a stir bar coated with poly (phthalazine ether sulfone ketone) (PPESK) was prepared using immersion precipitation technique by Guan *et al.* (2008). It was reported that the PPESK stir bar can extract OCPs in seawater and OPPs in juices. Hu *et al.* (2007) prepared a novel stir bar by introducing  $\beta$ -cyclodextrin into the coating layer using sol-gel technique. The PDMS/ $\beta$ -cyclodextrin stir bar showed better selectivity to polar compounds (estrogen and bisphenol A).

Sol gel technique has been selected numerous times to prepare the stationary phase on SPME but less can be said for SBSE. Research for coated stir bar using sol gel technique is progressing. The sol gel approach provides direct chemical binding of the stationary phase to the substrate, which results in higher thermal and solvent stability of the stationary phase compared to the physical deposition technique (Liu *et al.*, 2004). The technique is simple and gives excellent batch to batch reproducibility. Other than that sol gel technique produced end product that has better homogeneity, purity from their original raw materials while being prepared in a low temperature (Kumar *et al.*, 2008).

In this study, a new coating material for SBSE is produced using the sol-gel technique. 3-Aminopropyltrimethoxysilane (APTMS) was coupled with PDMS used as SBSE sorbent in the extraction of a polar OPP dicrotophos and mid-polar malathion.



### 1.3 Problem Statement

Currently the only stationary phase available commercially is PDMS and it only favors extraction of non-polar compounds. Thus, in the current work a new hybrid stationary phase is prepared to overcome the limitation for the extraction of moderately polar to polar organophosphorus pesticides (OPPs). APTMS was chosen to be functionalized with PDMS for the preparation of organic-inorganic hybrid APTMS/PDMS stationary phase onto glass jacketed stir bars by using sol-gel technique.

### 1.4 Aim and Objectives of Study

The aim of the study is to produce a new organic-inorganic hybrid coating material for use in SBSE using sol-gel technique for the extraction of organophosphorus pesticides. The objectives of the study are to:-

1. produce an in-house APTMS/PDMS sorbent material.
2. characterize the in-house APTMS/PDMS hybrid coating using Nitrogen Adsorption, Field Emission Scanning Electron Microscope, and Fourier Transform Infrared Spectrometry.
3. optimize extraction conditions for two selected organophosphorus pesticides using the in-house APTMS/PDMS SBSE.
4. validate SBSE method using the sol-gel APTMS/PDMS
5. compare the extraction performance of the in-house APTMS/PDMS coating with commercial PDMS coating (*TWISTER*).
6. application to real samples.

## 1.5 Scope of Study

This study was carried out with the purpose to produce a new coating material for SBSE using sol-gel process. The performance of the laboratory-made sol-gel hybrid APTMS/PDMS was compared with commercial PDMS SBSE from Twister<sup>TM</sup>. Selected organophosphorus pesticides used were mid-polar malathion and polar dicotophos. Analytes were separated using HPLC with UV detection at 230 nm. The calibration curve was used to determine the limit of detection and quantification, linear range as well as percentage of recoveries.

Physical characterizations of the sol-gel APTMS/PDMS was performed using Fourier transform infrared (FTIR) spectroscopy, nitrogen adsorption, and field emission-scanning electron microscopy (FE-SEM).

The optimization of commercial and laboratory-made SBSE was carried out to determine the effect of extraction parameters on the performance of the extraction. The parameters chosen are extraction time, desorption time, stirring rate of the bar, desorption solvents, and desorption volume. Parameter affecting sol produced (ratio APTMS to PDMS, water content used and type of acid catalyst) were studied. The optimum conditions of the in-house SBSE coating was applied to cucumber and grape samples.

## 1.6 Significance of Study

The new sol-gel organic-inorganic hybrid coating material is expected to show higher selectivity for the polar dicotophos than the current commercially available PDMS SBSE. Production of sorbent material with dual properties will extend the application range of SBSE to include more polar analytes.

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