



Solid phase microextraction for organochlorine pesticides in water samples using MWCNTs-doped polypyrrole coated on steel fiber before determination by gas chromatography electron capture detector

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ABSTRACT

The analysis of organochlorine pesticides (OCPs) residues has received an increasing attention in the last decades. The solid-phase microextraction (SPME) is a convenient and fast analytical method, which has been widely used for the determination of volatile and semivolatile organic compounds in aqueous samples. In this study, the multiwalled carbon nanotubes/polypyrrole composite (MWCNTs-PPy) coated on steel fiber was used for extraction OCPs from water samples by the SPME technique. The effects of various parameters on the efficiency of SPME process such as extraction time, extraction temperature, ionic strength, desorption time, and desorption temperature were studied. Under optimized conditions, the detection limits for the OCPs varied between 0.051 and 0.39 $\mu\text{g mL}^{-1}$, the inter-day and intra-day relative standard deviations for various OCPs using a single fiber were 6.5-11.5% and 3.6-11.5, respectively. The linear ranges varied between 0.001 and 1 ng mL^{-1} . The proposed method was successfully applied to the analysis of ground water samples with the recoveries from 86 to 110%

1. Introduction

Determination of OCPs has received great attention in recent decades. These compounds have been widely used worldwide in order to increase crops output and enhance quality of products. But most of these compounds have been eliminated or restricted in use after evidence of their toxicity and persistence in the environment [1-4]. For determination of trace pesticides/OCPs in complex matrices which contain a high number of interfering compounds, usually

require both efficient sample preparation techniques and high performance analytical instruments. Sample preparation before chromatographic analysis is one of the most important steps in analytical processes. The main conventional methods of sample preparation are liquid-liquid extraction (LLE) [5] and solid-phase extraction (SPE) [6]. Although these methods offer efficient and precise results but they have drawbacks. For example, LLE requires the use of a large amount of expensive and toxic solvents that can damage the environment. This method is also time-consuming, tedious, and very often requires solvent evaporation prior to introduction

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of the sample into the analytical instrument. Solid-phase extraction also has certain drawbacks, such as plugging of cartridges, solvent consumption for conditioning and elution steps and lack of elution selectivity. Alternative methods, such as dispersive liquid-liquid microextraction (DLLME) [7], single-drop microextraction (SDME) [8], membrane-protected micro-solid-phase extraction (μ -SPE) [9], dispersive solid-phase microextraction (DSPME) [10], stir bar sorptive extraction (SBSE) [11] have been developed to improve extraction efficiencies and reduce solvent consumption, etc. However, solid-phase microextraction (SPME) developed by Pawliszyn and coworkers [12] is a practical solvent-free alternative for the extraction of organic compounds. This method is easily automated, it simplifies the extraction process and meaningfully decreases the analysis time. In this method, analytes are generally extracted and concentrated by a thin layer of a sorbent coated on a silica fiber. The fiber is then introduced into a chromatographic system for separation and measurement. SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. Various sorbents have been used as SPME coating materials. Currently, the improvement in the applications of SPME is focused on the development of novel coatings to enhance the extraction efficiency. Some coatings include polyaniline [13], polythiophene [14], polypyrrole [15, 16], metalorganic frameworks (MOFs) [17], layered double hydroxide (LDH) [18], metal and metal oxide [19, 20], molecularly imprinted polymer (MIP) [21], carbon nanotubes [22, 23]. A multiwalled carbon nanotube-polypyrrole (MWCNTs/PPy) composite coated SPME fiber was first introduced in our laboratories for the extraction of phthalate esters from water [24]. In the present work, we present an application of MWCNTs/PPy composite polymer in direct immersion SPME/GC-ECD for the analysis of twelve OCPs residues in water.

