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# اندازه‌گیری دیازینون در نمونه‌های محیطی با استفاده از نانولوله‌های اصلاح‌شده کربنی با استفاده از سرسمپلر

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# Determination of Diazinon in Environmental Samples Using Modified Multi-Walled Carbon Nanotubes as Pipette-Tip Solid Phase Extraction Sorbent

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## چکیده

در این تحقیق یک تکنیک میکرواستخراج بر پایه استخراج فاز جامد بوسیله سرسمپلر برای پیش‌تغلیظ و تعیین مقدار دیازینون استفاده شد. نانولوله‌های کربنی توسط سولفید روی و اتیلن گلیکول عامل‌دار شد. دیازینون توسط دستگاه کروماتوگرافی مایع با عملکرد بالا تعیین مقدار شد. پارامترهای مهم مانند pH، مقدار جاذب، زمان استخراج و اثر نمک، حجم حلال و حجم محلول و تعداد دفعات پر و خالی کردن سمپلر که بر بازده استخراج مؤثر بودند، بهینه شد. نتیجه نشان داد که این روش برای گستره ۰,۵ تا ۱۰۰ میکروگرم بر لیتر خطی است. تکرارپذیری روش رضایت‌بخش است و زیر ۳,۷۸٪ می‌باشد و حد تشخیص و فاکتور تغلیظ روش ۰,۰۳ میکروگرم بر لیتر و ۱۰۰ بدست آمد که درستی روش را در تعیین دیازینون تأیید می‌کند.

## واژه‌های کلیدی

نانولوله کربنی؛ دیازینون؛ سر سمپلر پیش تغلیظ استخراج فاز جامد.

## Abstract

In this work, a microextraction technique based on pipette tip solid-phase extraction was used for preconcentration and determination of diazinon. Carbon nanotube functionalized by zinc sulfide and ethylene glycol was used as sorbent. Determination of diazinon was performed using high performance liquid chromatography and UV detection. Important parameters that influence the extraction efficiency (i.e. pH, amount of adsorbent, extraction time, salt addition, volumes of sample and eluting solvent and number of aspirating/dispensing cycles for both solvent and sample) were investigated and optimized. Results were showed that method was validated over the range of 0.50 - 100.0 µg $L^{-1}$. Repeatability was satisfactory, bellow 3.78% for 5 replicate measurements of 20 µg $L^{-1}$ of diazinon. The limit of detection of this method is 0.03 µg $L^{-1}$ with an enrichment factor of 100 and short extraction time of 8.5 min, which confirmed suggested method is a reliable and accurate for extraction and preconcentration of diazinon.

## Keywords

Carbon Nanotubes; Diazinon; Pipette Tip; Preconcentration; Solid Phase Extraction.

## 1. INTRODUCTION

Pesticides are widely used in the agriculture and household in many countries to prevent and destroy many annoyances including animals,

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*Corresponding Author: rezaei@zbmu.ac.ir unwanted plant and microorganism, during the growth process of plants. Organophosphorus pesticides (OPPs) are one class of pesticides, which are extensively used as insecticides to increase the agricultural production [1]. Diazinon (O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) is an organophosphorus compound often used in agriculture as a soil pesticide [2]. Large amounts of these compounds residues remain in agricultural soils after being applied [3], which leach into the groundwater and can also be found in run-off waters. Due to the mentioned toxicological effects, sensitive and reliable analytical methods are needed for the determination of trace amounts of this pesticide. Several methodologies have been reported for determining diazinon residues in aqueous samples preceded by different preconcentration procedures, including, solid phase microextraction (SPME) [4-5], reversed-dispersive solid phase extraction [6], dispersive liquid–liquid microextraction (DLLME) [7-8] and other techniques based on microextraction principles [9].

The pipette tip (PT) is a miniaturized format of SPE and has become essential tool for preconcentration and extraction of biological and environmental samples [10]. The small volume and sorbent mass in this method significantly reduce solvent consumption and analysis time. It differs from common SPE in that a small amount of sorbent is inserted into a pipette tip, and it is relatively inexpensive without special auxiliary device for extraction. In general terms, an advantage of pipet tips for sample preparation is that extraction can be carried out faster and more facile than conventional SPE cartridges [11-13]. The PT-SPE method is an effective means for purification, concentration, and isolation of proteins and peptides in genomics, proteomics, metabolomics, etc. However, most sorbents of PT-SPE suffer from low selectivity, especially for trace levels of analytes in complex samples. Therefore, improving affinity and specific recognition of PT-SPE sorbents is of great significance [14].

