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Malathion determination in Rice samples with Graphene oxide reinforced hollow fiber-solid phase microextraction by GC-MASS

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Abstract

A method for applicability of the solid phase microextraction (SPME) procedure for determination of trace amounts of the organophosphorus pesticide malathion by gas chromatography - mass spectrometry (GC-MS) was developed. Graphene oxide reinforced sol–gel which was placed in hollow fiber (HF-SPME) was used for pre-concentration of malathion. In the present study the Plackett-Burman (PB) factorial design was used as a method for first monitoring of Eight factors that have a significant impact and optimized them in next stage, optimization process of significant factor was carried out using a five-level CCD after screening by PBD. the following conditions were selected for the analytical method of Malathion in real sample: amount of GO (0.01gr), pH of aqueous solution (pH: 3), volume of aqueous solution (10000 µl), volume of organic solvent (250 µl), adsorption time (35 min), desorption time (30 min), stirring rate of solution (1000 rpm) and amount of salt (4%). Calibration curves were plotted using three spiking levels of malathion in the concentration ranges of 0.2–0.4-0.5 ng/mL with correlation coefficients (r^2) 0.9914 for analytes. Under the optimized extraction conditions, the method showed good linearity (0.05–0.5 ng/mL), repeatability, low limits of detections (3.9×10^{-3} ng/mL) and excellent pre-concentration factors (4000). The optimum conditions which were evaluated then applied for the analysis of malathion in the rice as a real sample.

Keywords: *Solid phase microextraction , graphene oxide, Hollow fiber, malathion , Sol–gel , experimental design.*

1. Introduction

For more than half a century, widely used organophosphorus pesticides for agricultural purposes. More than 300 different types of pesticides can be found in stores, of which almost 45% are most commonly used [1]. These pollutants have become ecosystems issue, especially in developing countries [2, 3]. One of the major concern for consumers is the presence of pesticide residues in foodstuff due to their possible long harmful health impact, particularly for children as they are the main consumers of fruits and vegetables and they are more sensitive to chemicals due to their low weight and early stage of development. Governmental an international organization has established the maximum residue limits (MRLs) of pesticides in foodstuff with the aim of protecting the health of consumers. Determining these (MRLs) are difficult to analyze because of interfering compounds in food matrix. It is therefore desirable to enhance the sensitivity and limit the number of sample handling steps involved in analytical methods of OPs. Considering that the effects of organophosphorus pesticides are similar to each other, studying one of this compound also recognizes the behavior of other compounds. In this study, malathion was selected as the target compound. Malathion (S-1,2-bis(ethoxicarbonyl)ethyl 0,0-dimethylphosphorodithioate) (Fig.1) is an insecticide of the nonsystematic organophosphorus group and its contact, digestive and oral effects which are capable of inhibiting cholinesterase enzyme in the nervous system of insects [4].

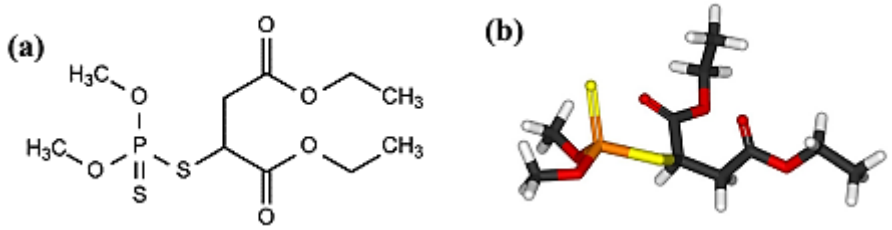

Fig. 1. (a) Skeletal formula and (b) 3D representation of the organophosphorus pesticide malathion ($C_{10}H_{19}O_6PS_2$).

Long-term and frequent contact with the pesticide can cause an acute problem. The first respiratory effect is in form of a coughing or dyspnea that occur after 12 hours it shows symptoms such as dizziness, nausea, abdominal cramping and visual impairment, pain and sweating, which, if untreated, cause death or heart failure. [5] there is evidence that malathion has an effect on damage to DNA at concentration of 24 mM [6] . In view of the above-cited considerations, a simple, rapidly and more selective analytical method for analysis of trace amount of malathion in nature should be developed. There are methods have been designed to measure and evaluate the residual of malathion , for instance kinetic spectrophotometric method [7] biosensor [8] gas chromatography (GC) [9] high-performance liquid chromatography (HPLC) [10] gas chromatography– mass spectrometry (GC-MS) [11] flow injection-tandem mass spectrometry (FI-MS/MS) [12] and high-performance liquid chromatography–mass spectrometry (HPLC-MS) [13] . preconcentration procedures for assessment of malathion can be carried out by means of liquid–liquid extraction (LLE) [9] SPE [14] and matrix solid-phase dispersion extract [15] Application of the conventional extraction methods were limited due to the disadvantages such as time-consumption, labor-intensive and large volumes of organic solvents are required. So far, most studies conducted on developed and applied Solid phase micro extraction (SPME) method that was introduced by Pawliszyn as a simple, solvent-free and sensitive and selective technique [16]. Malik and co-workers [17] introduced sol-gel coated fibers for SPME that eliminate some of the disadvantages of commercial SPME fiber, such as the lack of proper chemical bonding of the extraction-phase coating that causes low thermal and chemical stability. The porous structure of the sol-gel coating provides a large surface area; that increasing the extraction efficiency and the type of coating composition can be changed selectivity characteristics.

