

Selective and Simultaneous Solid Phase Extraction of Polar and Non-Polar Organophosphorus Pesticides Using Sol-Gel Hybrid Silica-Based Sorbent

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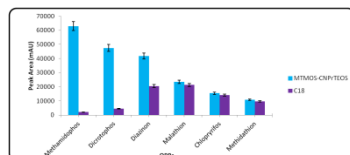
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Graphical abstract



Abstract

A new sol-gel hybrid silica-based sorbent, methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOS-CNPrTEOS) produced in our laboratory was used for highly selective and simultaneous solid phase extraction (SPE) of two polar organophosphorus pesticides (OPPs) and four non-polar OPPs from water samples. The two polar OPPs used as test analytes are dicrotophos and methamidophos while the four non-polar OPPs are diazinon, malathion, methidathion, and chlorpyrifos. Analysis of OPPs was performed using gas chromatography-mass spectrometry in scan mode. Extraction efficiency (based on peak area response) of the new sol-gel hybrid MTMOS-CNPrTEOS was superior to commercial C18 SPE sorbent. The new sorbent showed higher selectivity towards the polar dicrotophos and methamidophos and it was also able to simultaneously extract the four non-polar OPPs with higher extraction efficiency. The limit of detection at S/N=3 for the new sol-gel hybrid sorbent is 5-9× lower and similar accuracy for the six OPPs compared to commercial C18 SPE sorbent. The new sol-gel hybrid material showed high potential as an alternative sorbent material for solid phase extraction of OPPs of wide polarity. It was successfully applied to the selective and simultaneous extraction the six OPPs from tap water and lake water samples.

Keywords: Sol-gel hybrid; solid phase extraction; organophosphorus pesticides; gas chromatography-mass spectrometry

Abstrak

Satu bahan penyerap baru hibrid sol-gel berasaskan silika, metiltrimetoksisilana-sianopropiltrioksisilana (MTMOS-CNPrTEOS) yang dihasilkan dalam makmal telah digunakan untuk pengekstrakan fasa pepejal (SPE) berkepilihan tinggi dan serentak bagi dua pestisid organofosforus (OPPs) berketub dan empat OPPs tak berketub daripada sampel air. Dua OPPs berketub yang digunakan sebagai analit uji adalah dikrotofos dan metamidofos sementara empat OPPs tak berketub adalah diazinon, malation, metidation, and klorpirifos. Analisis OPPs dilakukan menggunakan kromatografi gas-spektrometri jisim dalam mod mengimbas. Kecekapan pengekstrakan (berasaskan gerak balas luas puncak) bahan penyerap baru MTMOS-CNPrTEOS adalah jauh lebih baik berbanding penyerap SPE C18 komersial. Penyerap baru ini menunjukkan kepilihan lebih tinggi terhadap dikrotofos dan metamidofos berketub dan ia juga berjaya mengekstrak secara serentak empat OPPs tak berketub dengan kecekapan pengekstrakan yang lebih tinggi berbanding penyerap SPE C18. Had pengesanan pada S/N = 3 bahan penyerap baru hibrid sol-gel ini adalah 5-9× lebih rendah dan kejituanannya adalah sama untuk enam OPPs berbanding bahan penyerap SPE C18 komersial. Bahan penyerap baru ini menunjukkan potensi tinggi sebagai bahan penyerap alternatif untuk pengekstrakan fasa pepejal bagi OPPs pelbagai ketubuhan. Ianya telah digunakan dengan jayanya untuk pengekstrakan berkepilihan dan serentak enam OPPs daripada sampel air paip dan air tasik.