In recent years, many researchers have been focused on synthesis and application of carbon nanotubes (CNTs) [15-16]. CNTs nanocomposites are one of major approaches for making use of dispersed carbon nanotubes. In recent decades, different methods and agents have been reported for functionalization of CNTs [17]. They can be well dispersed in water using either anionic, cationic, or nonionic surfactants such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS), cetyltrimethylammonium bromide (CTAB), Triton X and siloxane polyether copolymer (PSPEO)[18] .

In this work we used nano sized ZnS:Mn particles decorated on the CNTs surface for the preparation of a new solid phase sorbent. Because of a high agglomeration tendency of nanosized particles, ethylene glycol (EG) was used to optimize the dispersion of composites. Then pipette–tip solid phase extraction method were used and developed for preconcentration and extraction of diazinon.

## 2. EXPERIMENTAL

### *2.1. Reagents*

All chemicals were of analytical grade. Multiwalled carbon nanotubes (outer diameter of 5–20 nm, inner diameter of 2–6 nm, length of 1–10 µm, purity ≥95 %) were purchased from Plasmachem, Germany. Sodium sulfide hydrate ($Na_2S.XH_2O$, Across Organics, Belgium), Zinc acetate and manganese acetate (Merck KGaA, Germany) were used for the synthesis of ZnS:Mn nanoparticles. Ethylene Glycol (Merck) was used as surface modifiers. A 5000 µl filter tips (Extra GENE, USA) were used as column. Moreover, magnesium nitrate hexahydrate (Merck) was used for increasing the CNTs surface charge. Diazinon was purchased from Sigma-Aldrich (USA). All HPLC solvents were obtained from Scharlau (Spain).

### *2.2. Instrumental analysis*

The chromatographic analysis was carried out on Cecil HPLC system (Cecil, England), equipped with a UV detector. A reverse phase ACE-C18 column (250 mm × 4.6 mm i.d.) was used for separation of the analyte. The mobile phase was a mixture of methanol–water (40:60, v/v) at a flow rate of 1.0 mL $min^{-1}$. The column temperature was kept at 30 $^{o}C$ and the detection wavelength was set at 235 nm. The injection volume was 10 µL.

### *2.3. Synthesize of CNT–ZnS Nano composite*

The following procedure was used for synthesis of ZnS-CNTs nanocomposites: First, a suspension of CNTs were prepared by dispersing 100 mg of CNTs powder in 100 mL absolute ethanol under ultrasonication for 10 min. EG as a surface modifier was added to the CNTs suspensions in this step to make the surface of CNTs ready for absorption of analyte. Then 0.4 g sodium sulfide hydrate was added to the suspension during mixing (suspension A). In the second step, the cationic solution was prepared by dissolution of 1.124 g zinc acetate and 8.63 mL manganese acetate solution (0.04 g $L^{-1}$) in 100 ml deionized water (solution B). In the third step, solution B was added dropwise to suspension A for 30 min. The nanocomposites were dried in an electric oven at 60$^{o}$C for 24 h and used without further purification. Macro-features of the synthesized CNT–ZnS:Mn nano-composite (i.e. infrared spectrum and X-ray diffraction pattern) are similar to those we already reported [19].

### *4.4. Pipette- tip procedure*

Appropriate amounts of CNT-ZnS nanocomposite was put into the pipette-tip. The extraction of diazinon was performed by attaching this pipette-tip extractor to a 5000 µl pipette. Then 500 µl of the aqueous standard solution containing 10 mg L$^{-1}$ of diazinon in a 2 mL glass test tube was withdrawn into the sorbent and dispensed back into the same tube. Before the optimization of the number of aspirating and dispersing cycles, the extraction was performed with 10 cycles. The adsorbed analyte on the surface of the pipette-tip were eluted with 100 µL of an acetonitrile into a 2-mL amber vial, also with 10 aspirating/dispensing cycles.

## 3. RESULT AND DISCUSSION

### *2.1. Optimization of extraction conditions*

In order to reach the highest extraction efficiency, factors influencing the extraction were investigated and optimized as follows.

### *2.1.1. Type of eluting solvent*

Several solvents with different polarities were evaluated to desorb diazinon from the extracting media. Experiments showed that diazinon could not be desorbed by methanol and only 60% of it was eluted by acetone. Both hexane and acetonitrile could elute diazinon quantitatively because of the similarity in the polarity of them with the target analyte. Due to the incompatibility of hexane with octadecyl silane column, acetonitrile was chosen for the analyte desorption from pipette tip [20].