Recently, Es'haghi and coworkers [18] used a new solid phase microextraction, based on sol-gel techniques with the aim of hollow fiber . in this work the sol solution placed inside a treated hollow fiber and after appropriate time gel structure formed within the fiber this one-use fiber was applied in direct immersion sample solution during analysis. Polypropylene molecules in wall pores act as channels between analytes molecules and adsorbent sol-gel that cause more selectivity to analyte molecules. In the present study, a sol containing GO were used to obtain a sol-gel nanocomposite immobilized in HF. GO have a large number of oxygen group on its nanosheet surface[19] .Generally, oxygen groups in structure of GO include a lone electron pair and can efficiently bind and moreover this oxygenated lattice provides good dispersibility of GO in many solvents on of the outstanding feature of GO is its two dimensional plane structure as well as the single atom thickness of it providing an ultra-high specific surface area beside a high sorption capacity [20, 21]. These remarkable properties cause GO an excellent material for the solid phase microextraction of OPs.

2. Experimental Section

2.1 Chemicals and materials

The graphite powder (<150 mesh) were purchased from Merck (Darmstadt, Germany). Tetraethyl orthosilicate (TEOS), trifluoroacetic acid (TFA, 99%), poly (ethylene glycol) (PEG, MW 6000), and sodium chloride were purchased from Merck (Darmstadt, Germany). The Accurel Q 3/2 polypropylene hollow fiber membrane was provided from Membrana (Wuppertal, Germany). The fiber used has some specification as: wall thickness was 200 m, the inner diameter was 600 m, and the pore size was 0.2 m. Methanol, Acetonitrile with analytical quality (for organic trace analysis) were also provided by Merck (Darmstadt, Germany). Malathion standards (98%) purity were purchased from from Riedel-de Haen (Seelze-Hannover, Germany). Stock solutions of malathion (1000 g/mL) were prepared by dissolving certain amounts of concentrated malathion in methanol and stored in the dark at 4 ˚C. working solutions were prepared daily by diluting the stock solution in distilled water. All experiments were performed at room temperature, 22 ± 0.5 ˚C. Extra pure water was used from a Milli-Q® Direct Water Purification System (Merck). Iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate, Ferric Ammonium Sulfate dodecahydrate, Ferrous Ammonium Sulfate, potassium permanganate ($KMnO_4$), sulfuric acid, H_2O_2, NH_3 and graphite powder (<150 mesh) were all purchased from Merck (Darmstadt, Germany).

2.2 Instruments

GC–MS analysis carried out by an Agilent 7890A (GC)-Agilent 5975C inert MSD with triple axis detector. The temperatures were set at 300, 150 and 230 ˚C respectively for the interface, the quadrupole and the EI ionization source component. The system was perfumed by Agilent MSD ChemStation E.02.00.493 software. An a HP5 capillary column (30 m × 0.25 mm i.d, 0.25 m film thickness) from Agilent Technologies (Palo Alto, CA, USA) was applied for separation of the analytes .). Helium (99.999%) at a constant flow rate 2.0 mL min^{-1} was employed as carrier gas. Splitless mode was used for injection. After 1 min the split was opened on at a flow of 50 mL/min and the injector temperature was kept at 300˚C. The injection volume was 1µL.

Table 1. summarizes the condition of the GC oven temperature.

Ramp(˚C min^{-1})	Temp (˚C)	Hold time (min)	Total run time
	90 ˚C	0.5min	
10 ˚C min^{-1}	250 ˚C	0.5 min	17 min

A Heidolph MR3001 (Schwabach, Germany) heating magnetic stirrer was applied for stirring of the solution with a 8 mm × 1.5 mm magnetic stirring bar. an ultrasonic bath at a frequency of 42 kHz (Branson 1510, Branson Ultrasonic Co., Danbury, CT), was used to disperse and mix various solution. A pH-meter metrohm model 827 pH (Metrohm, Switzerland) and Vortex mixer (IKA.VORTEX 3) was used for mixing of solutions.

2.3. Fabrication of the HF-SPME fiber

2.3.1 Preparation of graphene oxide

GO was synthesis according to modified Hummer's method from graphite powder [22]. For this purpose,1g of graphite powder with 150 mesh in a 250 mL conical flask, 23 mL of H_2SO_4 (95 %) was added slowly and mixture in flask was stirred and then 0.50 g of Sodium nitrate in the meantime the mixture temperature was adjusted in 0°C in an ice bath and stirred. Afterward 3g $KMnO_4$ was added as oxidant and stirred for 1 h at 35°C. Then 45 mL H_2O was added slowly and mixture stirred for 35 min at 90°C. Next 10mL H_2O_2 10% was added and mixture color was changes to yellow and then 140 mL H_2O was added. In order to remove any of impurity the resultant precipitates (Go nano-sheetes) washed with HCl and EtOH and were dried in at 60°C.