Kata kunci: Hibrid sol-gel; pengekstrakan fasa pepejal; pestisid organofosforus; kromatografi gas-spektrometri jisim

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1.0 INTRODUCTION

Sample preparation is an important step in analysis and is needed to provide a sample solution free of matrix and interfering analytes and also to pre-concentrate analytes of interest present at trace level before detection. Sample preparation should also be fast, easy to use, inexpensive and compatible with a range of analytical instruments. There are many sample preparation methods available and one of them is solid phase extraction (SPE). SPE has been one of the most popular sample preparation methods and it is used actively in separation science [1]. Among the advantages of SPE is stability, reusability of sorbent, ease of separation, lower consumption of organic solvent compared to liquid-liquid extraction and also environmentally friendly [2]. Many different kinds of sorbent materials have been used in SPE. Silica-based materials are the most common SPE sorbents [3, 4] with C18-silica being the most commonly used [5]. Other sorbent materials include carbon-based [6, 7], molecularly imprinted polymers [7-11] and mixed-mode sorbents [12]. Most of the sorbents are designed to extract polar and non-polar analytes separately. The extraction of polar compounds posed problems as they are water soluble. Materials with both polar and non-polar moiety in their structure will enable simultaneous extraction of polar and non-polar analytes. This is most needed as it is time and energy saving.

Sol-gel process is known to produce porous structure with high surface area sorbent for extraction. In addition, the derivatization process of sol-gel sorbents is usually aimed to provide desired functional groups to the surface of solid support in order to obtain high selectivity of the extraction [2]. Several methods have been reported for the application of sol-gel process, e.g., solid phase microextraction [13-15] and stir bar sorptive extraction [16, 17]. Synthesis of SPE sorbent by sol-gel process has been demonstrated for the extraction of various analytes [18-20]. However, to the best of our knowledge only few previous works have reported on the use of sol-gel hybrid materials as SPE sorbents including metal extraction [21, 22], pesticide extraction [23] and N-containing compound extraction [24].

The present work demonstrated the potential of a new sol-gel hybrid silica-based material viz. methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOS-CNPrTEOS) as a selective sorbent for solid phase extraction (SPE) of a wide polarity range of organophosphorus pesticides (OPPs). Two polar and four non-polar OPPs were used. The order of decreasing polarity of the OPPs are methamidophos (log Kow = - 1.74), dicotophos (log Kow = - 0.50), methidathion (log Kow = 2.20), malathion (log Kow = 2.89), diazinon (log Kow = 3.86) and chlorpyrifos (log Kow=4.96) [25, 26]. To the best of the author's knowledge, this is the first work on the use of sol-gel hybrid MTMOS-CNPrTEOS as selective SPE sorbent for polar methamidophos and dicotophos and also for simultaneous extraction of the four non-polar OPPs from water samples. The extraction efficiency (based on OPPs area response) of the new sol-gel hybrid MTMOS-CNPrTEOS SPE for OPPs was found to be superior compared to a commonly used C18 SPE. The new sol-gel hybrid MTMOS-CNPrTEOS SPE sorbent was highly selective towards the two polar OPPs, methamidophos and dicotophos and it was also able to simultaneously extract the four non-polar OPPs with higher extraction efficiency than commercial C18 SPE.

2.0 MATERIALS AND METHODS

2.1 Pesticide Standards and Solvents

Standard pesticide solutions at 100 $\mu\text{g mL}^{-1}$ of methamidophos, dicotophos, diazinon, malathion, chlorpyrifos and methidathion were purchased from Dr. Ehrenstorfer GmbH laboratory (Augsburg, Germany). It was prepared in HPLC grade methanol which was obtained from J.T. Baker Inc. (Phillipsburg, NJ, USA). The pesticide solutions were stored at 4°C when not in use. HPLC grade methanol was purchased from Merck (Schuchardt, Germany) and deionized water was obtained from a Millipore Water purification system (MA, USA).

2.2 Solid Phase Extraction

The in-house synthesised sol-gel hybrid MTMOS-CNPrTEOS sample (100 mg) was ground using a pestle and mortar. It was then manually packed into an empty 3.0 mL SPE polypropylene tube with frits from Supelco (Bellefonte, PA, USA). The filled SPE cartridge was then placed in a Supelco 10-port SPE vacuum manifold (Bellefonte, PA, USA) and conditioned by passing 5.0 mL HPLC grade methanol, followed by 10 mL deionized water. For standard calibration process, spiked deionized water (1.0 mL) at the desired concentrations of OPPs were passed through the cartridge at a flow rate of 0.5 mL min⁻¹. The sorbent material in the cartridge was not allowed to dry at any moment. After the sample loading, the SPE cartridge was dried by passing air for 30 min. Trapped OPPs were eluted from the sorbent with 2.0 mL HPLC grade methanol and dried under a gentle stream of nitrogen gas to complete dryness. Finally, the residue was reconstituted in 100 μL of HPLC grade methanol prior to GC-MS analysis. Commercial 100 mg C18 SPE was obtained from Supelco (Bellefonte, PA, USA).

