CrossMark

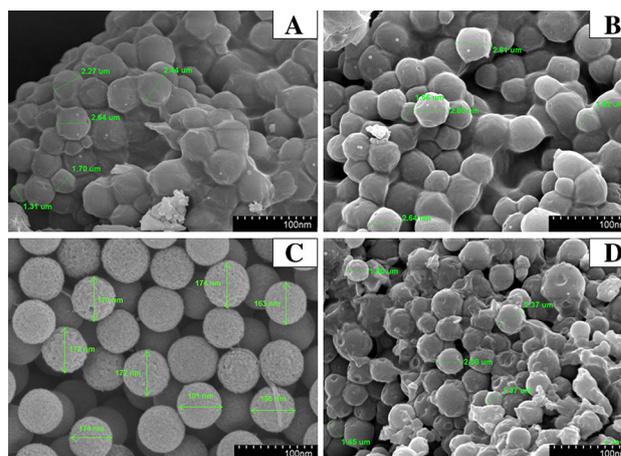ORIGINAL PAPER: INDUSTRIAL AND TECHNOLOGICAL APPLICATIONS OF SOL-GEL AND HYBRID MATERIALS

Application of sol–gel hybrid extraction sorbent for gas chromatographic analysis of organophosphorus pesticides

Wan Norfazilah Wan Ismail[1]

Abstract Sol–gel hybrid extraction sorbent based on methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOS-CNPrTEOS) was successfully synthesized by sol–gel process for use in solid-phase extraction (SPE) of organophosphorus pesticides (OPPs). Analysis was performed using gas chromatography–mass spectrometry. Several important sol–gel parameters were optimized. Fourier transform infrared spectroscopy, scanning electron microscopy and surface area analyses were used to characterize the composite structure and morphology in detail. The results showed that the specific area of sol–gel hybrid MTMOS-CNPrTEOS was $585\ m^2g^{-1}$ with perfect spherical shape with average size of 174 nm. Under the optimum sol–gel conditions (2:1 mol composition of MTMOS:CNPrTEOS, NH_4OH of pH 10.5 and drying temperature of 100 °C), the method using MTMOS-CNPrTEOS SPE showed good linearity with excellent limit of detection (10–70 pg mL^{-1}) at signal to noise ratio = 3 and good relative standard deviation (RSD < 9 %) for all the three OPPs analyzed.

Graphical Abstract

1 Introduction

Sample pre-treatment is a vital stage in chemical analysis, allowing for the final identification and quantitative determination of targeted analytes using a chosen detection method. Frequently used sample pre-treatment is solid-phase extraction (SPE), as it greatly reduces interferences of the matrix, enhancing sensitivity and facilitating unambiguous identification and confirmation [1, 2]. Stability and reusability sorbents require small solvent volumes, ease of separation and enrichment under dynamic

✉ Wan Norfazilah Wan Ismail
 norfazilah@ump.edu.my

1 Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

conditions; high pre-concentration factors are several highlighted advantages of SPE [3, 4].

The majority of the SPE sorbents available, such as silica-based materials [5, 6], carbon-based materials [7, 8], molecularly imprinted polymers [9–12] and mixed-mode sorbents [13], have been reported. The most commonly used SPE sorbent is commercially available C_8- or C_{18}-silica [14] which has low recoveries or too specific for analytes of interest, leading to difficulties in further steps of analysis due to dirty extracts or complex sample matrix. In addition, low thermal and solvent stability of the sorbents represent a major drawback of the SPE method. These problems are related to sorbent synthesis techniques [15]. Novel approaches to sorbent synthesis technique are very important for solving these problems.

Sol–gel technique is an approach to address the above-mentioned problem. It is known to produce porous structure with high surface area sorbent for extraction in order to obtained high recoveries of targeted analytes [3]. It provides a simple and convenient pathway to synthesize advanced material systems that can be used to prepare SPE sorbents. The advantages of sol–gel technology in the area of SPE sorbents are as follows: 1) it provides a single-step procedure making the whole manufacturing process of SPE sorbents very efficient and cost-effective; 2) it provides the possibility to combine organic and inorganic material properties in extraction sorbents providing tunable selectivity; 3) it offers the opportunity to create sorbents with a porous structure which significantly increases the surface area of the extracting phase and provides acceptable stationary phase loading and sample capacity; 4) it provides mild reaction temperature [16, 17]. Synthesis of SPE sorbent by sol–gel process has been demonstrated for the extraction of various analytes [18–20]. However, only a limited number of works have reported on the use of hybrid sol–gel materials as SPE sorbents [17, 21–25].

