



# Novel sol–gel hybrid methyltrimethoxysilane–tetraethoxysilane as solid phase extraction sorbent for organophosphorus pesticides

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## ABSTRACT

A novel sol–gel hybrid methyltrimethoxysilane–tetraethoxysilane (MTMOS–TEOS) was produced and applied as sorbent for solid phase extraction (SPE). Five selected organophosphorus pesticides (OPPs) were employed as model compounds to evaluate the extraction performance of the synthesized sol–gel organic–inorganic hybrid MTMOS–TEOS. Analysis was performed using gas chromatography–mass spectrometry. Several important SPE parameters were optimized. Under the optimum extraction conditions, the method using the sol–gel organic–inorganic hybrid MTMOS–TEOS as SPE sorbent showed good linearity in the range of 0.001–1  $\mu\text{g L}^{-1}$ , good repeatability (RSD 2.1–3.1%,  $n=5$ ), low limits of detection at  $S/N=3$  (0.5–0.9  $\text{pg mL}^{-1}$ ) and limit of quantification (1–3  $\text{pg mL}^{-1}$ ,  $S/N=10$ ). The performance of the MTMOS–TEOS SPE was compared to commercial C18 Supelclean SPE since C18 SPE is widely used for OPPs. The MTMOS–TEOS SPE method LOD was 500–600 $\times$  lower than the LOD of commercial C18 SPE. The LOD achieved with the sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent allowed the detection of these OPPs in drinking water well below the level set by European Union (EU) at 0.1  $\mu\text{g L}^{-1}$  of each pesticides. The developed MTMOS–TEOS SPE method was successfully applied to real sample analysis of the selected OPPs from several water samples and its application extended to the analysis of several fruits samples. Excellent recoveries and RSDs of the OPPs were obtained from the various water samples (recoveries: 97–111%, RSDs 0.4–2.8%,  $n=3$ ) and fruit samples (recoveries: 96–111%, RSDs 1–4%,  $n=5$ ) using the sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent. Recoveries and RSDs of OPPs from river water samples and fruit samples using C18 Supelclean SPE sorbent were 91–97%, RSD 0.9–2.6,  $n=3$  and 86–96%, RSD 3–8%,  $n=5$ , respectively). The novel sol–gel hybrid MTMOS–TEOS SPE sorbent demonstrate the potential as an alternative inexpensive extraction sorbent for OPPs with higher sensitivity for the OPPs.

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## 1. Introduction

In recent years, organophosphorus pesticides (OPPs) have been the largest type of pesticides used worldwide [1,2]. However, OPPs are known as the most poisonous class of pesticides [3]. It causes the inhibition of acetyl-cholinesterase in the central nervous systems [4]. Therefore, it is crucial to monitor the trace levels of OPPs in environment particularly in food samples for human health protection and environmental control. In the European Union, water intended for human consumption must meet minimum specified requirements, including for pesticides a maximum level for each pesticide of 0.1  $\mu\text{g L}^{-1}$  and a maximum of 0.5  $\mu\text{g L}^{-1}$  for total

pesticides, except for aldrin, dieldrin, heptachlor, and heptachlor epoxide, which are each limited to maximum levels of 0.03  $\mu\text{g L}^{-1}$  [5,6].

Since the concentrations of the OPPs are in trace amounts, pre-concentration techniques are required to determine these compounds in the real samples. The most common and conventional technique for the analysis of OPPs in water and food is solid phase extraction (SPE). In SPE, the choice of sorbent is the main key point in SPE because it controls parameters such as selectivity, affinity and capacity [7,8].

The most common and classic material used as sorbent media in SPE is chemically bonded silica, usually with a C8 or C18 organic group, carbon or ion-exchange materials to the polymeric materials based on styrene-divinylbenzene [9]. New materials have been developed in the last few years, since the above materials presents low recoveries for the polar compounds or are too specific for a particulate analyte.

Recent efforts focused on developing new sorbents which enhance selectivity. The selective sorbents are immunosorbents

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(ISs), molecularly imprinted polymer (MIPs) and restricted access materials (RAMs) [9].

Sol–gel has been one of the emerging technologies in the synthesis of inorganic polymers and organic–inorganic hybrid materials [10]. The sol–gel process notably can occur at very mild conditions and provides a versatile method to prepare size, shape, and charge selective materials of high purity and homogeneity. Many applications of sol–gel have been reported in the literature including chemical sensors [11,12], optical material [13], membrane [14], fibre [15] and sorbent [16]. The sol–gel approach brought new promises to provide high stationary phase stability and columns efficiency in separations as sol–gel is capable to chemically bind chromatography stationary phase to column inner surface [15,17].

Sol–gel sorbents have been proven to be quite successful in the extraction of wide range of analytes by SPME [18,19]. Further advances of sol–gel technologies included its application as sorbent media for stir bar sorptive extraction (SBSE) [20–23]. However, only limited numbers of applications of sol–gel hybrid as sorbent materials have been reported [19,22–26]. Thus, there are more hybrid materials that can be explored for its potential to be used in analytical extraction using sol–gel reaction since the reaction is easily carried out under mild synthetic conditions using various kinds of precursors and sorbent materials.