2.3 Gas Chromatography-Mass Spectrometry Analysis

Gas Chromatography analysis of methamidophos, dicotophos, diazinon, malathion, chlorpyrifos and methidathion was performed on a Hewlett Packard Model 6890N Gas Chromatography (GC) equipped with Hewlett Packard Model 6890N mass spectrometer (MS). An Ultra 2 column (25 m \times 0.20 mm i.d., and \times 0.33 μm film thickness) was used in the analysis. Purified helium was used as carrier gas at flow rate 1 mL min⁻¹. Sample (0.5 μL) with a solvent delay of 2.50 min was injected manually into the injection port under splitless mode. For the MS conditions, scan mode was used with a source temperature of 230°C, quad temperature at 150°C and transfer line temperature at 280°C.

2.4 Real Sample Analysis

Calibration graph of analyte peak area versus its concentration was constructed to validate the SPE-GC-MS method towards the six selected OPPs. Optimum SPE conditions (1 mL sample volume, dichloromethane as elution solvent and 1 mL elution solvent) was applied to the extraction of the six OPPs from deionized water at varying concentration to calculate the linearity range, correlation of determination, and limit of detection (LOD). For real sample analysis, tap water sample was taken from our laboratory while lake water sample was collected from the university lake. Both water samples were filtered through 0.45 μm pore size nylon membrane from Millipore (MA, USA) before use. For method validation, blank samples were spiked with the selected OPPs standard at 0.01 and 0.05 ng mL⁻¹ each using MTMOS-CNPrTEOS SPE, and spiked at 0.05 and 0.1 ng mL⁻¹

using commercial C18 SPE. The spiked level used for extraction with the sol-gel hybrid MTMOS-CNPrTEOS is well below (5-10 times lower) the maximum residue limit (MRL) allowed by European Union (EU) at 0.1 ng mL^{-1} each pesticide. All samples and standards were stored at 4°C when not in use.

3.0 RESULTS AND DISCUSSION

3.1 Comparison of Extraction Efficiency of In-House Sol-Gel Hybrid Sorbent with Commercial Sorbent

Solid phase extraction (SPE) was performed using the in-house sol-gel hybrid MTMOS-CNPrTEOS for the six selected OPPs of wide polarity range. Its extraction efficiency (measured based on peak area response) was compared in terms of peak area of OPPs extracted against commercial 100 mg C18 SPE sorbent. GC-MS (scan mode) was used to measure the OPPs extracted using both SPE sorbents. Figure 1 illustrates the comparison between the

peak areas of OPPs extracted using sol-gel hybrid MTMOS-CNPrTEOS and commercial C18 SPE from tap water samples (spiked at 1.0 ng mL^{-1} of each OPP). The sol-gel hybrid MTMOS-CNPrTEOS sorbent presented peak areas much higher than commercial C18 sorbent for all the six selected OPPs. The sol-gel hybrid MTMOS-CNPrTEOS showed a much higher selectivity towards the two polar OPPs, methamidophos and dicrotophos. The highest selectivity was observed for methamidophos, the most polar of the OPPs followed by dicrotophos (second most polar OPPs). The commercial C18 failed to extract the two polar OPPs efficiently. The trend of high selectivity for polar OPPs was also observed with another in-house sol-gel hybrid sorbent material, 3-(2-aminoethylamino)propyltrimethoxysilane-polydimethylsiloxane for methamidophos and dicrotophos (manuscript under preparation for submission). The extraction efficiency of the sorbent material for diazinon was the highest among the non-polar OPPs and showed significant difference between C18 extraction performances.