2.3.2. Preparation of the sol solution

Firstly, the polypropylene hollow fiber was cut into certain segments with a length of 2 cm. in order to eliminate the contamination in the pores and the surface of HF, all segments were stirred in an acetone solution and then all pieces were dried in the desiccator. The sol solution was prepared as follows: 10 mg GO and 100 mg PEG were added to 100 µL of tetraethylorthosilicate (TEOS) in an Eppendorf tube and dissolved thoroughly by ultrasonic agitation for 5 min. Then 70 µL of TFA containing 5% water was added to the solution and the mixture was sonicated for another next 5 min. At this stage, the sol solution was injected into the fiber by a 2 ml Hamilton syringe until all fiber pores were saturated with the sol solution.

2.3.3. Aging of the sol and in situ gelation process

In next step the prepared fiber was located in a desiccator at room temperature for 24 h. finally, for Conditioning, the fiber was conditioned in an oven at 60 -150°C temperature for 6 h in the GC oven with gradually rising temperature program.

2.4. SPME procedures

Extractions were performed according to the following steps: Optimized volume of aqueous solution containing the malathion pesticide was added into the sample vial with a 8 mm × 4 mm magnetic stirring bar. The SPME hollow fiber was placed in the aqueous sample solution. The vial was sealed and the stirrer turned on. At the end of the extraction for an optimized of time at room temperature the hollow fiber was taken out from the first vial and transferred into a Eppendorf tube containing the optimal organic solvent and the analytes were desorbed from fiber after optimize time. Finally, 1.00 µL of the organic solvent was withdrawn into the GC microsyringe and then injected into the GC-MS for further analysis. Due to the low cost, and to avoided the Memory effect, each HF piece was Disposable in the experiments.

2-5 Sample analysis

Rice samples were ground and mixed to uniform consistency. Fifty grams of uncontaminated rice samples were spiked by each malathion at three level 0.2, 0.4, 0.5 ng/mL. These samples have been transferred to a blender jar. Then, 200

mL acetone/water (50:50 v/v) was added to these samples and blended on high speed for about 5 min. Then, acetone was removed using a N_2 rotary vacuum evaporator. 15 ml of this diluted solution was used as real sample aqueous solution.

2-6 Experimental optimization for the GO

The FT-IR spectra were recorded for graphene oxide and TEM, SEM images of graphene oxide are presented in Fig. 2. As demonstrated, the number of absorption bands, corresponding to the presence of functional groups, showed. the characteristic absorption bands at 1250 and 1100 cm $^{-1}$ corresponding to C–O stretching of epoxy and alkoxy, respectively, at 1730 cm $^{-1}$ corresponding to C-O stretching of carboxyl group and at 1630 cm $^{-1}$ corresponding to aromatic C=C in the graphitic region. and confirms the successful synthesis of graphene oxide nanoparticle.

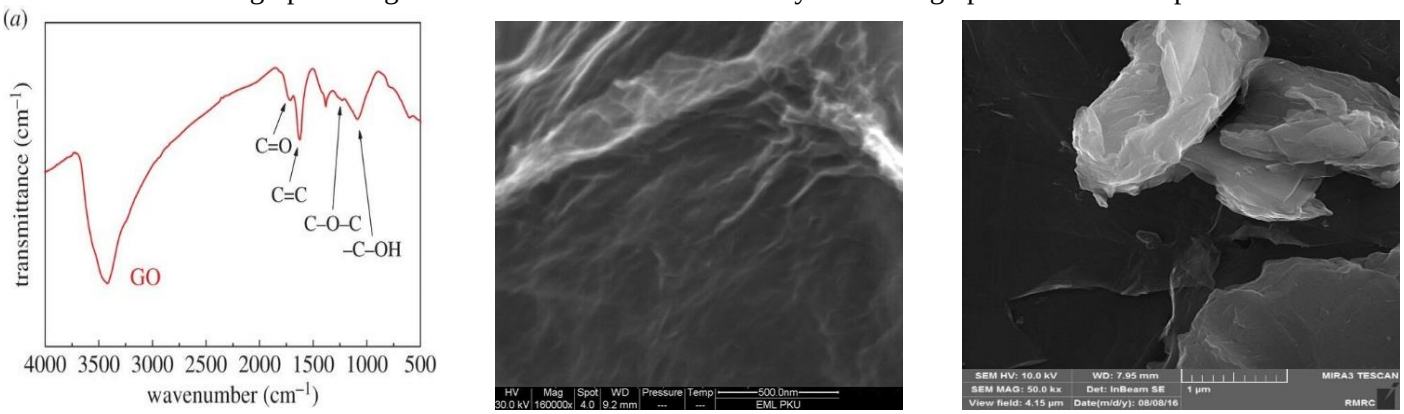

Fig. 2. (a) FTIR spectrum (b) SEM image of GO (c) TEM image of GO

3. Results and discussion

3.1. Optimization of experimental parameters

3-1-1-2 Selection of extraction solvent

One of the most important parameters affecting extraction efficiency in microextraction procedures is the type of organic solvent. This investigated factor is a kind of non–numerical factors. since the Plackett-Burman factorial design couldn't check more than two level, therefore this factor was studied in one at the time way. For this purpose, three solvents including methanol, acetonitrile and ethanol were tested. Result obtained in the microextraction process was shown in Fig. 3. According to this diagram it is revealed that methanol has the highest detector response for target analysis (malathion).