### *2.1.2. Effect of pH*

The effect of sample pH on the recovery was investigated between 2.0 and 10.0, adjusted by 1 M NaOH or 1M HCl. As shown in Fig. 1, pH values of 5.0 to 8.0 have no significant effect on the extraction efficiency of the developed extractor. However; in stronger acidic media, extraction efficiency is increased. At the pH of 3, the highest recovery was obtained. At pHs less than 3, unknown peaks were observed in chromatograms and recovery of diazinon was decreased. This is mainly due to dissolution of some component of the sorbent in strong acidic medium [21].

There are three type of surface complexation reactions of protonation, deprotonating and ion exchange between adsorbent (ZnS-CNTs) and the diazinon. Therefore, the best interaction between analyte and adsorbent takes place while it is in anionic form and the sorbent is protonated. In alkaline media, repulsion forces between analyte and surface of adsorbent caused decrease in extraction recovery. Also, comparison of ZnS-CNTs adsorbent with non-modified CNTs for extraction of diazinon showed that the nano sized Zns:Mn increased adsorption capacity of sorbent and therefore, extraction efficiency of diazinon was increased.

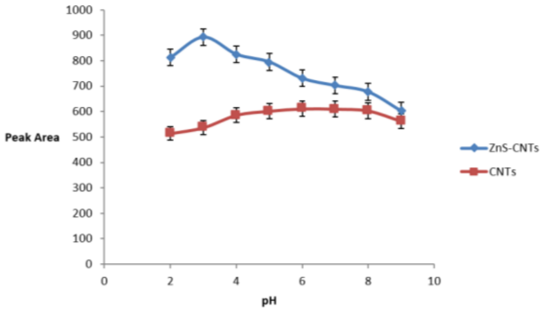

**Fig. 1.** Effect of pH on recovery of Diazinon.

### *2.1.3. Effect of amount of sorbent*

To achieve high extraction efficiency with good recoveries of diazinon pesticides, the amount of nanocomposite for pipette-tip extraction was changed between 20-100 mg. The adsorption ability of nanocomposite was increased by increasing amount of nanocomposite up to 70 mg. After that, the extraction recovery became constant and hence, amount of adsorbent were optimized at 70 mg (Fig. 2). Increasing amount of adsorbent, provide more adsorption sites on surface of nanocomposite and hence, extraction efficiency was increased. For non-modified CNTs highest extraction efficiency obtained at 100 mg of CNTs that showed in Fig. 2.

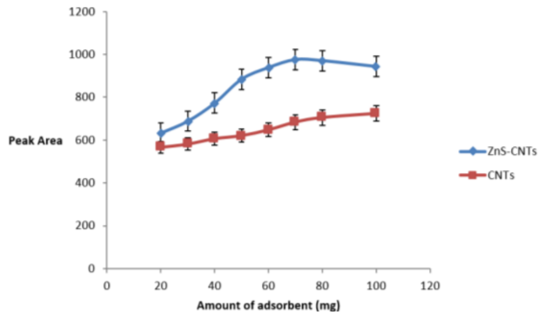

**Fig. 2.** Effect of adsorbent dose on recovery of Diazinon.

### *2.1.4. Effect of volume of eluting solvent*

We tried to obtain the smallest volume of desorption solvent which provides the highest enrichment factor. Volumes between 10 to 80 µL of acetonitrile were examined. As shown in Fig.

3, between 25 and 35 µL of the eluting solvent, the recovery of diazinon is in its highest value, which means these volumes of eluting solvent provides a better elution. Therefore, the eluting volume of 30 µL was selected for further experiments. Also, these volumes of acetonitrile were applied for extraction of diazinon from non-modified CNTs that results indicated that ZnS-CNTs is more effective adsorbent for extraction of diazinon.

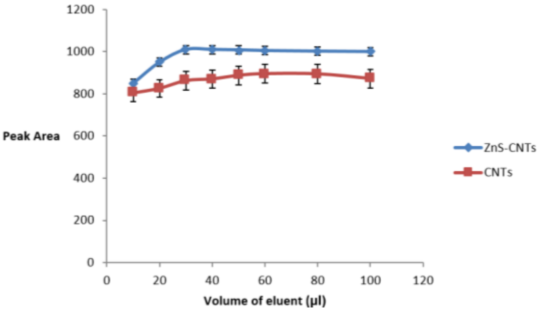

**Fig. 3.** Effect of volume of eluting solvent on recovery of Diazinon.

### *2.1.5. Effect of volume of sample solution*

Amount of sample solution taken for the analysis is an important parameter in solid phase extraction [22]. Different volumes of sample solution were tested at the range of 500 to 5000 µL. Fig.4 shows that with increasing of the sample solution, extraction recovery of diazinon is also increases. Therefore, 3000 µl of sample solution was selected as optimized volume.