The present study is focussed on the production of a novel sol–gel organic–inorganic hybrid based on methyltrimethoxysilane–tetraethoxysilane (MTMOS–TEOS) and its application as sorbent for use in SPE for the determination of five selected OPPs (chlorpyrifos, diazinon, methidathion, profenofos and quinalphos). Although many works have been reported previously on the developments of new sorbents for SPE, this is the first work to report the application of sol–gel organic–inorganic hybrid MTMOS–TEOS as sorbent for SPE for the determination of OPPs. The in-house sol–gel organic–inorganic hybrid MTMOS–TEOS SPE method exhibit low limit of detection ( $0.5\text{--}0.9\text{ }\mu\text{g mL}^{-1}$ ) compared to commercial Supelclean C18 SPE sorbent ( $0.3\text{--}0.45\text{ ng mL}^{-1}$ ). The proposed sol–gel hybrid SPE sorbent was successfully applied to the determination of OPPs in several water samples and its application extended to the determination of OPPs in several fruit samples. The LOD attained for the sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent in the parts per trillion level is useful for the determination of OPPs at levels lower than the levels set by the European Union for drinking water ( $0.1\text{ }\mu\text{g L}^{-1}$  for each individual pesticides) [5,6]. In the current work, the OPPs were spiked at a concentration  $20\times$  lower than the allowed limit with quantitative recoveries (96–111%) and good repeatability (RSDs 1–4%,  $n = 5$ ).

## 2. Experiment

### 2.1. Standards, reagents and materials

Chlorpyrifos, diazinon, methidathion, quinalphos, profenofos, and vinclozolin (used as internal standard) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methyltrimethoxysilane (MTMOS), tetraethoxysilane (TEOS) and ammonia solution ( $\text{NH}_3$ ) were obtained from Sigma Aldrich (St. Louis, MO, USA). HPLC grade acetonitrile was purchased from Merck (Schuchardt, Germany) and analytical grade methanol (99.99%) was from Fisher Scientific (Loughborough, UK). Working standard solutions were prepared by diluting the stock solution with acetonitrile. The stock solutions and the working standards were stored at  $4^\circ\text{C}$  when not in use. Double distilled deionized water was purified by a Millipore Simplicity 185 (UV) water system from Thermo Scientific (Barnstead, MA, USA).

C18 SPE cartridge (3 mL) was from Supelco (PA, USA). Green apple, red apple, strawberry and grape samples were purchased

from a local hypermarket in Skudai, Johor and used without washing.

### 2.2. Instrumentation

OPP were analyzed using an Agilent 7890A GC system with an Agilent 5975C Series GC/MSD from Agilent Technologies Inc. (Santa Clara, CA, USA). The GC column used was a HP-5MS column ( $30\text{ m} \times 0.32\text{ mm i.d. and } \times 0.25\text{ }\mu\text{m}$  film thickness). Helium was used as carrier gas at a flow rate of  $1.0\text{ mL min}^{-1}$ . The surface morphology of the sol–gel hybrid MTMOS–TEOS was determined at 15 kV using a JSM-6390 scanning electron microscope from JEOL (Tokyo, Japan). The FTIR spectrum was obtained using KBr pellet method on a 1600 Series Perkin Elmer spectrophotometer (MA, USA) in the range of  $400\text{--}4000\text{ cm}^{-1}$ . The surface area and pore size of the sol–gel hybrid MTMOS–TEOS were collected using a surface analyzer model ASAP 2010 Micromeritics from Delta Analytical Instruments Inc. (PA, USA) at 77 K.

### 2.3. Chromatographic conditions

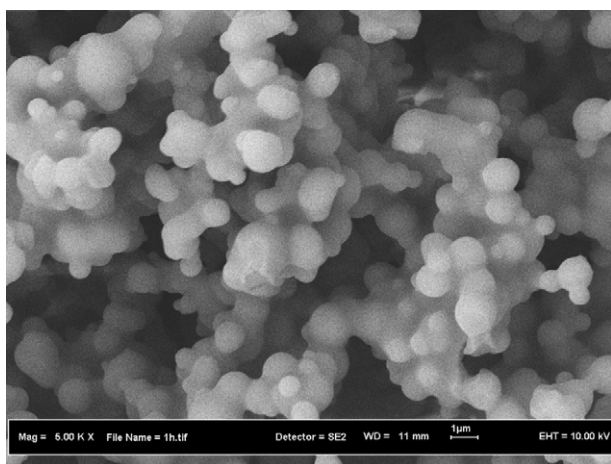
The injection port and detector temperature was set at  $260^\circ\text{C}$  and  $300^\circ\text{C}$ , respectively. Gas chromatography temperature profile was set at  $150\text{--}300^\circ\text{C}$ , start at  $150^\circ\text{C}$  (hold 1 min) ramp at  $10^\circ\text{C min}^{-1}$  to  $200^\circ\text{C}$  (hold 1 min) and ramp at  $4^\circ\text{C min}^{-1}$  to  $300^\circ\text{C}$  (hold 5 min). Sample ( $1\text{ }\mu\text{L}$ ) with the solvent delay of 3.00 min was injected manually into the injection port under splitless mode. For the MS conditions, SCAN mode was used with source temperature of  $230^\circ\text{C}$ , quad temperature at  $150^\circ\text{C}$ , transfer line temperature of  $280^\circ\text{C}$  and multiplier voltage auto tune voltage at 17 kV.

### 2.4. Preparation of sol–gel organic–inorganic hybrid MTMOS–TEOS

The sol–gel organic–inorganic hybrid MTMOS–TEOS were prepared by mixing optimum amount of MTMOS (7 mmol), TEOS (2.5 mmol),  $\text{H}_2\text{O}$  (830.9 mmol), methanol (12.4 mmol),  $\text{NH}_3$  solution (25.2 mmol). The resulting mixture was magnetically stirred for  $\sim 15$  min, and left at room temperature for 3 days till the formation of aerogel. The aerogel was then washed with  $3 \times 10\text{ mL}$  acetone, followed by  $3 \times 10\text{ mL}$  deionized water. The product was finally dried at  $100^\circ\text{C}$  for 5 days. The sorbent with the molar ratio MTMOS/TEOS of 2.8 was selected for further use in SPE of OPPs from water and fruit samples as it gave the highest extraction efficiency (peak area obtained).