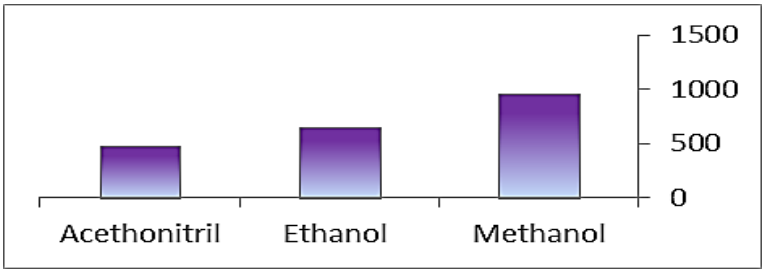

Fig. 3. Evaluation of extraction organic solvent.

3-1-1 evaluation of significant parameters using Plackett-Burman design

A large number of quantitative and qualitative factors potentially affect the micro-extraction process and the evaluation of the analyte. Therefore, the Plackett-Burman (PB) factorial design was used as a method for first monitoring and

determining the factors that have a significant impact and optimized them. we study a large number of variables with a small number of experiments.

Table 2. Factors and their signs and levels used in PBD

Variable	Symbol	Low(-)	High(+)
amount of GO(gr)	a s	0.01	0.02
pH of aqueous solution	pH	3	9
volume of aqueous solution (ml)	v aq	3000	10000
volume of organic solvent (ml)	v org	300	700
adsorption time (min)	t ad	5	30
desorption time (min)	t de	5	30
stirring rate of solution (rpm)	s r	500	1000
salting effect(%)	salt	0%	5%

Table 3. The results of PB experimental design matrix.

pH	**v aq**	**v org**	**t ad**	**t de**	**a s**	**s r**	**salt**	**Response (peak area)**
9	3000	300	5	5	0.02	500	5	966
9	10000	700	5	5	0.02	1000	0	122
3	10000	300	30	30	0.02	1000	0	1856
3	10000	300	30	5	0.02	1000	5	1822.75
9	10000	300	30	30	0.01	500	0	1587.5
3	10000	700	5	30	0.02	500	0	527.66
3	3000	300	30	5	0.02	500	5	1307.25
3	10000	700	30	30	0.01	500	5	751.33
3	3000	300	5	30	0.01	1000	0	541.33
3	10000	700	5	5	0.01	500	5	663.75
3	3000	300	5	5	0.01	500	0	786.5
9	3000	700	30	30	0.02	500	0	435.66
3	3000	700	5	30	0.01	1000	5	1049
9	3000	700	5	30	0.02	1000	5	447.5
9	3000	700	30	5	0.01	500	0	468.5
9	10000	700	30	5	0.01	1000	5	1073.5
9	10000	300	5	5	0.01	1000	0	478
3	3000	700	30	5	0.02	1000	0	628
9	3000	300	30	30	0.01	1000	5	2918.5
9	10000	300	5	30	0.02	500	5	674.25

Eight factors that affected on efficiency of HF SPME procedure such as amount of graphene oxide used in the composition of sol gel, pH of aqueous solution, stirring rate of solution, adsorption time, desorption time, volume of

organic solvent and aqueous solution, salting effect were scanned. Each factor was examined at two levels as defined in Table 2. This PB design were performed in 20 experiments that the conditions for each run were listed in Table 3. Each experiment was performed twice and the response (peak area) for each run were reported. The statistical evaluation of significant parameters by the PBD at 90% confidence level ($p \leq 0.1$) are shown in Pareto chart in Fig. 4. As can be seen from this figure, positive signs such as Vaq , tad, tde, stirring rate of solution and salt effect indicate factors that can improve response by changing from low to high values and negative variables such as pH, Vorg , and amount of graphen oxide in sol gel matrix in their low levels lead to an improvement in response. Vorg, t ad and salt are statistically significant variables and were selected for more optimization in next statistical procedure. Other factors were used at the optimal levels reported by PBD. This Optimum Curve for suggested factors was shown in Fig. 5.