The present study is focused on the application of a sol–gel hybrid-based methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOS-CNPrTEOS) as sorbent for use in SPE method for the determination of three selected organophosphorus pesticides (OPPs). The appropriate sol–gel precursor was chosen depending on the characteristics of analytes selected. The three OPPs (diazinon, malathion and chlorpyrifos) selected have different polarity. Therefore, sorbent considered must be favorable in the extraction of these analytes. The CNPrTEOS possess polar cyano functional groups which are able to attract polar and semipolar analyte(s). MTMOS was chosen as the starting material because it contains three hydrolysable methoxy groups which can undergo rapid hydrolysis and condensation reactions to form a three-dimensional silica network as compared to other common sol–gel precursors. In addition, MTMOS also yields narrow and uniform pores

with high surface area and can overcome undesirable effects such as collapse structure during drying process [26].

The in-house sol–gel hybrid MTMOS-CNPrTEOS SPE method exhibits low limit of detection and is successfully applied for determination of OPPs in two different complex sample matrices. Most exposures to organophosphates occur from skin absorption and very likely to affect exposed workers and population. However, the exposure via foodstuffs is always possible and should be monitored as well. In the field, the degradation of organophosphate occurs slowly by hydrolysis. Their possibility of distribution in environment is under the influence of pH, oxygen and light intensity, producing residues with altered physical properties and potentially more toxic as well. Therefore, it is crucial to monitor the trace levels of OPPs in environment particularly in food samples for human health protection and environmental control.

2 Materials and methods

Standard solution at 100 µg mL^{-1} of diazinon, malathion and chlorpyrifos (purchased from Dr. Ehrenstorfer GmbH laboratory (Augsburg, Germany)) was prepared in methanol (HPLC grade which was obtained from J.T. Baker *Inc.* (Phillipsburg, NJ, USA)) and stored at 4 °C when not used. SPE-GC analysis of diazinon, malathion and chlorpyrifos was performed on a Hewlett-Packard Model 6890 N gas chromatography (GC) equipped with Hewlett Packard Model 6890 N mass spectrometer (MS). An Ultra-2 column (25 m × 0.20 mm i.d., and ×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 the solvent delay of 2.50 min was injected manually into the injection port under splitless mode. For the MS conditions, SIM mode was used with source temperature of 230 °C, quad temperature of 150 °C and transfer line temperature of 280 °C.

Initially, the sol–gel hybrid MTMOS-CNPrTEOS of mol composition 1:1 MTMOS:CNPrTEOS was prepared by putting 0.36 mL of water (reaction medium) and 0.85 mL of NH$_4$OH catalyst (pH 10.0) into 5 mL beaker followed by dropwise addition of MTMOS in water (MTMOS 0.14 mL and water 0.54 mL). Then, CNPrTEOS solution (CNPrTEOS 0.24 mL and water 0.54 mL) was added dropwise till completion. The mixture was stirred for half an hour at ambient temperature. The process was repeated with other mol composition 2:1, 3:1 and 1:2 MTMOS:CNPrTEOS. The resulting particles were separated by centrifugation (12 000 rpm for 5 min) and the supernatant was discarded. The collected particles were washed with deionized water (2 × 5 mL) to remove

residual catalysts. The washed powder was air-dried for 15 min and then dried at 80 °C for a day and finally ground using pestle and mortar. Other sol–gel synthesis parameters were kept constant as follows: NH_4OH pH 10.0 and drying temperature of 80 °C.

For optimization of pH value (9.0, 9.5, 10.0, 10.5 and 11.0), other sol–gel synthesis parameters were kept constant as follows: 2:1 mol ratio MTMOS:CNPrTEOS and drying temperature of 80 °C. In sol–gel process, base-catalyzed reactions lead to highly cross-linked sol particles which are suitable for synthesizing SPE sorbent materials. Thus, only basic pH values were varied in this study. For optimization of drying temperature (70, 80, 90, 100, 110 and 120 °C), other sol–gel synthesis parameters were kept constant as follows: 2:1 mol ratio MTMOS:CNPrTEOS and NH_4OH pH 10.5. Drying temperature is an important parameter to be studied to ensure that the particles are completely dried. In this study, the drying temperatures were carried out using an oven after the washed powder was air-dried for 15 min.