2. Experimental

2.1. Chemicals

The twelve organochlorine pesticides namely

lindane, heptachlor, aldrin, p,p'-DDE, dieldrin, endrin, endosulfan I, endosulfan II, p,p'-DDD, o,p'-DDD, p,p'-DDT and methoxychlor were of standard grade and obtained from PolyScience (IL, USA, <http://www.polysciences.com>). Pyrrole ($\geq 97\%$ pure) was obtained from Merck (Darmstadt, Germany, <http://www.merck.com>) and was distilled and stored in a dark bottle under nitrogen atmosphere in a refrigerator. Multiwalled carbon nanotubes (MWCNTs) purchased from PlasmaChem GmbH (Berlin, Germany, <http://www.plasmachem.com>) was 20-40 nm in diameter and 1-10 μ m in length. Stainless Steel wire (type 100-014, 350 μ m O.D.) was obtained from Ortho Organizers (Carlsbad, USA, <http://www.orthoorganizers.com>) and used as the SPME fiber. A 200 μ g mL⁻¹ stock solution of the mixture of OCPs was prepared in acetone. Working solutions were prepared by appropriate dilution of the stock solution in distilled water. Highly pure helium and nitrogen gases ($\geq 99.999\%$) were obtained from Sabalan Co. (Tehran, Iran). They were used as GC carrier gas and make-up gas, respectively. Other reagents used were of highest purity available. Double distilled water was used in all experiments.

2.2. Apparatus

The SPME device was home made. It consisted of a 23 gauge, 9.0-cm stainless steel spinal needle Dr. Japan Co., (Tokyo, Japan, <http://www.drjapan-jp.com>), housed in a 6.0-cm hollow cylinder of Al with two nuts and two pieces of rubber septum. A 17-cm piece of the stainless steel wire passing through the septum acted as the SPME fiber. One end of the fiber was attached to a cap and 3 cm of the other end was coated with MWCNTs/PPy coating. Electrochemical polymerization of pyrrole was carried out with a Behpajuh potentiostat/galvanostat, model BHP 2061-C (Esfahan, Iran, <http://www.behpajoooh.com>). The Pt counter electrode and the Ag/AgCl reference electrode used in the electrochemical process were from Azar Electrode (Urmieh, Iran). For stirring and heating the samples during the SPME procedure, a Corning model PC-351 hot plate-stirrer (MA, USA) was used.

The chromatographic analysis of OCPs was performed by a Shimadzu model 16A gas chromatograph (Kyoto, Japan, <http://www.Shimadzu.com>), equipped with a split-splitless injector, electron capture detector (ECD) and a BP-10 (25 m $\times$ 0.33 mm. I.D. and 0.5- μ m film thickness) capillary column. The flow rates of helium carrier gas and nitrogen make-up gas were adjusted at 1 mL min⁻¹ and 30 mL min⁻¹, respectively. The column temperature was initially kept at 50 °C for 1 min, then increased at 25 °C min⁻¹ to 170 °C, ramped at 4 °C min⁻¹ to 250 °C, and was kept for 3 min. Injector and detector temperatures were adjusted at 250 °C and 300 °C, respectively. A Shimadzu QP 2000 GC-MS instrument (Kyoto, Japan, <http://www.Shimadzu.com>) equipped with quadrupole analyzer and electron impact ion-source (EI) was used for the identification of pesticides in real samples. A Bandelin Sonorex ultrasonic bath (Berlin, Germany, <http://www.bandelin.com>) was used for sonication.

2.3. Preparation of composite coating

Briefly MWCNTs were refluxed in concentrated nitric acid. The resultant MWCNTs-COOH was collected on a filter paper and washed with distilled water until neutralized and was dried at room temperature. The composite coating of MWCNTs and polypyrrole was synthesized electrochemically via in-situ polymerization from a solution containing both the acid oxidized-MWCNTs and the pyrrole monomer. The deposition was carried out at room temperature. Stainless steel wire, platinum electrode and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. The coating procedure was as follows. The oxidized-MWCNTs were ultrasonically dispersed in water for 1 h at 28 °C and then pyrrole was added and sonicated for 15 min. The composite polymer coating was directly deposited on the steel wire from this solution by applying a constant potential. To make the coating adhere firmly to the surface of the wire, the wire surface was first roughened by a smooth sand paper and then washed in acetone while sonicating. Thermal conditioning of the coated fiber was carried out by heating at 100 °C for 30 min in an oven, and

then at 250 °C for 2 h in the GC injector port under a helium atmosphere. This removes the volatile compounds remaining in the fiber and a smooth chromatographic baseline is obtained.