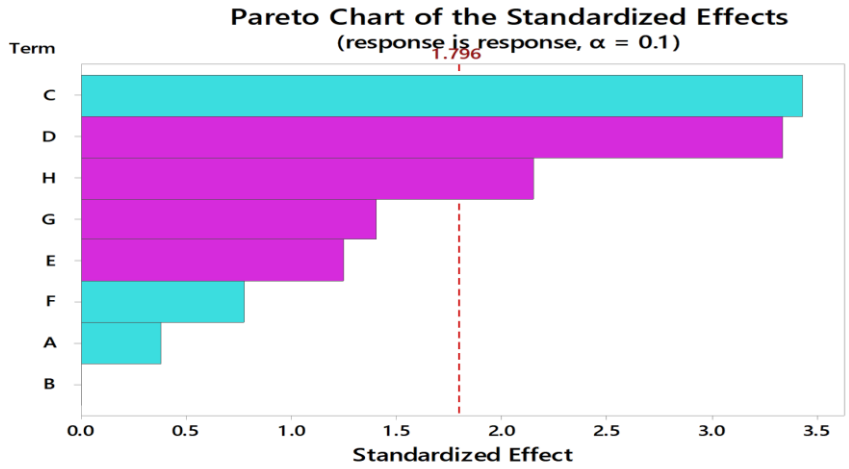

Fig. 4. Pareto chart of the standardized effects in 90% confidence Level.

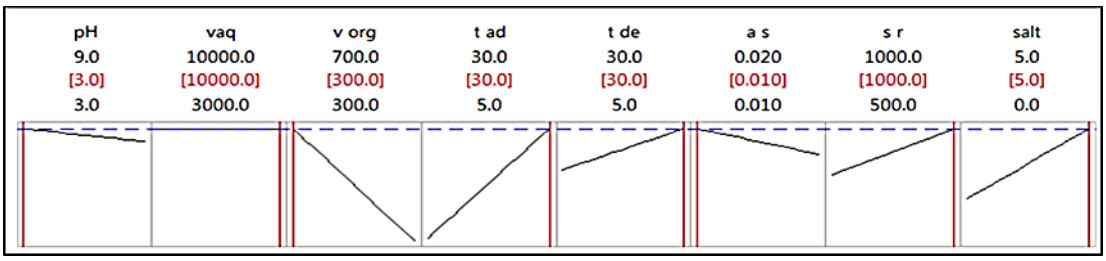

Fig. 5. Optimum Curve for sugesed factors by PBD.

3.1-2. Optimization using central composite design

In this study all significant factors were further optimized using a central composite design (CCD). In the current study, optimization process of malathion determination by HF-SPME was carried out using a five-level CCD after screening by PBD. total number of experiments (N) at CCD equals to $N = 2^k + 2k + C_0$. This design includes a full factorial design (2^3 hypercube points, 2×3 axial points, and 6 replicates of center points). totally 20 runs were randomized designed and CCD design and the corresponding response (peak area) of each run are presented in Table 4. The results of CCD were fitted with a polynomial equation for each response by regression analysis on experimental data. The quadratic model equation expressed an experiential relationship between response and input factors in uncoded values:

Table 4. Matrix table for central composite design

Run	V org	t ad	salt%	Response
1	250	35	4	4388
2	250	25	4	1773
3	350	25	6	2176
4	350	35	4	1750
5	300	30	5	1421
6	300	20	5	1395
7	400	30	5	1956
8	300	40	5	4133
9	250	35	6	4269
10	300	30	7	2087
11	300	30	5	2089
12	350	25	4	804
13	300	30	3	1524
14	300	30	5	1910
15	350	35	6	2253
16	300	30	5	1996
17	250	25	6	2558
18	300	30	5	1700
19	200	30	5	3635
20	300	30	5	1938

Final Equation in Terms of Coded Factors:

$R1=+1877.70 -585.19 * A +676.56* B +229.19 * C -412.87 * A * B +151.13 * A * C - 221.62 * B * C +255.98* A^2 +248.10 * B^2 +8.48 * C^2$ (1)

Final Equation in Terms of Actual Factors:

$R1=+1563.81250 -38.70580 * V\ org +256.94205* t\ ad +567.41477* salt -1.65150* V\ org * t\ ad +3.02250* V\ org * salt -44.32500* t\ ad * salt +0.10239 * V\ org^2 +9.92409* t\ ad^2 +8.47727* salt^2$ (2)

For this model, R^2 and R^2_{adj} were acquired 0.9472 and 0.8997, respectively. The Model F-value of 19.93 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A (V org), B (t ad), C(salt), and AB, A^2, B^2 are significant model terms. The "Lack of Fit F-value" of 2.46 implies the Lack of Fit is not significant relative to the pure error. There is a 17.24% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good thus The lack-of-fit test shows the selected model is adequate to describe the observed data. Furthermore, result of ANOVA (Table 5) indicated Lack of fit (p value = *0.1724*) was desirable and was not meaning full. Fig. 6 shows the response surface developed by the model considering t adsorption and V org. The response is maximum at 35 minutes when the volume of organic desorption solvent is 250µL.