The raw MTMOS, CNPrTEOS and sol–gel hybrid MTMOS-CNPrTEOS with different mol ratios were characterized using Fourier transform infrared spectroscopy (FT-IR) from Massachusetts, USA, and recorded in the range between 4000 cm^{-1} and 400 cm^{-1} using sodium chloride (NaCl) plate for sample in liquid form and potassium bromide (KBr) plate for sample in solid form. The liquid sample was put carefully on a semitransparent NaCl plate, and the plate was scanned to obtain the spectrum. Small amount of solid samples and potassium bromide (KBr) (ratio 1:100) was mixed using a ground mortar and pestle. The mixture was placed in a mini-press at 100,000 psi, and the screws were tightened to squeeze the KBr and sol–gel mixture into a semitransparent thin disk. The mini-press containing the disk was then placed into the FT-IR instrument.

The morphology of the prepared sol–gel hybrid MTMOS-CNPrTEOS was determined using field emission scanning electron microscope (FE SEM, Hitachi S-4800, Hitachi High-Tech., Tokyo, Japan). The sample was fixed on a carbon tape and coated with platinum to ensure the stability of sample toward electron bombardment without charging effect. The sample was bombarded using an electron gun with a tungsten filament to obtain required magnification image. The surface area, pore size and pore volume of the synthesized sol–gel hybrid were determined using nitrogen adsorption model ASAP 2010 Micromeritics surface analyzer.

The sol–gel hybrid sample (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

1×5 mL methanol, followed by 1×10 mL deionized water. 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 1×5 mL acetonitrile and dried under a gentle stream of nitrogen gas to complete dryness. Finally, the residue was reconstituted in 100 µL of acetonitrile prior to GC–MS analysis. Analyses of blank samples were also performed for comparison purposes.

In this study, the linearity range, limit of detection (LOD) and limit of quantification (LOQ) were calculated to evaluate the sensitivity of the instrument and also the SPE method.

3 Results and discussion

3.1 Preparation and sol–gel parameter optimization

MTMOS-CNPrTEOS-based sol–gel hybrid was prepared by using four main materials including MTMOS as a sol–gel precursor, CNPrTEOS as a sol–gel derivative, NH_4OH as a base catalyst and water as a solvent. The applicability of the synthesized material as sorbent for SPE was assessed by selecting OPPs, namely chlorpyrifos, diazinon and malathion, as the target analytes.

The solid-phase extraction (SPE) was performed using the four mol ratios, 1:1, 1:2, 2:1 and 3:1, of sol–gel MTMOS:CNPrTEOS to compare the extraction efficiency of each composition to find the optimum composition and then used in method validation. MTMOS:CNPrTEOS ratio of 2:1 gave the highest peak area of OPPs extracted (Fig. 1). The total extraction time taken was 4.37, 8.07, 3.01 and 4.39 min for 1:1, 1:2, 2:1 and 3:1 mol ratio MTMOS:CNPrTEOS, respectively. The extraction efficiency of the sorbent is affected by the porous structure of the material. The more porous the material (high surface area) is, the higher the extraction efficiency is [27]. The mol ratio 2:1 MTMOS-CNPrTEOS gave the shortest extraction time (3.01 min), indicating the most porous of the material synthesized. Other sol–gel synthesis parameters were kept constant as follows: NH_4OH pH 10.0 and drying temperature of 80 °C.