2.4. SPME procedure

A 0.1 ng mL⁻¹ working solution of the mixture of OCPs in distilled water was prepared from the stock solution on a daily basis. SPME extractions were performed by placing 10.0 mL samples into a 12.0 mL sample vial capped with a septum. Magnetic stirring with a 1-cm long Teflon-coated stirring bar was used to agitate the samples at the highest but constant possible rate. Extractions were carried out by exposing a 3.0 cm length of the composite coated fiber to the sample solution. The extraction temperature was adjusted by placing the extraction vial in a water bath placed on the magnetic stirrer. After the extraction, the fiber was withdrawn into the needle, removed from the sample vial and immediately introduced into the GC injector port for thermal desorption.

3. Results and discussion

3.1. SPME optimization

In this study, the effect of various parameters on the efficiency of SPME process, such as desorption time and temperature, salting out effect, pH, extraction time and extraction temperature were studied on a one-at-a-time strategy. Stirring the sample during the extraction is also an important parameter. This is to generate a continuously fresh layer of the sample solution near the surface of the fiber coating in order to improve the extraction efficiency. In addition, efficient agitation reduces the depth of the boundary layer and thus improves the speed of extraction. Therefore, all the experiments were performed under maximum but constant stirring rate.

3.1.1. Desorption time and desorption temperature

Study of desorption processes can provide useful information on the absorbent and the absorption processes. Desorption of extracted analytes was carried out in the GC injection port at temperatures between 160 and 280 °C. **Figure 1** shows that at the desorption temperature of 250 °C, nearly all

of OCPs were fully desorbed from the fiber and no carryover effect was observed. Therefore in subsequent experiments a desorption temperature of 250 °C was used.

The time necessary for desorbing analytes from the SPME fiber in the injection part of GC was also

studied. For this purpose, desorption times between 1 and 20 min were used. After a desorption time of 5.0 min at 250 °C, analytes were almost fully desorbed from the fiber, but to avoid memory effect or carry over an extra 5.0 min was considered in the desorption step. Therefore all desorptions were

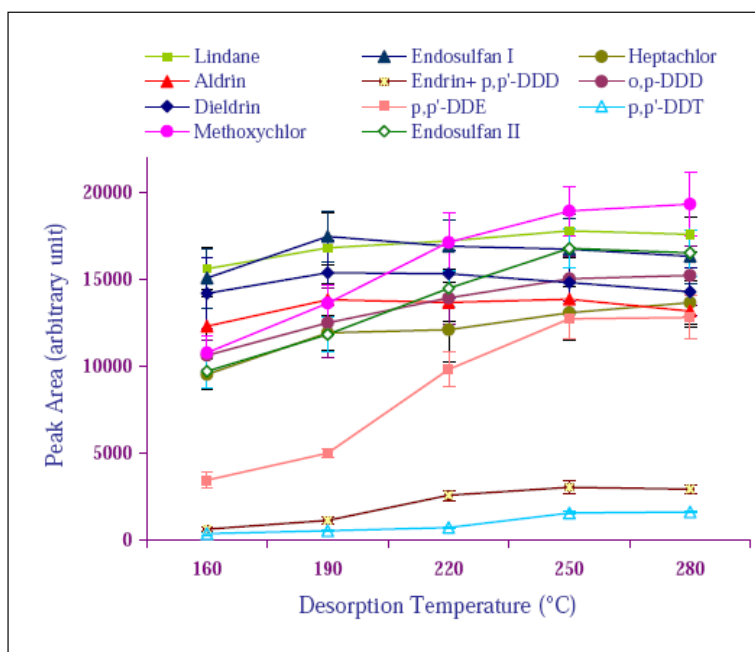


Fig. 1. Effect of desorption temperature on extraction efficiency. Extraction conditions: [OCPs] = 0.1 ng mL⁻¹ each; extraction time = 40 min; extraction temperature = 25 °C, no sample pH and salt was adjusted or added.