Table 5. ANOVA table

Source	Sum of Squares	df	Mean of Square	F Value	p-value Prob > F	
Model	1.84E+07	9	2.04E+06	19.93	< 0.0001	significant
A-V org	5.48E+06	1	5.48E+06	53.44	< 0.0001	
B-t ad	7.32E+06	1	7.32E+06	71.43	< 0.0001	
C-salt	8.40E+05	1	8.40E+05	8.2	0.0169	
AB	1.36E+06	1	1.36E+06	13.3	0.0045	
AC	1.83E+05	1	1.83E+05	1.78	0.2115	
BC	3.93E+05	1	3.93E+05	3.83	0.0787	
A^2	1.65E+06	1	1.65E+06	16.07	0.0025	
B^2	1.55E+06	1	1.55E+06	15.09	0.003	
C^2	1806.87	1	1806.87	0.018	0.897	
Residual	1.03E+06	10	1.03E+05			
Lack of Fit	7.29E+05	5	1.46E+05	2.46	0.1724	not significant
Pure Error	2.96E+05	5	59193.87			
Cor Total	1.94E+07	19				

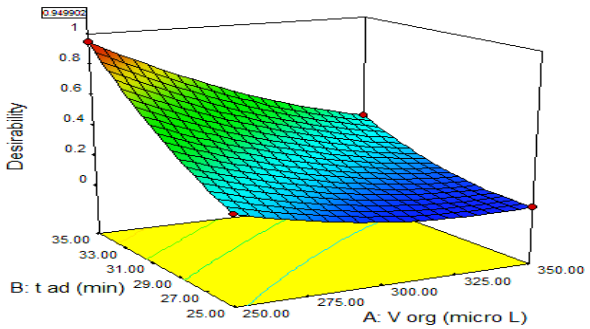

Fig. 6. Three-dimension (3D) surface response graph for two interaction of tad and Vorg desorption.

3.2 Investigating the effect of important factors

Solid phase microextraction is an equilibrium method and has a direct relationship between the amount of extracted analyte with extraction time. In this method the mass transfer between the donor and acceptor phase depends on time. The results indicated that the extraction efficiency was increased with increasing extraction time from 5 to 35 min. When the extraction time was 35 min, the extraction recovery for analyte reached to the maximum .by increasing at extraction time over the 35 minutes,there was insignificant change the recovery for analyte .Maybe, the analyte returned from sorbent to aqueous solution at higher than equilibrium time In this work, the positive effects of salt lead to an increase in extraction efficiency. In this way, by increasing salt ions to the environment, the salt ions interact with the water molecules, and subsequently, the aqueous solvation analyte ions are released to a degree and easily enter the solid phase. in other words, salt reduces the solubility of the analyte in the aqueous phase. The optimum concentration 4 (w/v) of salt cause the maximum extraction recoveries. In this study for optimizing of elution solvent volume, in the range of 200-400 µL were studied to elute malathion molecules from the sorbent composites. Finally, the results of optimization

showed the optimal amount of 250 µL eluent was adequate .in high volumes can be expressed that dilution of malathion solution occurred.

3.3 Analytical figures of merit

Based on the new approach to analysis the Malathion as method described above, the following conditions were selected for the analytical method of Malathion in real sample: amount of GO(0.01gr), pH of aqueous solution (pH: 3), volume of aqueous solution (10000 µl), volume of organic solvent (250 µl), adsorption time (35 min), desorption time (30 min), stirring rate of solution (1000 rpm), amount of salt (4%). Calibration curved under optimized condition were plotted. The equation of calibration curve obtained ($y = 2\times10^{10}x + 98312$). Desirable linearity regression in the concentration range of 0.05 to 0.50 ng/mL was obtained (R^2= 0.9914). Limit of detection (LOD), relative standard deviation (RSD), correlation coefficient (R^2) and pre-concentration factor (PF) for pre-concentration and determination of Malathion were investigated and reached values shown in Table 6.

Table 6. Figures of merit in the determination of Malathion by proposed SPME method.

Analyte	LOD [a] ng/mL	LOQ [b] ng/mL	R^2 [c]	PF [d]	RSD% [e]	LDR [f] ng/mL
Malathion	3.90×10^{-3}	1.30×10^{-2}	0.9914	4000	4.69	0.05-0.50

[a] Limit of detection (S/N = 3), (ng/mL)

[b] Limit of Quantification µg/L (S/N = 10), (ng/mL)

[c] Coefficient of determination

[d] Pre-concentration factor

[e] Relative standard deviation (n = 5).

[f] Linear dynamic range(ng/mL)

The pre-concentration factors (PF) were calculated based on the following equation:

$$PF = \frac{A\,RP,final}{A\,PS,initial} \times \frac{Vaq}{VIn} \qquad (3)$$

where $A_{RP,final}$ and $A_{SP,initial}$ are the final and initial peak areas at after and before micro-extraction of the malathion in the organic solvent respectively, that obtained based on direct injection of the OP compound solutions in methanol into the GC-MASS for analysis. Vaq and Vin are volume aqueous sample and internal volume of hollow fiber.

The method was compared with the other previous works (Table 7) In comparison with the other conventional sample preparation methods, the developed method has the merits of considerable analysis speed, good separation efficiency and elevated preconcentration, notable precision and high sensitivity.