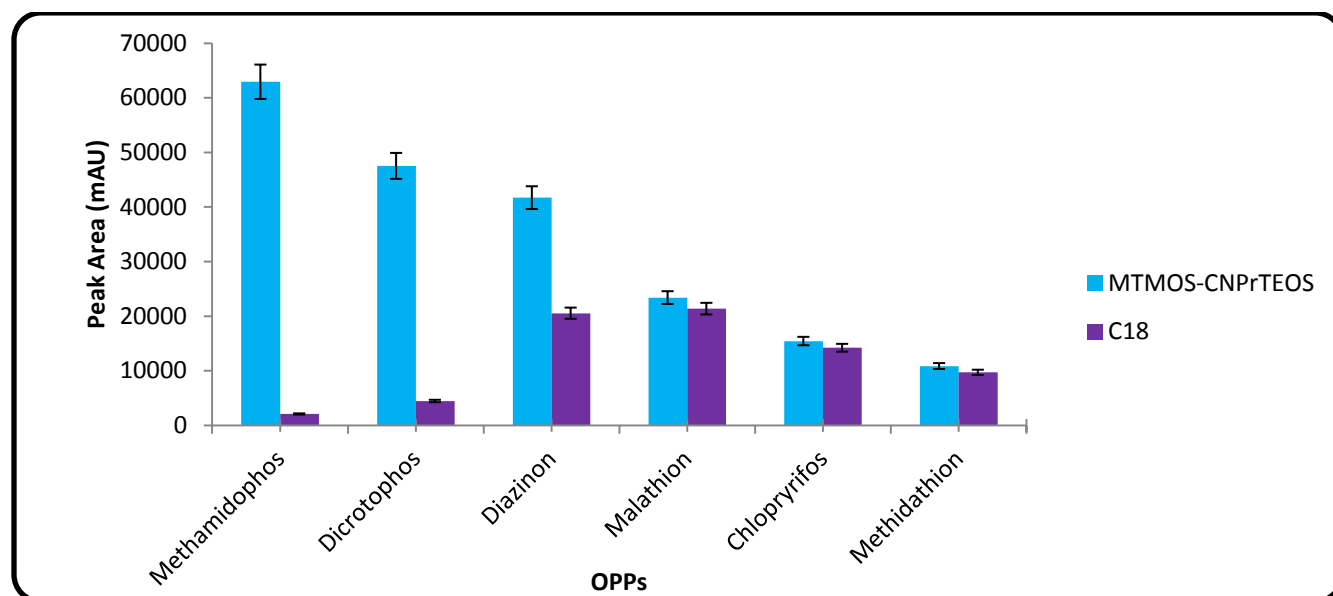


Figure 1 Comparison of extraction efficiency (based on peak area response) of the in-house sol-gel hybrid MTMOS-CNPrTEOS as SPE sorbent material and commercial C₁₈ SPE sorbent towards the six selected OPPs of varying polarities

3.2 Method Validation

The analytical characteristics of the MTMOS-CNPrTEOS SPE and C18 SPE method in terms of its linear range, precision, limits of detection (LODs) were investigated to estimate the efficiency and the feasibility for application to the analysis of environmental samples. Calibration graph for the sol-gel hybrid MTMOS-CNPrTEOS SPE was linear in the range studied $0.1\text{-}1.0 \text{ ng mL}^{-1}$ with good coefficient of determination ($R^2 > 0.9994$) and good RSD ($< 4\%$, $n=3$). The LOD at $S/N=3$ obtained ($0.01\text{-}0.02 \text{ ng mL}^{-1}$) was $5\text{-}10\times$ lower than the maximum residue limit (MRL) of individual pesticides from water samples set by the European Union (EU) [28]. Calibration graph obtained using commercial C18 SPE was linear in the range studied $0.1\text{-}5.0 \text{ ng mL}^{-1}$ with good coefficient of determination ($R^2 > 0.9991$) and the LOD at $S/N=3$ obtained was in the parts per billion range ($0.05\text{-}0.16 \text{ ng mL}^{-1}$) with good RSD ($< 1.5\%$, $n=3$). The LOD obtained using the MTMOS-CNPrTEOS SPE was $5\text{-}8\times$ lower than the LOD obtained from commercial C18 SPE. This can be explained

because the sol-gel hybrid MTMOS-CNPrTEOS sorbent produced possess high surface area ($585 \text{ m}^2 \text{ g}^{-1}$) and porous surface which increased the extraction efficiency. Similar observation was noted by Faraji *et al.* [27] in the determination of phenolic compounds using β -cyclodextrin bonded silica particles in stir bar sorptive extraction and also by Wang *et al.* [28] in the determination of trace organochlorine pesticides in water using novel Benzo-15-Crown-5 sol-gel coating in SPME. The sol-gel hybrid MTMOS-CNPrTEOS SPE provides a potential method for the determination of OPPs at trace levels in water samples with higher responses than commercial C18 SPE.