### 2.5. SPE procedure

The sol–gel hybrid material (100 mg) was ground using a pestle and mortar and packed manually into an empty 3 mL SPE polypropylene tube with frits. The filled SPE cartridge was then placed in a 12-port SPE vacuum manifold from Supelco (Bellefonte, PA, USA) and conditioned by passing  $1 \times 5\text{ mL}$  methanol, followed by  $1 \times 10\text{ mL}$  deionized water. For optimization process, 10 mL of spiked ( $1\text{ }\mu\text{g mL}^{-1}$  of each pesticide) deionized water sample was passed through the cartridge at a flow rate of  $0.5\text{ mL min}^{-1}$ . 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. Retained OPPs were eluted from the sorbent with  $1 \times 5\text{ mL}$  acetonitrile and dried under a gentle stream of nitrogen gas to dryness. The residue was reconstituted in  $100\text{ }\mu\text{L}$  of acetonitrile prior to GC–MS analysis. Blank sample analysis was also performed for comparison purposes. For C18 SPE, a 3 mL cartridge was used for extraction and a similar procedure as the MTMOS–TEOS SPE was followed.



**Fig. 1.** Micrograph of sol-gel organic-inorganic hybrid MTMOS-TEOS at 2500 $\times$  magnification.

The optimum SPE conditions for the C18 SPE sorbent are 10 mL sample loading, acetonitrile as the eluting solvent and 5 mL solvent volume used. C18 SPE was selected for comparison of extraction performance as it is often used in environmental analysis for sample enrichment of OPPs [27,28].

### 2.6. Real sample and its preparation

Water samples namely tap water, bottled drinking water (processed water, reverse osmosis and filtration process), bottled mineral water (from underground water source) and river water was used as real samples. Bottled drinking water and bottled mineral water were purchased from a local shop. Tap water was obtained from the laboratory and river water samples were collected from Skudai River, Johor in Teflon bottles pre-cleaned with acetone. The pre-cleaned bottles were covered with aluminium and stored in the dark at  $-4^{\circ}\text{C}$  until analysis. All water samples were used as received.

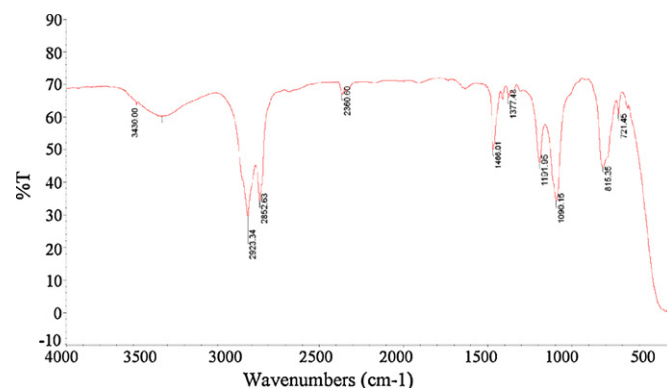
For recovery analysis, the river water, tap water, bottled drinking water and bottled mineral water samples were spiked with mixture of OPPs standard at  $0.005\ \mu\text{g L}^{-1}$  of each OPP and water sample pH was adjusted to pH 7. The spiked water samples were allowed to stand overnight before being extracted with both C18 SPE and MTMOS-TEOS SPE.

Representative portion of green apple, red apple, strawberry, and grape samples were each separately homogenized in a blender and analytical portion (12.0 g) was weighed into a 50-mL centrifuge tube and 20 mL of acetonitrile was added into each tube. The samples were left to be extracted for 30 min in a Branson 3510 ultrasonic bath (Danbury, CT, USA). After ultrasonication, the aliquot was filtered through a  $0.45\ \mu\text{m}$  Whatman filter paper (NJ, USA) and made up to 10 mL. Preliminary analysis showed the fruit samples to be analyte free. Accuracy of developed method was assessed by spiking fruit samples with  $0.005\ \mu\text{g L}^{-1}$  each OPPs for MTMOS-TEOS SPE and  $10\ \mu\text{g L}^{-1}$  each OPPs for C18 SPE. Different spiking levels were used for both SPE sorbent as the LOD achieved were different. Repeatability of extraction was determined using 5 replicates.

## 3. Results and discussions

### 3.1. Characterization of sol-gel hybrid

The morphology of sol-gel hybrid MTMOS-TEOS was investigated using scanning electron microscope (SEM) (Fig. 1). The



**Fig. 2.** FTIR spectrum of KBR pellets of sample of sol-gel organic-inorganic hybrid MTMOS-TEOS.

sol-gel hybrid material formed a porous microstructure contributed by the cross-linking and self-condensation reaction occurred during the process of MTMOS chain bonded to the surface of TEOS particles through Si-O-Si combination. The pore size and surface area of MTMOS-TEOS sorbent is 5.09 nm (mesoporous material) and  $565\ \text{m}^2\ \text{g}^{-1}$ , respectively. The particle size of the hybrid MTMOS-TEOS sorbent is 0.75–1.02  $\mu\text{m}$ .