3-4 Real sample

3-4-1 Rice samples

The reliability and versatility of the HF-SPME methodology coupled to the GC-MS system was evaluated by determining Malathion in rice samples. The analytical results and the typical chromatograms are shown in Table 8 and Fig. 7, respectively. To evaluate the accuracy of the method, the recoveries of the OPP were investigated by spiking the standard solution of the OPP into the rice samples at the concentrations of 0.2 and 0.4 0.5 ng/mL. For each concentration level, three replicate experiments were performed. The relative recoveries of the method were expressed as the mean

ratios between the amounts found and the ones spiked. As shown in Table 8, satisfactory recoveries ranging from 88 to 108% were obtained by the sol-gel graphene oxide hollow fiber for studied analyst.

Table 7. Comparison of analytical parameters of the current method and other techniques for analysis of malathion in various samples.

Analitical method	Matrix	Linear dynamic range ($ng.mL^{-1}$)	LOD ($ng.mL^{-1}$)	RSD	Recovery (%)	Reference
DLLME-GC–MS	Apple juice	-	1.24	>8 (6)	78–104	[23]
DLLME-GC-FPD	Water	0.80–50	0.21	10.3 (5)	86–102	[24]
HF-LPME-GC-FPD	Water	4.00–300	1.16	3.4 (5)	94–104	[24]
SPME-GC–MS	Water	0.1–2.0	-	4 (5)	62–87	[25]
Amperometric	Vegetables	0.033–23.1	0.033	<5	99–105	[26]
HS-SMPE-GC-ECD	Cucumber and strawberry	0.1–5000	0.01	<4 (3)	83–86	[27]
Spectrophotometry	Water and vegetables	500–11,000	130	<2 (5)	-	[28]
DLLME-CD-IMS	Apple and water	4–200	1.8	<7.2 (5)	81–96	[29]
HF-SPME-GC-MS	rice	0. 05-0. 5	0.0039	4.69	88- 97	current method

[a]The replicates, *n*, are indicated in the parentheses

Table 8. Results of real sample analysis for determination of malathion by proposed method.

Samples	Added, ng/mL	Found, ng/mL	Recovery, %
Rice sample	0	0.37×10^{-4}	-
	0.2	0.194± 4.69	96.86
	0.4	0.375± 4.29	93.60
	0.5	0.441± 4.76	88.20

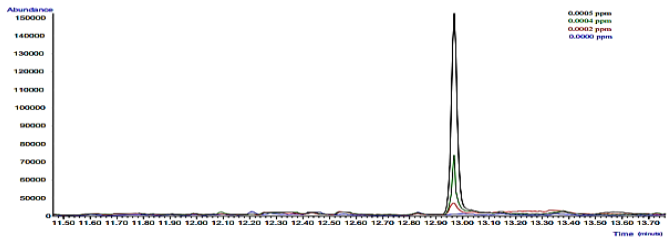

Fig. 7. Chromatograms of extracted solutions of a real samples contaminated with malathion (spiked amount 0.2-0.4-0.5 ng/mL) in rice sample .

Conclusion

The present sol-gel PEGg graphene –oxide SPME-GCMS procedure was employed for the determination of malathion as an organophosphate pesticide at ultra-trace levels in rice samples. Due to the outstanding properties of GO and furthermore the performance of the sol-gel coating technology, this fiber supplies a high porosity surface and also good precision and accuracy, high selectivity and sensitivity. This sol-gel coating increases the surface area on the fiber, the speed of extraction and desorption steps and sample capacity by its porous structure. Based on these features, in this article, a rapid and facile method for routine ultra-trace analysis of OP pesticide in real samples was introduced. Therefore, it could be expected to have a potential use in the other complex matrix samples. On the other hand, there

are still some areas of research left to modify GO with other functional groups to increase coating fiber selectivity for highly complex samples. The obtained LOQ are almost always below the maximum residue limits (MRLs) fixed by the European legislation (Council Directives 90/642/EEC, 1990).