Another sol–gel synthesis parameter that was optimized is the pH value. In this work, five basic pH values (pH 9.0, 9.5, 10.0, 10.5 and 11.0) were chosen. Other sol–gel synthesis parameters were kept constant as follows: 2:1 mol ratio MTMOS:CNPrTEOS and drying temperature of 80 °C. At pH 9.0, 9.5 and 11.0, the extraction using the MTMOS-CNPrTEOS produced took a long time to complete (198, 57 and 20 min, respectively). At pH 10 and 10.5, the extraction time is comparable which are 2.52 and
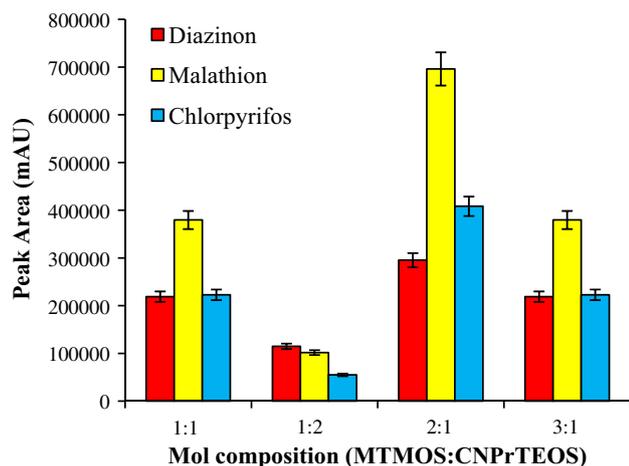
Fig. 1 Effect of different mol composition of the synthesized sol–gel hybrid MTMOS-CNPrTEOS on the extraction efficiencies of the three selected OPPs. Sol–gel parameters: NH$_4$OH pH 10.0 and 80 °C drying temperature
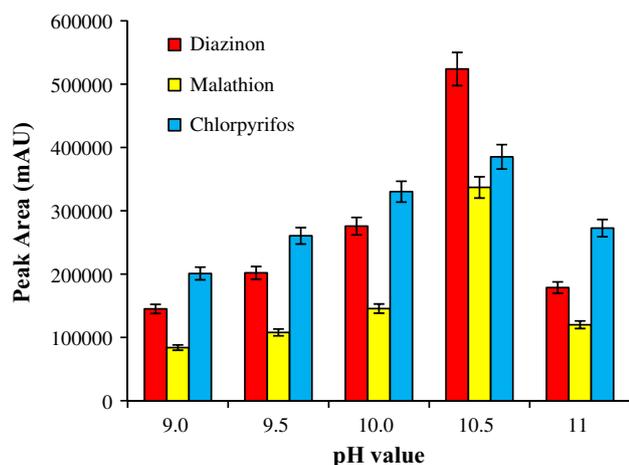

Fig. 2 Extraction performances of the sol–gel hybrid of composition 2:1 mol ratio MTMOS-CNPrTEOS synthesized using four different basic pH values toward the three selected OPPs. Sol–gel parameters: drying temperature 80 °C

Fig. 3 Variation of extraction efficiency with drying temperature for three selected OPPs using sol–gel hybrid of mol composition 2:1 mol ratio MTMOS-CNPrTEOS as SPE sorbent. Sol–gel parameters: NH$_4$OH pH 10.5

However, only one day was needed to completely dry the particles when drying temperatures of 100, 110 and 120 °C were used. The drying temperature 100 °C was chosen for further analysis as the peak area of OPPs extracted started to become constant starting from 100 to 120 °C. From the results obtained, the optimum sol–gel synthesis parameters can be summarized as follows: 2:1 mol composition of MTMOS:CNPrTEOS, NH$_4$OH of pH 10.5 and drying temperature of 100 °C.

3.2 Characterization of sol–gel hybrid MTMOS-CNPrTEOS sorbents

The first characterization of sol–gel hybrid MTMOS-CNPrTEOS is found by using FT-IR. The spectrum of raw MTMOS, CNPrTEOS, sol–gel hybrid MTMOS-CNPrTEOS with composition of 1:1, 1:2, 2:1 and 3:1 MTMOS:CNPrTEOS was shown in Fig. 4. All of the spectrum shows a broad peak around 3400 cm^{-1} which indicates the peak of O–H bonds stretching and is attributed to non-condensed silanol and residual water. In all the sol–gel hybrid MTMOS-CNPrTEOS FT-IR spectra, there are existences of functional group from MTMOS and also CNPrTEOS which are C–H (around 2800–2900 cm^{-1}), Si–O–Si (around 1100–1300 cm^{-1}) and C ≡ N (around 2200–2300 cm^{-1}). This indicates that the hybridization process between MTMOS and CNPrTEOS was successful.

The morphology of four different mol compositions of sol–gel hybrid MTMOS-CNPrTEOS was analyzed using SEM and is shown in Fig. 5 (a, b, c, d). The SEM images show synthesized sol–gel hybrid MTMOS-CNPrTEOS were spherical particles with average diameter around 1.30–2.65 μm for 1:1 MTMOS:CNPrTEOS (A), 1.55–2.85 μm for 1:2 MTMOS-CNPrTEOS (B), 160–254 nm for 2:1 MTMOS:CNPrTEOS

2.49 min, respectively. Figure 2 shows the extraction efficiency of 2:1 MTMOS:CNPrTEOS synthesized using different basic pH values. The basic pH value of 10.5 was chosen for further analysis as it showed the highest extraction efficiency as well as shorter extraction time.