Fig. 2 shows the FTIR spectrum of the sol-gel hybrid 0.5:1 molar ratio of MTMOS-TEOS. Bands at  $2923\ \text{cm}^{-1}$  and  $2852\ \text{cm}^{-1}$  are characteristics of C-H symmetry and anti-symmetry stretching vibrations of  $\text{CH}_3$  group. The strong absorption band at  $1192\ \text{cm}^{-1}$  and  $1090\ \text{cm}^{-1}$  are assigned to asymmetric stretching vibration of Si-O-Si. The peak at  $1466\ \text{cm}^{-1}$  corresponds to the C-H bending band and the peak at  $815\ \text{cm}^{-1}$  corresponds to stretching of Si-C bond (Si- $\text{CH}_3$ ) presence in the hybrid. The band at  $3430\ \text{cm}^{-1}$  is the Si-OH band (H-bonded).

### 3.2. SPE optimization

Several important SPE optimization parameters namely sample volume, types of eluting solvents, and eluting solvent volumes were studied. Sample volume is important in determining the loading capacity of SPE device as well the overall time required by the sorbent, to reach equilibrium with analyte. Sample volumes also play an important role in the recovery of the analyte. As large as possible sample volume is necessary to obtain highest sensitivity and sample enrichment. The sample size is governed by the breakthrough volume of the sorbent. Nine different sample volumes (1–100 mL) were examined at a flow rate of  $0.5\ \text{mL min}^{-1}$ . Increasing sample volume increased the peak area of OPPs extracted. However, beyond 10 mL the peak area of OPPs extracted started to decrease significantly probably due to the sorbent breakthrough being exceeded. Thus, 10 mL was selected as the optimum sample volume (Fig. 3).

In SPE, eluent is very important to elute retained analytes from sorbent to obtain best sensitivity. Six eluting solvents of different polarities namely acetonitrile, ethyl acetate, methanol, ethanol, hexane and dichloromethane were investigated to determine the best eluting solvent. Results indicated that acetonitrile was the most effective eluent and thus selected as it gave the highest recovery for all of the OPPs studied (Fig. 4).

Eluent solvent volumes from 1 to 20 mL acetonitrile were investigated to ensure that minimum but sufficient volume is needed to elute retained OPPs to obtain the highest sensitivity. On increasing solvent volume from 1 mL to 5 mL, the peak area of OPPs extracted increased. The highest peak areas for the OPPs were obtained when 5 mL of eluting solvent were used (Fig. 5). Thus, 5 mL acetonitrile was selected as the optimum eluent volume. Based on the results,

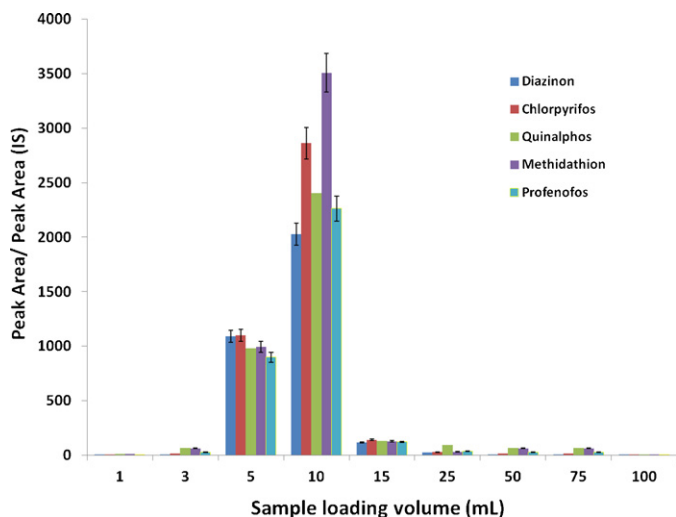


Fig. 3. Effect of different sample loading volume on extraction efficiency of OPPs from sol-gel organic-inorganic hybrid MTMOS-TEOS.

the optimized parameters obtained for the extraction of OPPs using sol-gel hybrid MTMOS-TEOS are 10 mL sample loading volume, acetonitrile as the eluting solvent and 5 mL volume used. Optimum SPE conditions for the C18 SPE sorbent are 10 mL sample loading and 5 mL acetonitrile as the eluting solvent.

### 3.3. Method validation

To validate the applicability of the proposed SPE method using the sol-gel hybrid MTMOS-TEOS sorbent, linearity, limit of detection (LOD) and limit of quantification (LOQ) for both MTMOS-TEOS sol-gel hybrid SPE sorbent and commercial C18 SPE sorbent were assessed using the optimum extraction conditions. The linearity of the extraction technique was studied by spiking deionized water samples using 5 different concentration levels of OPPs in the range  $0.001\text{--}1\ \mu\text{g L}^{-1}$  for MTMOS-TEOS SPE and  $5\text{--}1000\ \mu\text{g L}^{-1}$  for C18-SPE.

Table 1 show that good linearities were obtained for both SPE extractions using the sol-gel organic-inorganic hybrid

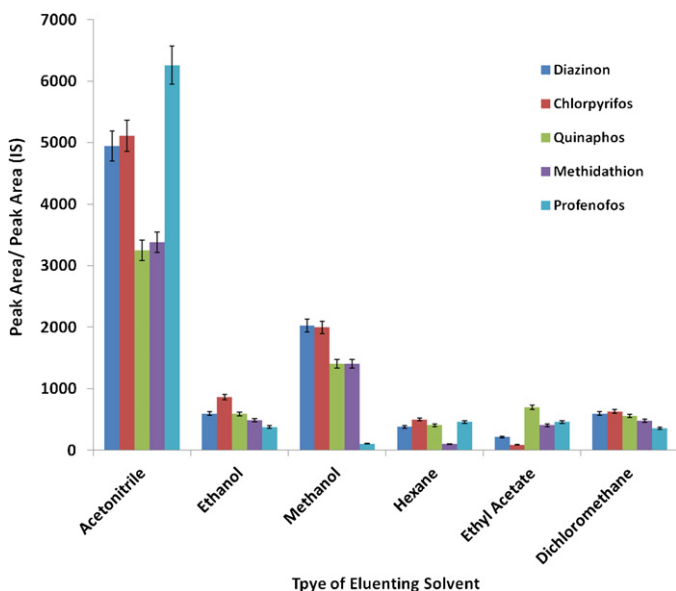


Fig. 4. Effect of eluent types on extraction efficiency of OPPs from using sol-gel organic-inorganic hybrid MTMOS-TEOS sorbent with 10 mL of sample volume.