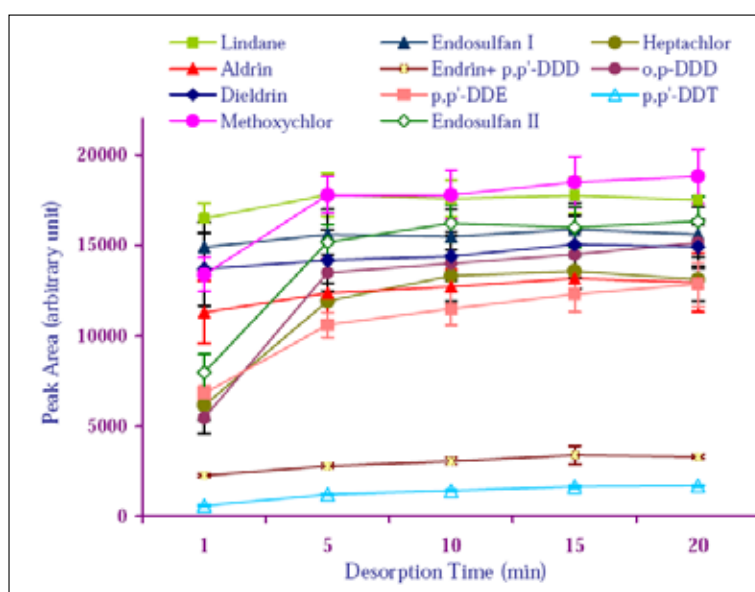


Fig. 2. Effect of desorption time on extraction efficiency. Extraction conditions: [OCPs]=0.1 ng mL⁻¹ each; extraction time=40 min; extraction temperature=25 °C and desorption temperature=250 °C, no sample pH and salt was adjusted or added.