By increasing of sample solution more analytes can be adsorbed on ZnS-CNTs nanocomposite. After a certain volume of sample solution, equilibrium condition takes placed and extraction efficiency is constant.

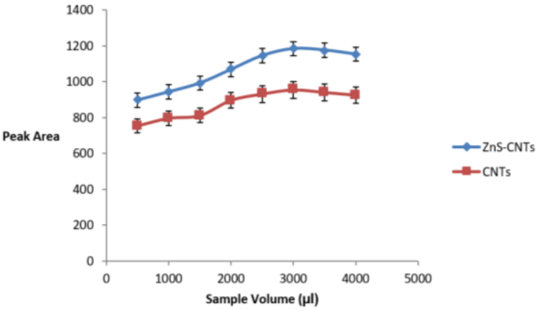

**Fig. 4.** Effect of sample volume on recovery of Diazinon.

### *2.1.6. Effect of number of aspirating/dispensing of sample*

The number of aspirating/dispensing cycles is another important parameter that affects the adsorption efficiency of the extraction. The time of extraction depends on the number of cycles and the volume of solution that passed through the extractor. The results show that the highest recoveries for diazinon were 10 cycles, while used a 3000 µL of sample. At a higher number of cycles, the back extraction of analytes from adsorbent into the sample solution might occur, causing a decrease in the recovery [22].

### *2.1.7. Effect of number of aspirating/dispensing cycles of elusion solvent*

During desorption, the analyte was eluted from the extractor into a 5-mL glass test tube by repetitive aspirating/dispensing of 450 µL of the acetonitrile through the tip. The optimal number of aspirating/dispensing cycles used for desorption of adsorbed analytes (provided the highest recovery) was found to be 20 cycles at 8.5 min.

### *2.1.8. Salting out effect*

The effect of salt on the extraction efficiency was evaluated by adding enough solid NaCl to the solution to have a concentration of 0 to 2 M of NaCl in sample solution. In the presence of 2 M of NaCl, highest recovery of the analyte was obtained. However, there was no further improvement at higher concentrations of salt. Presence of salt increases the ionic strength of the sample solution and reduces the solubility of diazinon that results in an increase of the adsorption ability onto the surface of the adsorbent.

## *2.2 Analytical performances and method validation of the developed method*

### *2.2.1 Analytical Figures of Merit*

The analytical performance of the suggested pipette-tip extraction coupled with HPLC–UV was evaluated, and the results are summarized in Table 1.

**Table 1.** Analytical figures of merit for pipette-tip extraction of diazinon

| Parameter | Analytical feature |
|---|---|
| Dynamic range (µg $L^{-1}$) | 0.50-100.0 |
| $R^2$(determination coefficient) | 0.991 |
| Repeatability[b] (RSD %) | 3.78 |
| Limit of detection[a] (µg $L^{-1}$) | 0.030 |
| Enrichment factor (fold) | 100 |
| Total extraction time (min) | ≤ 10 |

[a] LOD, was based on $3S_b/m$ criterion for 10 blank measurements; [b] RSD, relative standard deviation, for 5 replicate measurements of 20 µg $L^{-1}$ of Each analyte

Limit of detection (LOD) was obtained based on a signal-to-noise ratio of 3. The linearity range was studied by varying the concentration of the standard solution from 0.1 to 100 µg $L^{-1}$. The repeatability of the method, expressed as relative standard deviation (RSD), was calculated for five replicates of the standard at an intermediate concentration (20 µg $L^{-1}$) of the calibration curve. The enrichment factor (EF), which was calculated as the ratio between the analyte concentration after pipette-tip extraction ($C_{PT}$) and the initial concentration of analyte ($C_0$) within the sample Eq. (1) was found to be 100 folds [23].

$$EF = C_{PT}/C_0 \qquad (1)$$

*2.2.2 Comparison of this method with other methods*

A comparison of the proposed method with the other previously reported methods demonstrates the feasibility of PT-SPE-HPLC method and its reliability for the analysis of diazinon (Table 2). The LOD and LDR in this work are comparable with and lower than some studies. RSD is better than some and comparable with those of the other studies. It can be concluded that PT-SPE-HPLC is a sensitive method that can be used for the ultra preconcentration and determination of diazinon from environmental samples.