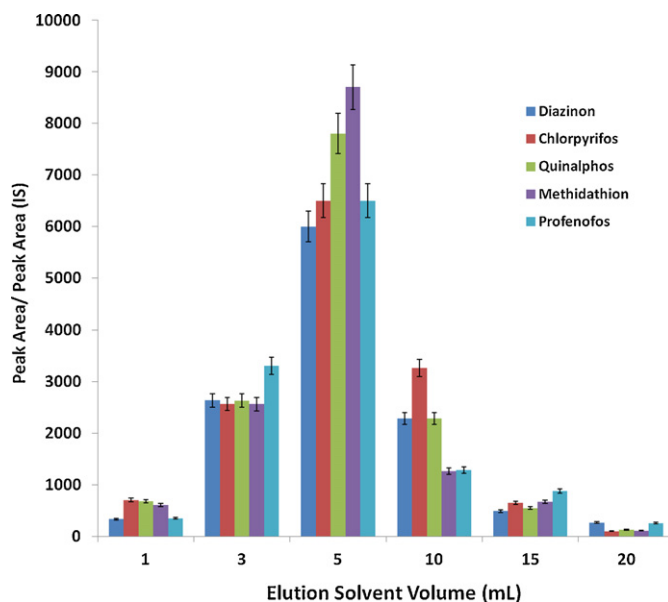


Fig. 5. Effect of eluent volumes on extraction efficiency of OPPs from using sol-gel organic-inorganic hybrid MTMOS-TEOS sorbent using 10 mL sample volume and acetonitrile as eluent.

MTMOS-TEOS and commercial C18 sorbent with coefficient of determination,  $r^2 > 0.9994$ . The LOD was calculated at a signal-to-noise ratio (S/N) of 3 while the LOQ measured at S/N=10. The LOD and LOQ achieved by sol-gel organic-inorganic hybrid MTMOS-TEOS sorbent were absolutely superior ( $500\text{--}600\times$  and  $730\text{--}1500\times$  more sensitive) compared to the LOD and LOQ for C18 sorbent (Table 1). The repeatability (RSD 2.5–4%,  $n=5$ ) and reproducibility (RSD 2.9–4.1%,  $n=25$ ) were good for C18 SPE. Slightly lower repeatability (RSDs 2.1–3%,  $n=5$ ) and reproducibility (RSD 2–2.9%,  $n=25$ ) were achieved using sol-gel organic-inorganic hybrid MTMOS-TEOS SPE. Both the sol-gel organic-inorganic hybrid MTMOS-TEOS SPE and C18 SPE cartridge were found practically reusable for all the extractions performed.

The potential regeneration and stability of the SPE-MTMOS-TEOS cartridge were studied up to at least 25 adsorption-elution cycle. The column was washed with 5 mL of MeOH followed by 10 mL deionized water after each extraction. It was observed that MTMOS-TEOS SPE could be repeatedly used (up to at least 25 adsorption-elution cycles) without significant loss of uptake capacity in the extraction OPPs from water and fruit samples. The interday precision (RSDs) after 25 cycles of use is 2–2.9% for MTMOS-TEOS and 2.9–4.1% for C18 (Table 1). However, the cost of producing the in-house sol-gel organic-inorganic hybrid material is low and the process involve is simple and easily performed. The sol-gel hybrid MTMOS-TEOS sorbent SPE was able to enrich analytes far superior (even with a small volume of sample loading) than the commercial C18 sorbent SPE.

### 3.4. Determination of OPPs in water and fruit samples

The proposed method using the sol-gel hybrid MTMOS-TEOS SPE sorbent was applied to the analysis of four water samples (tap water, mineral water, and river water). None of the target analytes were detected in these water samples under the experimental conditions described. Since no targeted OPPs were detected, all the water samples were spiked ( $0.005\ \mu\text{g L}^{-1}$ ) to assess recovery (accuracy of proposed method) and also to assess matrix effect. Analyses of a blank sample was performed for comparison purposes. C18 Supelclean SPE was also used for extraction of the OPPs from the water samples for comparison (chromatogram not shown). The



**Table 1**

Qualitative data comparisons between sol–gel hybrid MTMOS–TEOS SPE and C18 SPE: linearity, repeatability (% RSD,  $n = 5$ ), reproducibility (%RSD,  $n = 25$ ), limit of detection and limit of quantification of OPPs.

OPPs	Coefficient of determination ( $r^2$ )	MTMOS–TEOS SPE GC–MS				Coefficient of determination ( $r^2$ )	C18 SPE GC–MS			
		RSD (%, $n = 5$ ) <sup>a</sup>	RSD (%, $n = 25$ ) <sup>a</sup>	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	LOQ <sup>b</sup> ( $\mu\text{g L}^{-1}$ )		RSD (%, $n = 5$ ) <sup>**</sup>	RSD (%, $n = 25$ ) <sup>**</sup>	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	LOQ <sup>b</sup> ( $\mu\text{g L}^{-1}$ )
Chlorpyrifos	0.9995	3	2.7	0.0007	0.002	0.9997	3	3.5	0.3	2
Diazinon	0.9999	2.3	2.8	0.0009	0.001	0.9997	4	4.1	0.45	1.5
Methidathion	0.9997	3.1	2.9	0.0006	0.003	0.9994	4	3.5	0.42	1.7
Profenofos	0.9997	2.2	2	0.0008	0.001	0.9995	2.5	2.9	0.33	2.1
Quinalphos	0.9996	2.1	2.3	0.0005	0.002	0.9998	3.2	3.8	0.43	2.3

Linearity range: 0.001–1  $\mu\text{g L}^{-1}$  (MTMOS–TEOS SPE) and 5–1000  $\mu\text{g L}^{-1}$  (C18 SPE).