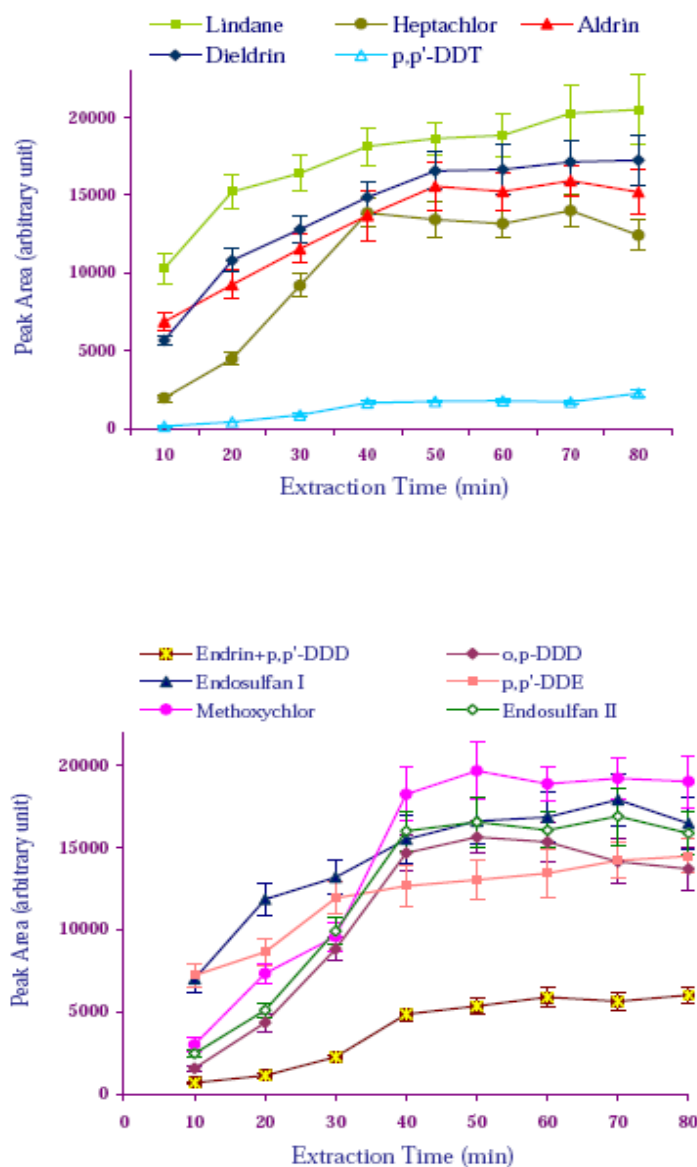


Fig. 3. The effect of extraction time on extraction efficiency. Extraction conditions: [OCPs]=0.1 ng mL⁻¹ each; extraction temperature=25 °C; desorption temperature=250 °C; desorption time=10 min; no sample pH and salt was adjusted or added.

carried out for a period of 10 min (Fig. 2).

3.1.2. Extraction time

The SPME process depends on the equilibrium involving partitioning of the analytes from the sample liquid phase to the sorbent phase on the fiber. Therefore, the resistance to the mass transfer of analytes should be overcome to reach equilibrium between the aqueous phase and the fiber. For this reason, the fiber was exposed to a mixed aqueous solution of the OCPs under study (0.1 ng mL⁻¹ each)

for a period of 10 to 80 min. The results found are shown in Figure 3. As this figure shows, the peak areas sharply increase with increases in the extraction time until 50 min, after which no significant improvement in the extraction efficiency was observed. Therefore, in all subsequent experiments, 50 min was selected as the extraction time.

3.1.3. Extraction temperature

Extraction temperature is a very important

parameter. An increase in the extraction temperature leads to an increase in diffusion coefficient and at the same time a decrease in distribution constant, leading to faster extraction, but reduced extraction efficiency. After optimizing the extraction time, the extraction temperature was varied between 20 and 70 °C. **Figure 4** shows, the extraction efficiencies for most OCPs increase by increasing extraction temperature up to 40 °C, after which it levels off. This may be due to more favorable mass transfer for these analytes. In some cases, at temperatures above 40 °C, the extraction efficiency decreased, because the distribution constant at these temperatures

decreased. This may be due to exothermic nature of the absorption process. Therefore, 40 °C was chosen as the optimum extraction temperature for all subsequent analyses.

3.1.4. Ionic strength

Ionic strength can vary the mechanism of mass transfer of analytes in SPME, depending on the structure, analyte properties and matrix [25]. In addition, the solubility of the non-polar organic solutes in water decreases in the presence of salts. Thus, it is expected that the addition of salts should modify the sorption of analytes by the fiber. For this