Four drying temperatures were chosen (70, 80, 90, 100, 110 and 120 °C) as one of the sol–gel synthesis parameters. Other sol–gel synthesis parameters were kept constant as follows: 2:1 mol ratio MTMOS:CNPrTEOS and NH$_4$OH pH 10.5. Lower drying temperature needs more time for the sorbent materials to dry. In addition, it gives lower extraction efficiency of the selected OPPs (Fig. 3). This may be due to incomplete dried particles. Three days were needed to dry the particles with low drying temperature.
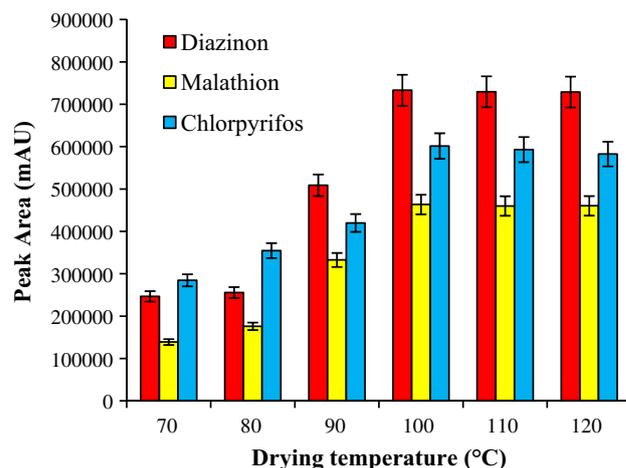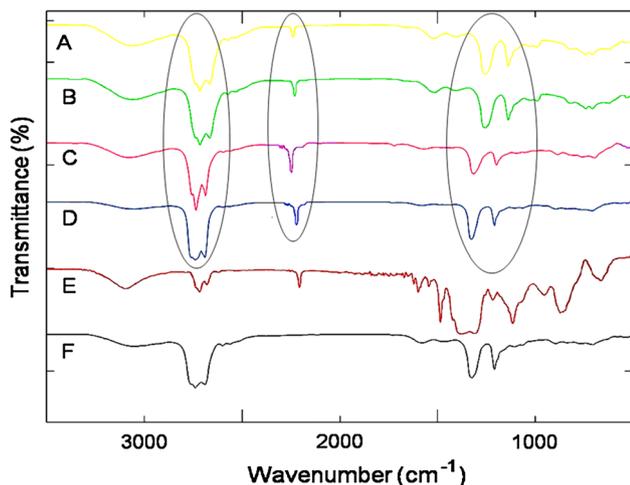
Fig. 4 Fourier transform infrared spectra of sol–gel hybrid with molar ratio of *a* 3:1 MTMOS:CNPrTEOS, *b* 2:1 MTMOS:CNPr-TEOS, *c* 1:2 MTMOS:CNPrTEOS, *d* 1:1 MTMOS:CNPrTEOS, *e* raw CNPrTEOS and *f* raw MTMOS

(C) and 130–270 nm for 3:1 MTMOS:CNPrTEOS. The sol–gel sorbent with mol ratio of 2:1 MTMOS:CNPrTEOS shows uniform and perfect sphere-type particles with no agglomeration.

The physical characteristic of optimum sol–gel hybrid MTMOS-CNPrTEOS was measured using nitrogen gas adsorption where it can determined the Brunauer, Emmet and Teller (BET) surface area, pore volume and pore size distribution. The BET surface area of prepared sol–gel hybrid MTMOS-CNPrTEOS with mol ratio of 2:1 is 585 m^2g^{-1}, the average pore diameter is 104 nm and total pore volume is 3.15 cm^3g^{-1}.

3.3 Peak identification of OPPs

Direct injection of a mixture of three OPPs used in the study showed that they were well separated within 10 min. Generally, compound with low molecular weight (MW) will be eluted first followed by compound with high MW when using gas chromatography with mass spectrometry. The OPPs were eluted according to its MW. Based on the chromatogram (Fig. 6), (1) diazinon having the smallest MW was eluted first followed by (2) malathion and lastly (3) chlorpyrifos, which has the highest MW among the OPPs used in this study.