3.3 Real Sample Analysis

For real sample analysis, the water samples namely tap and lake water were spiked (after confirming the non-presence of the OPPs) at 10 and 50 pg mL^{-1} ($5\text{-}10\times$ lower than MRL of EU) of each OPP for extraction using sol-gel hybrid MTMOS-CNPrTEOS SPE and 50 ($2\times$ lower than MRL of EU) and 100 pg

mL⁻¹ (MRL limit set by EU) for C18 SPE. In terms of extraction recoveries, both sorbent gave similar recoveries of the six OPPs at the spiking levels used, with recoveries between 84-99% for both

SPE sorbent and with RSDs ranging from 0.07-6.50% (n = 3) (Table 1).

Table 1 Average percentage recoveries and RSD of OPPs from two types of water samples studied at two spiked levels using sol-gel hybrid MTMOS-CNPPrTEOS and commercial C18 SPE

Sample	OPPs	MTMOS-CNPPrTEOS			Commercial C ₁₈			
		Spiked level (pg mL ⁻¹)	Average recovery (%)	RSD (%; n = 3)	Spiked level (pg mL ⁻¹)	Average recovery (%)	RSD (%; n = 3)	
Tap water	Methamidophos	10	95.52	1.41	50	92.83	4.73	
		50	98.15	1.28	100	95.91	2.11	
	Dicrotophos	10	97.19	2.20	50	91.23	5.23	
		50	99.03	0.44	100	95.03	3.03	
	Diazinon	10	91.76	4.27	50	92.90	3.73	
		50	99.34	0.07	100	96.76	1.43	
	Malathion	10	97.28	1.27	50	98.07	1.07	
		50	98.82	1.59	100	97.75	1.00	
	Chlorpyrifos	10	96.36	4.06	50	95.87	2.21	
		50	99.45	0.37	100	97.43	1.88	
	Methidathion	10	94.09	3.78	50	93.70	5.17	
		50	98.20	1.50	100	97.76	1.15	
	Lake water	Methamidophos	10	94.74	4.29	50	92.11	4.70
			50	94.17	1.79	100	94.79	2.24
Dicrotophos		10	98.32	1.04	50	90.48	5.16	
		50	91.54	5.70	100	92.19	3.37	
Diazinon		10	84.68	6.46	50	93.43	4.42	
		50	84.80	6.50	100	96.10	2.72	
Malathion		10	97.88	1.90	50	93.87	0.74	
		50	96.60	0.65	100	94.91	1.69	
Chlorpyrifos		10	91.16	6.10	50	97.97	1.63	
		50	95.09	2.70	100	97.38	1.99	
Methidathion		10	90.58	1.31	50	94.36	5.39	
		50	97.53	2.87	100	98.68	0.69	

4.0 CONCLUSION

A new sol-gel hybrid MTMOS-CNPPrTEOS as SPE sorbent material with high potential for highly selective extraction of two polar OPPs from water samples was successfully demonstrated. The sorbent was also able to simultaneously extract four non-polar OPPs in the process thus saving time and money. The in-house MTMOS-CNPPrTEOS sol-gel sorbent material exhibit superior extraction performance for the six selected OPPs compared to commercial C₁₈ SPE. The introduction of CNPPrTEOS to MTMOS has helped to increase the hydrophilicity of the material and promote the interaction between both the polar and non-polar OPPs with the hybrid sorbent materials. LOD at sub-part per billion level OPPs was achieved using this sol-gel hybrid material. Quantitative recoveries (84-99%) and good precision (0.06-6.5%) of OPPs from water samples was achieved with the new sol-gel hybrid sorbent. The new sorbent showed promising alternative sorbent material for selective and simultaneous SPE of OPPs of wide range polarities from water samples at a level much lower than the allowable MRL.

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