**Table 2.** Comparisons of proposed method with other methods for extraction of diazinon.

| Method | LOD (µg $l^{-1}$) | LDR[a] (µg $l^{-1}$) | RSD (%) | Ref |
|---|---|---|---|---|
| SPME | 0.3 | 1.0-50 | 5.0-8 | 24 |
| MWCNTs /SPME | 0.02 | 0.0003-10 | 0.76 | 25 |
| Magnetic/SPE | 14-19 | - | 7.2 | 26 |
| SPE/DLLME | 0.0003 | 0.001-10 | 4.9 | 27 |
| PT/SPE | 0.03 | 0.05-100 | 3.78 | this work |

[a]LDR, linear dynamic range is the minimum detectable concentration and the largest concentration that the response factor ® falls outside.

*2.3. Application of proposed method in real samples*

The suggested pipette-tip procedure was applied on five environmental samples. Water samples (from two different farms close to the university campus) were filtered through 0.45 µm nylon membranes prior to analysis. Soil samples (collected from three different farms) were milled finely and 5.0 g of it, was added to a 1:1 mixture of 10 mL of 50 ◦C distilled water and acetone. This mixture was sonicated for 15 min and the slurry was centrifuged at 4000 rpm for 10 min. The extraction procedure was repeated three times on each liquid and soil sample. Since no diazinon pollution was observed in all samples, the samples were spiked with 3 different concentrations to investigate the matrix effect on its determination. For soil samples, 0.5 mL of diazinon standard solution with proper concentration was sprayed to 5.0 g of the soil. The spiked sample was allowed to stand overnight before extraction. An unspiked (blank) soil sample was also extracted and analyzed. The results are shown in Table 3. As can be seen, recoveries are adequate; therefore, we can justly this assumption that matrix effect is negligible for the analysis of the target analyte. Example chromatograms are depicted in Fig. 5.

## 4. CONCLUSIONS

In this study, pipette-tip solid phase extraction based on CNT–ZnS nano particles followed by high performance liquid chromatography has been developed for the determination of diazinon in water and soil samples. Due to very high surface areas and short diffusion rate, high adsorption capacities can obtain in a very short time. The optimized method is found to be fast, economical, sensitive, accurate and simple.

**Table 3.** Application of proposed methods in environmental samples.

| Sample | Added (µg $l^{-1}$) | Found (µg $l^{-1}$) (SD[1]) | Recovery (%) |
|---|---|---|---|
| Farm water | 10 | 9.65(0.64) | 96 |
| | 25 | 24.31(0.80) | 97 |
| | 50 | 47.6(0.95) | 95 |
| River water | 10 | 9.72(0.32) | 97 |
| | 25 | 24.11(0.38) | 96 |
| | 50 | 46.2(1.10) | 92 |
| Soil 1 | 10 | 9.35(0.52) | 93 |
| | 25 | 24.89(0.77) | 99 |
| | 50 | 49.95(0.96) | 99 |
| Soil 2 | 10 | 9.88(0.83) | 98 |
| | 25 | 24.92(0.65) | 99 |
| | 50 | 49.92(0.72) | 99 |
| Soil 3 | 10 | 9.30(0.28) | 93 |
| | 25 | 24.70(0.31) | 98 |
| | 50 | 48.90(0.78) | 97 |

[1]-Standard Deviation

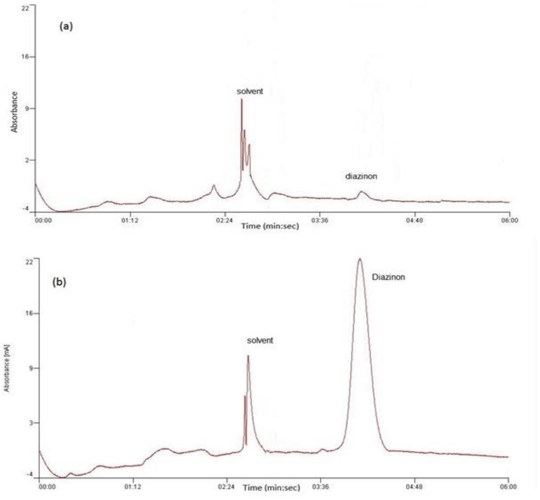

**Fig. 5.** HPLC chromatograms obtained from extraction of (a) water sample and (b) soil sample spiked by 25 µg.$L^{-1}$ of diazinon.

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