<sup>a</sup> LOD:  $S/N = 3$ .

<sup>b</sup> LOQ:  $S/N = 10$ .

<sup>\*</sup> Spiked at 0.1  $\mu\text{g L}^{-1}$  (distilled water).

<sup>\*\*</sup> Spiked at 100  $\mu\text{g L}^{-1}$  (distilled water).

**Table 2**

Percentage recovery and % RSD ( $n = 3$ ) for spiked OPPs from river water samples using developed organic–inorganic hybrid MTMOS–TEOS SPE and C18 SPE method with GC–MS analysis.

OPPs	MTMOS–TEOS SPE GC–MS Recovery ( $\pm$ RSD%, $n = 3$ )				C18 SPE GC–MS Recovery ( $\pm$ RSD%, $n = 3$ )			
	River water <sup>*</sup>	Tap water <sup>*</sup>	Mineral water <sup>*</sup>	Drinking water <sup>*</sup>	River water <sup>**</sup>	Tap water <sup>**</sup>	Mineral water <sup>**</sup>	Drinking water <sup>**</sup>
Chlorpyrifos	98 (2.8)	99 (1.4)	100 (1.9)	98 (2)	92 (2.4)	97 (2.8)	98 (3.5)	99 (1.2)
Diazinon	99 (1.9)	100 (2.5)	99 (1.5)	101 (2)	95 (2.6)	95 (4.9)	97 (3.9)	97 (3.4)
Methidathion	107 (1.5)	108 (0.6)	111 (0.9)	104 (1.7)	91 (1.5)	89 (6)	94 (2.8)	95 (3.1)
Profenofos	100 (0.7)	98 (1.5)	98 (0.4)	100 (0.9)	96 (1.5)	93 (3.7)	92 (7)	90 (6)
Quinalphos	101 (2)	100 (0.9)	97 (1)	101 (2)	97 (0.9)	91 (4)	97 (0.9)	92 (3.9)

<sup>\*</sup> Spiked level: 0.005  $\mu\text{g L}^{-1}$  MTMOS–TEOS SPE.

<sup>\*\*</sup> Spiked level: 10  $\mu\text{g L}^{-1}$  C18 SPE.

OPPs was spiked at 10  $\mu\text{g L}^{-1}$  (100 $\times$  higher than the LOD) for the C18 SPE.

The developed MTMOS–TEOS SPE and C18 SPE method were extended to the analysis of OPPs from four real fruit samples namely green apple, red apple, strawberry and grapes. Since, no targeted analytes were detected, the fruit samples too were spiked at the same level as the water samples for both the MTMOS–TEOS SPE sorbent and C18 SPE sorbent. Analyses of a blank sample were also performed for comparison purposes for both sorbent. Table 2 shows the comparison of recovery and precision (repeatabilities) obtained using sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent and C18–SPE sorbent, respectively for several water samples. The level of OPPs spiked into the river water samples (0.005  $\mu\text{g L}^{-1}$ ) for MTMOS–TEOS SPE is 20 $\times$  lower than the MRL set by European Union (EU). The LOD obtained for the OPPs using the C18 SPE from the current study (0.3–0.45  $\mu\text{g L}^{-1}$ ) and this is above the limit set by EU for individual pesticides (0.1  $\mu\text{g L}^{-1}$ ). The LOD obtained for the OPPs analyzed using C18 SPE with GC analysis is comparable to literature values as obtained by Pittarch et al. [29]. The spiked level used for assessing recovery using C18 SPE was 10  $\mu\text{g L}^{-1}$ . The recovery and RSD observed with the sol–gel hybrid MTMOS–TEOS

**Table 4**

Maximum residue limit (MRL) of OPPs in several fruits as given by European Union (EU) Regulations (EC) No 600/2010.

OPPs	MRL (mg/kg)			
	Red apple	Green apple	Strawberry	Grape
Chlorpyrifos	0.5	0.5	0.2	0.5
Diazinon	0.01	0.01	0.01	0.01
Methidathion	0.05	0.05	0.02	0.02
Profenofos	0.05	0.05	0.05	0.05
Quinalphos	0.05	0.05	0.05	0.05

SPE was 98–107% and 0.7–2.8%, respectively, while the recovery and RSD from the C18 SPE was 91–97% with an RSD of 0.9–2.6%. Both sorbents showed quantitative recovery and excellent RSD but the MTMOS–TEOS SPE sorbent was able to detect the OPPs even at a concentration 20 $\times$  lower than the set value of EU which was not possible with the C18 SPE.

Table 3 shows the comparison of recovery and precision (repeatabilities and reproducibilities) obtained using sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent and C18–SPE

**Table 3**

Comparison of % recovery and % RSD ( $n = 5$ ) for fruit samples using sol–gel organic–inorganic hybrid MTMOS–TEOS SPE and C18 SPE with GC–MS analysis.