Reference

1. D. Echobichan, and R. Joy, CRC Pesticides and Neurological Diseases. CRC Press, Boca Raton, FL, 1994: p. 381.
2. M. Driss, M.-C. Hennion, M. Bouguerraca, Determination of carbaryl and some organophosphorus pesticides in drinking water using on-line liquid chromatographic preconcentration techniques. Journal of Chromatography A, 1993. 639(2): p. 352-358.
3. W.E. Johnson, N.J. Fendinger, and J.R. Plimmer, Solid-phase extraction of pesticides from water: possible interferences from dissolved organic material. Analytical chemistry, 1991. 63(15): p. 1510-1513.
4. T.C. Kwong, Organophosphate pesticides: biochemistry and clinical toxicology. Therapeutic drug monitoring, 2002. 24(1): p. 144-149.
5. M.H. Dehghani, et al., Optimizing the removal of organophosphorus pesticide malathion from water using multi-walled carbon nanotubes. Chemical Engineering Journal, 2017. 310: p. 22-32.
6. P.D. Moore, C.G. Yedjou, and P.B. Tchounwou, Malathion-induced oxidative stress, cytotoxicity, and genotoxicity in human liver carcinoma (HepG2) cells. Environmental toxicology, 2010. 25(3): p. 221-226.
7. G.P. Pandey, et al., A novel and sensitive kinetic method for the determination of malathion using chromogenic reagent. Microchemical Journal, 2014. 113: p. 83-89.
8. Raghu, P., et al., Acetylcholinesterase based biosensor for monitoring of malathion and acephate in food samples: a voltammetric study. Food chemistry, 2014. 142: p. 188-196.
9. H.M. Lofty, A.E.-A.A.A. El, and H.H. Monir, Determination of insecticides malathion and lambda-cyhalothrin residues in zucchini by gas chromatography. Bulletin of Faculty of Pharmacy, Cairo University, 2013. 51(2): p. 255-260.
10. N.G. Tsiropoulos, et al., Evaluation of solid sorbents for the determination of fenhexamid, metalaxyl-M, pyrimethanil, malathion and myclobutanil residues in air samples: application to monitoring malathion and fenhexamid dissipation in greenhouse air using C-18 or Supelpak-2 for sampling. Analytica chimica acta, 2006. 573: p. 209-215.
11. M.A.Z. Chowdhury, et al., Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography–mass spectrometry. Food Control, 2013. 34(2): p. 457-465.
12. H. Nakazawa, et al., Rapid and simultaneous analysis of dichlorvos, malathion, carbaryl, and 2, 4-dichlorophenoxy acetic acid in citrus fruit by flow-injection ion spray ionization tandem mass spectrometry. Talanta, 2004. 64(4): p. 899-905.
13. E. Sobhanzadeh, et al., Low temperature followed by matrix solid-phase dispersion-sonication procedure for the determination of multiclass pesticides in palm oil using LC-TOF-MS. Journal of hazardous materials, 2011. 186(2): p. 1308-1313.
14. C. Sánchez-Brunete, et al., Determination of pesticide residues by GC-MS using analyte protectants to counteract the matrix effect. Analytical sciences, 2005. 21(11): p. 1291-1296.
15. A.J. Nieto-García, R. Romero-González, and A.G. Frenich, Multi-pesticide residue analysis in nutraceuticals from grape seed extracts by gas chromatography coupled to triple quadrupole mass spectrometry. Food control, 2015. 47: p. 369-380.
16. C.L. Arthur, and J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers. Analytical chemistry, 1990. 62(19): p. 2145-2148.

17. S.L. Chong, et al., Sol− gel coating technology for the preparation of solid-phase microextraction fibers of enhanced thermal stability. Analytical chemistry, 1997. 69(19): p. 3889-3898.
18. Z. Es'haghi, et al., Synthesis and application of a novel solid-phase microextraction adsorbent: hollow fiber supported carbon nanotube reinforced sol–gel for determination of phenobarbital. Analytica chimica acta, 2011. 689(1): p. 122-128.
19. H. He, et al., A new structural model for graphite oxide. Chemical physics letters, 1998. 287(1): p. 53-56.
20. R. Sitko, B. Zawisza, and E. Malicka, Graphene as a new sorbent in analytical chemistry. TrAC Trends in Analytical Chemistry, 2013. 51: p. 33-43.
21. D. Chen, H. Feng, and J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications. Chemical reviews, 2012. 112(11): p. 6027-6053.
22. Marcano, D.C., et al., Improved synthesis of graphene oxide. 2010.
23. S. Cunha, J. Fernandes, and M. Oliveira, Fast analysis of multiple pesticide residues in apple juice using dispersive liquid–liquid microextraction and multidimensional gas chromatography–mass spectrometry. Journal of Chromatography A, 2009. 1216(51): p. 8835-8844.
24. J. Xiong, and B. Hu, Comparison of hollow fiber liquid phase microextraction and dispersive liquid–liquid microextraction for the determination of organosulfur pesticides in environmental and beverage samples by gas chromatography with flame photometric detection. Journal of Chromatography A, 2008. 1193(1): p. 7-18.
25. J. Ma, et al., Determination of organophosphorus pesticides in underground water by SPE-GC-MS. Journal of chromatographic science, 2009. 47(2): p. 110-115.
26. N. Chauhan, and C.S. Pundir, An amperometric acetylcholinesterase sensor based on Fe 3 O 4 nanoparticle/multi-walled carbon nanotube-modified ITO-coated glass plate for the detection of pesticides. Electrochimica Acta, 2012. 67: p. 79-86.
27. C.M. Kin, and T.G. Huat, Headspace solid-phase microextraction for the evaluation of pesticide residue contents in cucumber and strawberry after washing treatment. Food Chemistry, 2010. 123(3): p. 760-764.
28. N. Venugopal, and B. Sumalatha, Spectrophotometric determination of malathion in environmental samples. Journal of Chemistry, 2012. 9(2): p. 857-862.
29. M.T. Jafari, and F. Riahi, Feasibility of corona discharge ion mobility spectrometry for direct analysis of samples extracted by dispersive liquid–liquid microextraction. Journal of Chromatography A, 2014. 1343: p. 63-68.