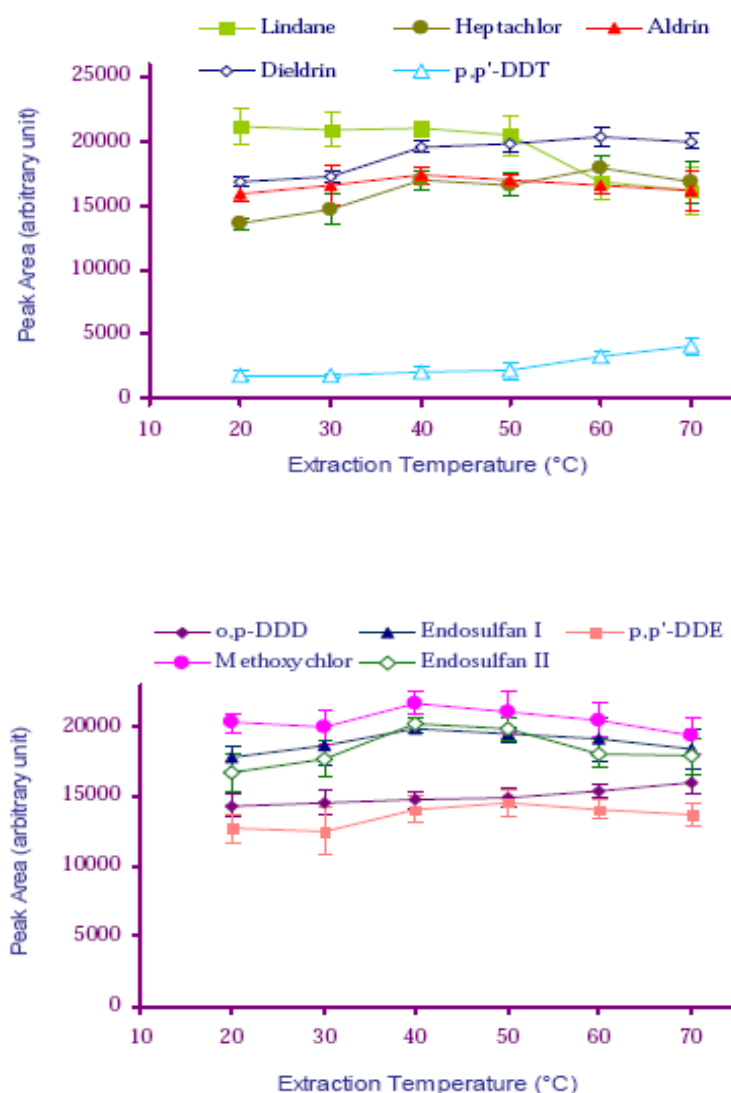


Fig. 4. The effect of extraction temperature on extraction efficiency. Extraction conditions: [OCPs]=0.1 ng mL⁻¹ each; desorption temperature=250 °C; extraction time=50 min; desorption time=10 min; no sample pH and salt was adjusted or added.

reason, the effect of this parameter on extraction efficiency was investigated. Here, extractions were carried out from solutions in the presence of NaCl from 0 to 20% (w/v). **Figure 5** shows that for most analytes no significant improvement in the extraction efficiency is observed up 10% NaCl. However, a decrease in the extraction efficiency is observed at higher NaCl concentrations. This can be explained

by the fact that the present composite coating is a solid porous sorbent, and the extraction occurs on the surface of pores. It seems that large amounts of NaCl in the sample solution occupies the surface of the coating material and have a negative effect on the extraction efficiency. Based on the results obtained, it was decided to carry out all subsequent extractions without adding any salt to sample solutions.

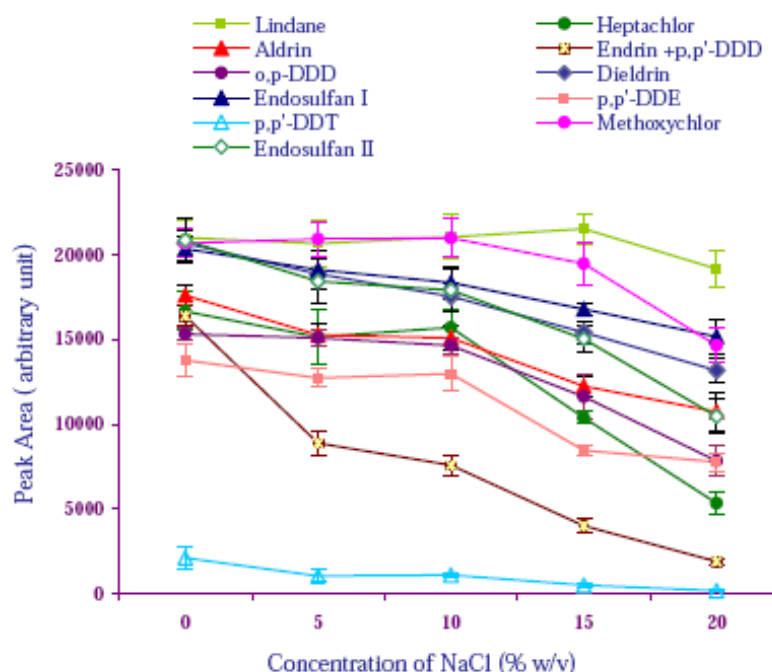


Fig. 5. The effect of NaCl concentration on extraction efficiency.