OPPs	MTMOS–TEOS SPE–GC–MS <sup>*</sup> Recovery ( $\pm$ RSD%, $n = 5$ )				C18 SPE–GC–MS <sup>**</sup> Recovery ( $\pm$ RSD%, $n = 5$ )			
	Green apple	Red apple	Grape	Strawberry	Green apple	Red apple	Grape	Strawberry
Chlorpyrifos	99 (1)	100 (1)	97 (3)	96 (4)	96 (3)	91 (6)	92 (6)	89 (7)
Diazinon	98 (1)	101 (1)	98 (3)	97 (3)	96 (4)	90 (4)	92 (7)	88 (8)
Methidathion	107 (1)	107 (1)	99 (3)	96 (3)	96 (3)	88 (8)	90 (7)	90 (6)
Profenofos	100 (2)	102 (1)	100 (3)	97 (4)	93 (4)	90 (5)	92 (6)	86 (8)
Quinalphos	101 (3)	111 (2)	98 (2)	98 (4)	90 (4)	92 (6)	93 (6)	88 (7)

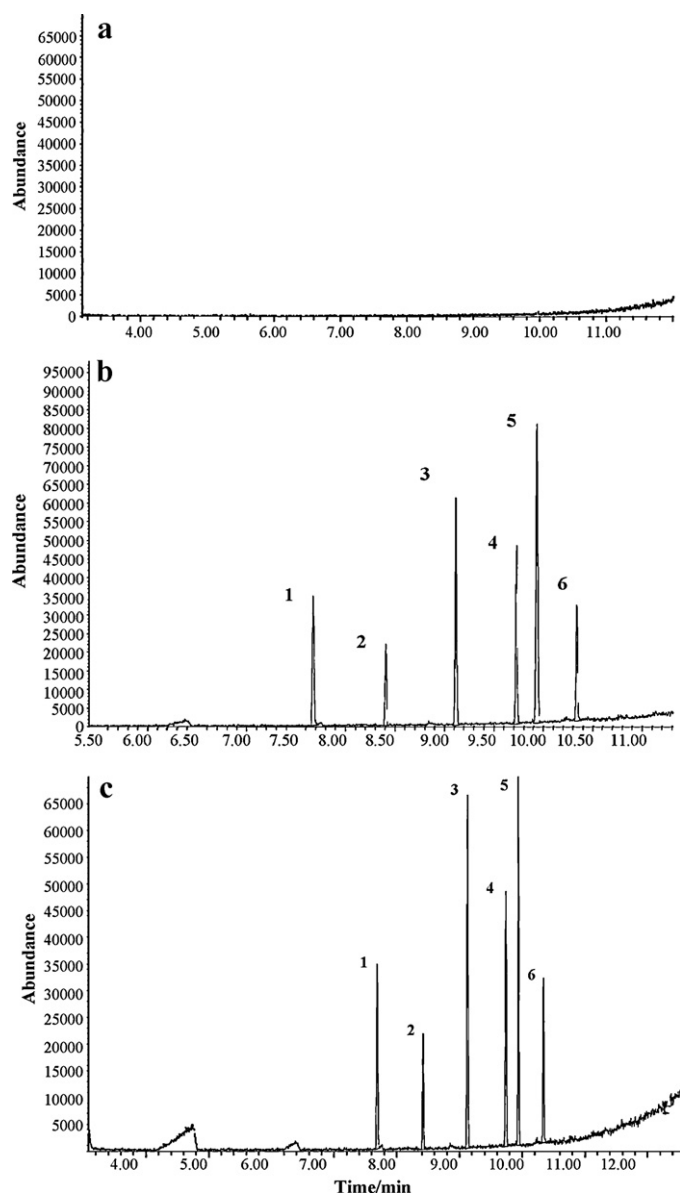
<sup>\*</sup> Spiked level: 0.005  $\mu\text{g L}^{-1}$ .

<sup>\*\*</sup> Spiked level: 10  $\mu\text{g L}^{-1}$ .

**Table 5**  
Comparison of LOD of current work using sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent compared to other recent sol–gel hybrid materials for OPPs determinations.

Year	Sol–gel	Analyte	LODs	Matrix	Extraction method	Detection method	Ref.
2011	Methyltrimethoxysilane–tetraethoxysilane (MTMOS–TEOS)	Chlorpyrifos, diazinon, profenofos, methidathion and quinalphos	0.5–0.9 pg mL <sup>-1</sup>	Water	SPE	GC–MS (scan mode)	Current work
2010	Polydimethylsiloxane–2-hydroxymethyl–18-crown–6 (PDMS–2OHMe18C6)	Chlorpyrifos, diazinon, profenofos	4.5–4.8 ng g <sup>-1</sup>	Red apple green apple and strawberry	SPME	GC–ECD	
2010	3-(Trimethoxysilylpropyl)amine–poly(dimethylsiloxane) (TMSPA/PDMS)	Disulfoton, sulfotep, phorate, parathion, O,O,O-triethylthiophosphate	0.05–1 pg mL <sup>-1</sup>	Water	SPME	GC–MS (SIM)	[26]
2008	Tetramethoxysilane and dimethyldimethoxysilane (TMOS–DMDMOS)	Fenclorphos, pirimiphos-methyl, chlorpyrifos, ethion, quinalphos	5.2–34.6 ng L <sup>-1</sup>	Water	SPME	GC–FTD	[31]
2008	Hydroxy-terminated silicone divinylbenzene (OH-TSO/DVB)	Dichlorvos, diazinon, methyl parathion, ethyl parathion, malathion	0.007–0.07 ng g <sup>-1</sup>	Packchoi	HS-SPME	GC–NPD	[32]
2008	Polydimethylsiloxane/polyvinylalcohol (PDMS–PVA)	Phorate, fenitrothion, malathion, parathion, and quinalphos	0.013–0.081 µg L <sup>-1</sup>	Honey	SBSE	LVI–GC–FPD	[33]
2007	Polydimethylsiloxane/polyvinylalcohol (PDMS/PVA)	Fenthion, methyl parathion, malathion	0.3–3.9 ng mL <sup>-1</sup>	Complex herbal <i>Passiflora L.</i>	SPME	FIMS (Fibre Introduction Mass Spectrometry FPD)	[34]
2006	PDMS–DVB (vinyl crown ether)	Dichlorvos, diazinon methyl parathion, ethion, fenitrothion, malathion parathion, phorate	0.003–0.09 ng g <sup>-1</sup>	Apple juice, apple and tomato	SPME		[35]
2006	PDMS with 3% vinyl coating	Monocrotopos, phorate, dimethoate, parathion-methyl, malathion, ethion, fenitrothion, fenthion, chlorpyrifos, parathion, methidathion, triazophos	0.39–19.9 ng L <sup>-1</sup>	Orange juice, red wine and water	SPME	GC–TSD	[36]
2004	Sol–gel-derived bisbenzo crown ether/hydroxyl-terminated silicone oil (OH-TSO)	Dichlorvos, phorate, ethion, dimethoate, diazinon, methyl parathion, fenitrothion, malathion, fenthion, chlorpyrifos, triazophos	0.003–1.0 ng g <sup>-1</sup>	Honey, juice, orange and pakchoi	SPME	GC–FPD	[37]