3.4 Method validation

The extraction of three selected OPPs using sol–gel hybrid MTMOS-CNPrTEOS sorbent was carried out to validate the developed method. The validation parameters studied were linearity, limit of detection (LOD) and limit of quantification (LOQ). The coefficient of determination for
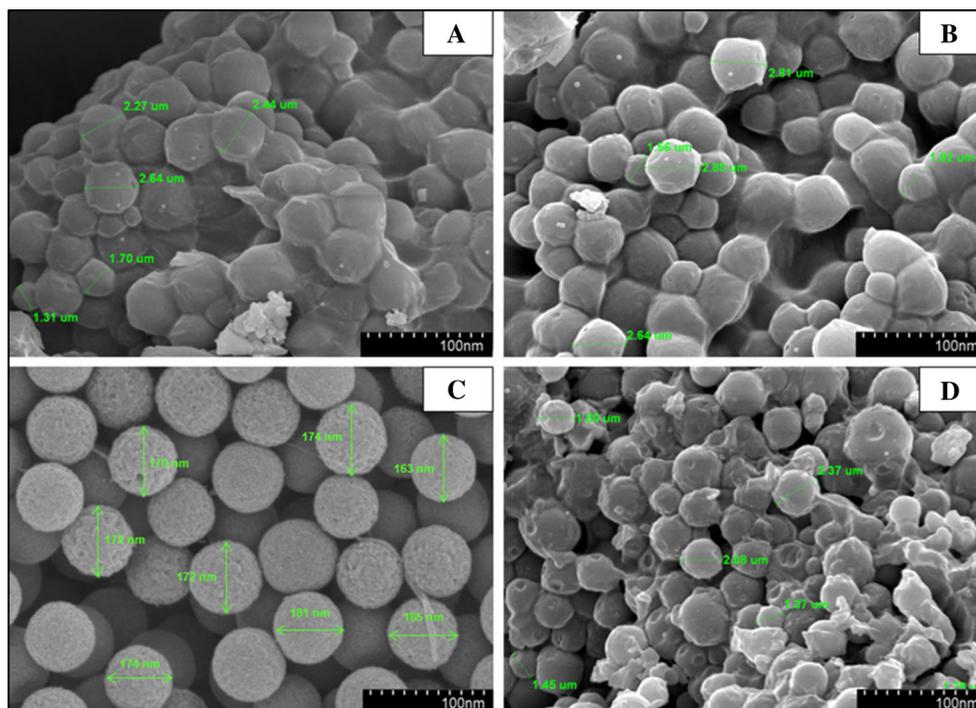

Fig. 5 SEM micrographs of sol–gel hybrid MTMOS-CNPrTEOS with mol composition of (**a**) 1:1 MTMOS:CNPrTEOS at ×5 k magnification, (**b**) 1:2 MTMOS:CNPrTEOS at ×5 k magnification, (**c**) 2:1 MTMOS:CNPrTEOS at ×30 k magnification and (**d**) 3:1 MTMOS:CNPrTEOS at ×30 k magnification
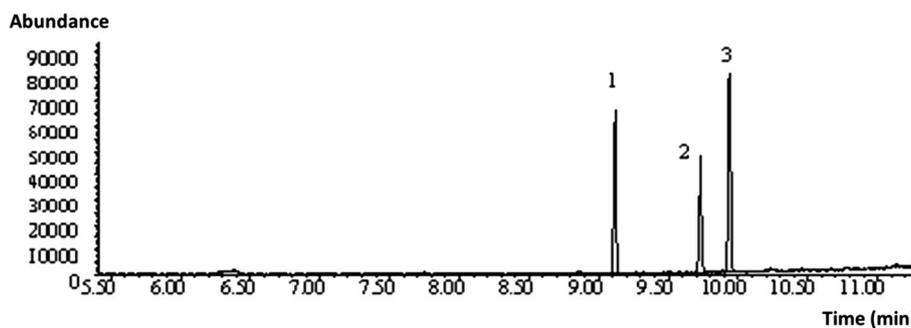
Fig. 6 GC Chromatogram of OPPs mixture from direct injection: **1** diazinon, **2** malathion and **3** chlorpyrifos with concentration of 100 μg mL^{-1}. GC conditions: HP-5 column (25 m × 0.20 mm i.d., and ×0.33 μm film thickness). Carrier gas: Helium gas at a flow rate of 1.0 mL min^{-1}. Detector: Mass spectrometry (MS). Injection port temperature: 260 °C, detector temperature: 230 °C