Extraction conditions: [OCPs]=0.1 ng mL⁻¹ each; desorption time=10 min; desorption temperature=250 °C; extraction time=50 min; extraction temperature=40 °C; no sample pH adjusted.

3.1.5. pH optimization

Further investigations were carried out on pH value of sample solution. The effect of sample pH on the extraction efficiency was experimented in the range from 4 to 9. For the group of OCPs studied, no significant changes were found in the pH values tested. The OCPs are little affected by pH because they are nonionizable compounds in aqueous solution. Therefore, extraction of OCPs was carried out using the original solution.

3.2. Method Validation

Figures of merit including linear range (LR), precision (RSD %) and limit of detection (LOD) were evaluated for the method developed in this work. The linear range was determined by extracting a series of aqueous solutions of the mixture of OCPs in the range between 0.001 and 1.0 ng mL⁻¹ for lindane and heptachlor, 0.01 to 1 ng mL⁻¹ for p,p'-DDT, and 0.005 to 1 ng mL⁻¹ for aldrin, endosulfan I, p,p'-DDE, dieldrin, endrin + p,p'-DDD, endosulfan II, o,p'-DDD and

methoxychlor. As shown in Table 1, the coefficient of determination (r^2) obtained for different OCPs varied from 0.9871 to 0.9979. The repeatability of the method was determined by seven replicate analyses from mixed aqueous solutions containing 0.02 ng mL⁻¹ of each OCP. As Table 1 shows, the intra-day relative standard deviations (RSD%) varied from 3.6 % for lindane to 11.5 % for endosulfan II, while the inter-day RSD% varied from 6.5% for methoxychlor to 11.5% for dieldrin. The limits of detection based on S/N = 3 in this DI-SPME/GC/ECD method varied between 0.051 and 0.39 pg mL⁻¹ (Table 1). To evaluate the accuracy

of the method, a water sample was collected from the university campus and subjected to the present SPME and GC analysis without any pretreatment. No pesticide was detected in this sample using both ECD and MS detection. Therefore, this water sample was used as blank and spiked at 0.01 and 0.075 ng mL⁻¹ of each OCP. The percent recoveries found were reasonable and between 86 and 110% (Table 1). The validation parameters obtained here were compared with results obtained by other methods which show that they are comparable or better than the values reported by other groups (Table 2).

Table 1. Analytical performance of OCPs residues in water: Limit of detection (LOD), percent recovery, linear range (LR), coefficient of determination (r^2) and RSD%.

Compound	LOD (pg mL ⁻¹)	Recovery (%)		LR (ng mL ⁻¹)	Coeff. Det r^2	RSD%	
		0.01 ng mL ⁻¹	0.075 ng mL ⁻¹			Intra-day (N=7)	Inter-day (N=7)
Lindane	0.08	91	103	0.001 - 1	0.9958	3.6	6.8
Heptachlor	0.17	89	94	0.001 - 1	0.9926	8.6	8.1
Aldrin	0.11	89	93	0.005 - 1	0.9879	8.8	10.1
Endosulfan I	0.18	95	93	0.005 - 1	0.9954	5.2	7.1
Endrin+p,p'-DDD	0.16	86	89	0.005 - 1	0.9938	8.6	9.5
p,p'-DDE	0.17	105	101	0.005 - 1	0.9894	7.3	9.8
Dieldrin	0.095	95	88	0.005 - 1	0.9871	6.2	11.5
Endosulfan II	0.065	92	94	0.005 - 1	0.9940	11.5	11.1
o,p'-DDD	0.051	106	101	0.005 - 1	0.9932	9.8	9.4
p,p'-DDT	0.39	110	98	0.05 - 1	0.9976	7.5	9.2
Methoxychlor	0.1	102	98	0.005 - 1	0.9979	6.8	6.5

Table 2. Comparison of limit of detection (LOD) and relative standard deviation (RSD%) of the present SPME-GC analysis based on MWCNTs-pPy coating for OCPs with other works.