GC–TSD: gas chromatography–thermionic specific detector; GC–FTD: gas chromatography–flame thermionic detector; GC–ECD: gas chromatography–electron capture detector; GC–NPD: gas chromatography–nitrogen phosphorus detector; LVI–GC–FPD: large volume injection–gas chromatography–flame photometric detector.



**Fig. 6.** Chromatogram obtained using sol–gel organic–inorganic hybrid MTMOS–TEOS SPE from red apple samples for (a) unspiked, (b) spiked OPPs ( $0.005 \mu\text{g L}^{-1}$ ) and (c) spiked red apple samples ( $10 \mu\text{g L}^{-1}$ ) using commercial C18 SPE cartridge. GC–MS performed in SCAN mode with solvent delay of 3 min and experimental condition as in Section 2. Peaks: 1. Diazinon; 2. Vinclozolin (IS); 3. Chlorpyrifos; 4. Quinalphos; 5. Methidathion; 6. Profenofos.

sorbent, respectively for fruits sample. The level of OPPs spiked onto the fruit samples ( $0.005 \mu\text{g L}^{-1}$  for MTMOS–TEOS SPE) is well below the MRL set by European Union (EU) while the spiked level for extraction using C18 SPE meets the lower limit of  $0.01 \mu\text{g g}^{-1}$  set by EU. The maximum residue limit (MRL) according to EU Regulations (EC) No 600/2010 in the fruit samples analyzed is given in Table 4 [30]. The recoveries and repeatability obtained from fruit samples using the sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent were 96–111% and RSDs 1–4%,  $n = 5$  while the recoveries and repeatability for the C18 SPE sorbent were 88–96%, and 3–8%,  $n = 5$ , respectively.

The extraction recovery of any method is dependent on the sample matrix. Based on the results, it is clearly seen that sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent showed higher extraction recoveries for fruit samples compared to C18 SPE sorbent. This indicates that matrix effects were less when

sol–gel organic–inorganic hybrid MTMOS–TEOS SPE sorbent was being used. Fig. 6(A) and (B) shows the chromatogram of blank analysis and spiked red apple extracts respectively, while Fig. 6(C) is the chromatogram for GC–MS runs of red apple extract using C18 SPE.

### 3.5. Comparison with other results

Table 5 gives a comparison of the LOD attained with the developed sol–gel organic–inorganic hybrid MTMOS–TEOS SPE as compared to the LOD obtained using other kinds of sol–gel hybrid from recent years. The sensitivity of the proposed method is much higher ( $1000\times$  lower LOD) than our previous sol–gel hybrid 2OHMe18C6-PDMS SPME in the extraction of 3 common OPPs [19]. Generally, the sensitivity of the proposed sol–gel hybrid SPE method was higher than most of the other sol–gel hybrid materials except for 3-trimethoxysilylpropylamine–poly(dimethylsiloxane) (TMSPA/PDMS) [26].

## 4. Conclusion

Novel organic–inorganic hybrid MTMOS–TEOS has been successfully prepared using sol–gel technique and applied as sorbent for SPE coupled with GC–MS for the determination of five selected OPPs from several water and four fruit samples. LOD at part per trillion level OPPs in water was achieved using this sol–gel hybrid material. The SPE method presented here offers an interesting and effective option for the analysis of OPPs and other GC-amenable trace contaminants in similar sample types or similar analytes from other sample types. A comparison of sol–gel hybrid MTMOS–TEOS SPE with commercial C18 SPE indicates that MTMOS–TEOS sorbent is better in terms of LOD (sensitivity), reproducibility (precision), and linearity, and accuracy (recovery). Sol–gel hybrid MTMOS–TEOS sorbent is also cost effective and easy to prepare. The sorbent also showed superior extraction performance as compared to other sol–gel hybrid material most probably due to the porous nature and large surface area of the sol–gel material. The introduction of the MTMOS to TEOS helped to increase the hydrophobicity of the material and promote the increase in the interaction between the hydrophobic OPPs and the sorbent materials. The high surface area and the mesoporous nature of the material also facilitate in the adsorption process and its increase in sensitivity.

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