sol–gel hybrid MTMOS-CNPrTEOS SPE obtained was $R^2 > 0.9960$. The linearity range was tested in the range of 0.1–1.0 ng mL^{-1} for all the three OPPs. The LOD obtained was in the range of 10–70 pg mL^{-1} with acceptable RSD ($n = 3 < 9$ %). The LOD of the MTMOS-CNPrTEOS SPE was very low probably because the MTMOS-CNPrTEOS sorbent using sol–gel technique produced high surface area and porous surface, which increased the extraction efficiency.

4 Conclusion

Hybrid MTMOS–CNPrTEOS has been successfully prepared using sol–gel technique and applied as sorbent for SPE coupled with GC–MS for the determination of three selected OPPs from complex sample matrices. LOD at part per trillion level OPPs was achieved using this sol–gel hybrid material. The introduction of the CNPrTEOS to MTMOS helped to increase surface area of the porous structure sorbent in order to obtain high recoveries of targeted analytes. With the good recoveries obtained in real sample analysis and rapid and simple pre-treatment step, the newly developed SPE method has high potential for advanced applications.

References

1. Shi L, Liu X, Li H, Niu W, Xu G (2006) Anal Chem 78:1345
2. Blasco C, Vazquez-Roig P, Onghena M, Masia A, Picó Y (2011) J Chromatogr A 1218:4892
3. Azimi G, Zolgharnein J, Sangi MR, Ebrahimi S (2009) Anal Sci 25:711
4. Ferreira V, Jarauta I, Ortega L, Chacho J (2004) J Chromatogr A 1025:147
5. Lu Q, Chen X, Nie L, Luo J, Jiang H, Chen L, Hu Q, Du S, Zhang Z (2010) Talanta 81:950
6. Jiang X, Zhao C, Jiang N, Zhang H, Liu M (2000) Food Chem 108:1061
7. Ensafi AA, Ghaderi AR (2007) J Hazard Mater 148:319
8. Zhang Z, Zhang H, Hu Y, Yao S (2010) Anal Chim Acta 661:173
9. Jin G, Zhang B, Tang Y, Zuo X, Wang S, Tang J (2011) Talanta 84:644
10. Yin Y-M, Chen Y-P, Wang X-F, Liu Y, Liu H-L, Xie M-X (2012) J Chromatogr A 1220:7
11. Silva RGC, Vigna CRM, Bottoli CBG, Collins CH, Augusto F (2010) J Sep Sci 33:1319
12. Zhu R, Zhao W, Zhai M, Wei F, Cai Z, Sheng N, Hu Q (2010) Anal Chim Acta 658:209
13. Zheng M-M, Ruan G-D, Feng Y-Q (2009) J Chromatogr A 1216:7739
14. Geller AM, Stedile FC, Peralba MCR, Pizzolato TM, Santos JHZ (2006) J Colloid Interface Sci 299:163
15. Ibrahim WAW, Ismail WNW, Sanagi MM (2013) J Teknol 62:83
16. Kabir A, Hamlet C, Malik A (2004) J Chromatogr A 1047:1
17. Ibrahim WAW, Veloo KV, Sanagi MM (2012) J Chromatogr A 1229:55
18. Ca DV, Cox JA (2004) Microchim Acta 147:31
19. Farrington K, Regan F (2009) Talanta 78:653
20. Lordel S, Chapuis-Hugon F, Eudes V, Pichon V (2010) J Chromatogr A 1217:6674
21. de Moraes SVM, Passos JB, Schossler P, Caramão EB, Moro CC, Costa TMH, Benvenutti EV (2003) Talanta 39:1039
22. Kim M, Stripeikis J, Tudino M (2009) Spectrochem Acta Part B 64:500
23. Seneviratne J, Cox JA (2000) Talanta 52:801
24. Ibrahim WAW, Ismail WNW, Keyon ASA, Sanagi MM (2011) J Sol-gel Sci Technol 58:602
25. Ibrahim WAW, Farhani H, Sanagi MM, Aboul-Enein HY (2010) J Chromatogr A 1217:4890
26. Sinkó K (2010) Mater 3:704
27. Sarafraz-Yazdi A, Vatani H (2013) J Chromatogr A 1300:104