Compound	References						
	Present work	[13]	[16]	[26]	[27] ^a	[27] ^b	[4] ^c
Lindane	0.08 ^d	0.3	0.25	3.8	5	0.2	0.34
	3.6 ^e	6	5.6	3.7	5.1	7.1	7.1
Heptachlor	0.17	1.6	0.27	2.7	10	-	0.32
	8.6	3	4.7	4.2	12.4	-	6.7
Endrin	0.16	0.6	0.125	3.7	51	-	3.4
	8.6	6	8.7	3.7	14.6	-	10.2
p,p'-DDD	0.16	-	0.095	-	2	-	-
	8.6	-	6.3	-	7.3	-	-
Aldrin	0.11	0.2	0.66	2.6	14	-	0.39
	8.8	3	9.6	3.9	35.3	-	8.1
p,p'-DDE	0.17	0.1	0.015	5.7	1	-	0.33
	7.3	8	9.1	5.7	15.3	-	9.6
Dieldrin	0.095	0.1	0.015	2.8	9	0.5	0.36
	6.2	12	9.1	3.8	11.5	7.7	8.9
Endosulfan II	0.065	0.1	0.051	3.6	18	1	1.41
	11.5	10	6.5	4.3	11.2	7.8	12.1
o,p'-DDD	0.051	-	0.24	-	-	-	-
	9.8	-	9.7	-	-	-	-
p,p'-DDT	0.39	0.1	0.26	3.7	13	-	0.34
	7.5	5	7.3	3.7	14.7	-	8.2
Endosulfan I	0.18	0.1	0.17	2.9	10	0.8	1.29
	5.2	4	8.3	4.3	10.8	5.8	11.2
Methoxychlor	0.1	-	0.048	-	-	-	0.26
	6.8	-	7.3	-	-	-	11.8

^a: Full scan MS^b: MS/MS^c: Membrane-protected micro-solid-phase extraction^d: The first row of figures for each compound indicates detection limit (ng mL⁻¹)^e: The second row of figures for each compound indicates RSD%

3.3. Real samples

To apply the proposed method in real analysis, four water samples were collected and stored in glass containers and stored at 4 °C. They were then subjected to the present SPME/GC method without any pre-treatment. The results found are shown in **Table 3**. None of the organochlorine

pesticides were detected in the samples collected from the campus of Shahid Bahonar University (SBUC) and Saadi village, but the two samples from Noogh and Zarand area were found to be contaminated. The analysis of real samples based on MWCNTs-PPy for determination OCPs by

Table 3. The OCPs analysis in real samples based on MWCNTs-PPy by SPME-GC procedure

Compound	Location			
	Noogh	Saadi	Zarand	SBUC
	Concentration (pg mL ⁻¹)			
Lindane	N.D	N.D	N.D	N.D
Heptachlor	N.D	N.D	N.D	N.D
Aldrin	N.D	N.D	N.D	N.D
Endrin + p,p'-DDD	N.D	N.D	N.D	N.D
o,p-DDD	8.6	N.D	N.D	N.D
Dieldrin	N.D	N.D	N.D	N.D
Endosulfan I	65	N.D	54	N.D
p,p'-DDE	11	N.D	7.3	N.D
p,p'-DDT	N.D	N.D	N.D	N.D
Methoxychlor	N.D	N.D	N.D	N.D
Endosulfan II	8	N.D	6.1	N.D

N.D: not detected

4. Conclusions

The determination of organochlorine compounds from water samples was successfully performed by SPME-based electrodeposition of MWCNTs/PPy on stainless steel fiber, followed by GC-ECD analysis. The SPME-GC-ECD method is selective, sensitive, precise, reproducible and linear over a wide range. Due to the widespread use of the organochlorine pesticides until 1970's and the high persistence of these pollutants can still be detected some of these in the environment. The proposed method showed good reproducibility, wide linear range, low detection limit and good recovery for the various OCPs studied.

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