

# Determination of Diazinon Pesticide in Water Using Continuous Solvent Extraction - Steam Distillation

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## الخلاصة

تم استخدام طريقة الاستخلاص المستمر- التقطير البخاري لاستخلاص المبيد ديازنون، المستخدم كثيرا محليا، في العينات المائية متضمنة الظروف المثلى للاستخلاص باستعمال المذيبات العضوية الأثقل من الماء كلوريد المثيلين أو الكلوروفورم. إن نسبة الاسترجاع للمبيد لمحللول تركيزه 10 ملغم / لتر كانت 100 % تقريبا بعد تعديل حامضية العينة المائية ( الأس الهيدروجيني = 1,5 - 2 ) وزمن استخلاص مستمر - تقطير بخاري 3.5 ساعات لعينة مائية ذات حجم 500 مللتر باستعمال حجم 150 مللتر من الكلوروفورم أو كلوريد المثيلين. أعطى الاستخلاص بدفعة واحدة لعينة صغيرة من المبيد نسبة تراوحت بين 70 - 78 % لمدى تركيز 1 - 10 ملغم / لتر باستعمال الكلوروفورم أو كلوريد المثيلين . استخدمت طريقة امتصاص الأشعة فوق البنفسجية - المرئية لتقدير وتحليل المبيد ديازنون باستعمال خلايا مصنوعة من زجاج الكوارتز ذات سمك 1 سم . تم حساب قيم الدقة والضبط لهذه الطريقة باستعمال عينات مائية قياسية محضرة مختبريا لمبيد ديازنون ، وبأجراء المعالجات الإحصائية أظهرت النتائج وجود خطأ نسبي منوي R.E % يتراوح ما بين ± 0.2 إلى 4.8 % وكان الانحراف المعياري النسبي R.S.D % لا يزيد على 8.19 % . هذه الطريقة بسيطة وطبقت باستعمال معدات بسيطة ورخيصة متوفرة في المختبرات الكيميائية لمدى واسع من العينات المائية.

## ABSTRACT

A continuous solvent extraction-steam distillation method of water by heavier solvents was used for the extraction of diazinon pesticide, locally widely used, in aqueous samples involving the optimal conditions for extraction with chloroform or dichloromethane as extractor. The recovery for a concentration about 10 mg.L<sup>-1</sup> of diazinon approaches to 100% using acidification of the water sample (pH=1.5-2) and a extraction- distillation time of 3.5 hour for an aqueous sample 500 ml with 150 ml of chloroform or dichloromethane as extractor. One extraction with small volumes of chloroform or dichloromethane, diazinon could be recovered to the extent of 70-78 % in the range 1-10 mg . L<sup>-1</sup> . A UV- spectrophotometric method has been used for the determination and analysis of diazinon using 1cm quartz cells. The accuracy and precision of the method were determined by preparing laboratory samples of diazinon , the results showed relative error ranging from ± 0.2 to 4.8 % and the Relative standard deviation did not exceed 8.19 % . This method is simple and could be implemented with relatively low-coast equipment which is already available in chemical laboratories and it may be applicable to a wide range of aqueous samples.

## INTRODUCTION

It is important to determine small concentration of pesticides in aqueous samples such as waste streams, natural water used as raw water for drinking water supplies. The organophosphates are more soluble and have half lives in fresh water on the order of one to four week (1) . Hunt J. W. et al (2) study organophosphates diazinon and chlorpyrifos in a central California watershed because of their high toxicity, their common usage and their previously reported association with biological effects. The concentration of diazinon, chlorpyrifos and malathion in

water was reported by using polyester foams, the sorption efficiency and the recovery were found to be up to 95.5%(3). Athanasius C. Kimbris et al (4) reported a method for analyzed organophosphates with FT-Raman spectroscopy which is simple, rapid and non-destructive for the sample. H. B. Mathur et al (5) found a method for analysis of organophosphates pesticides in soft drinks using methylene chloride as solvent. Methods for the determination of trace pesticides pollutants in aqueous samples generally include solvent extraction(6), continuous solvent extraction-steam distillation(7) and concentration step (8) or concentration on solid adsorbents by adsorption and subsequent elution from XAD resins(9,10). W. John et al(11) have reported a method for the determination of diazinon residues in sheep's wool using petroleum spirit as solvent and analysis using GC-Mass spectrometer. A. Neicheva et al. (12) reported good method for simultaneous determination of organophosphorus pesticides in plant products and water, the pesticides were extracted with acetonitrile or chloroform. A continuous liquid-liquid extraction apparatus based on mixed settling is described (13). The recovery of pesticides is 83-96% for different pesticides and different pump rates. Size Exclusion Chromatography SEC is used of extraction of pesticides with ethyl acetate , recoveries better than 90% are obtain for organophosphorus pesticides from fats, fish oils, vegetable, fruits, cereal and liver (14). V. Janda and K. Krijt (15) used continuous distillation- continuous liquid-liquid extraction for the isolation of phenols from water using diethyl ether as the extraction solvent, the recovery approaches 100% for a concentration range about 0.1-30 mg. L<sup>-1</sup> at distillation- extraction time of 1.5 hour. Pesticides residue in raw wool wax were removed by continuous counter current extraction with hexane and DMF in mixer-settler contactor (16), the caffeinate wool wax produced by this process after conventional neutralization met all BP and USP specification for pharmaceutical lanolin. Hunt J. W.et al (17) found relationships between water quality and organophosphorus pesticides application rates in agricultural watersheds, to evaluate the usefulness of pesticides application data in regional monitoring sites. Nguyen Van Cong et al (18) were tested level from 0.008 to 0.52 mg. L<sup>-1</sup> of diazinon to assess the effects on the brain cholinesterase activity of the snakehead fish.

This work was aimed to improve the analytical methodology for the determination of diazinon, widely used in Iraq, in polluted aqueous samples by optimization the continuous solvent extraction-steam distillation and analysis by a UV-spectrophotometer. It was also desirable to minimize the analysis time required by avoiding further clean-up steps and avoid time-consuming.

## MATERIALS AND METHODS

### Apparatus

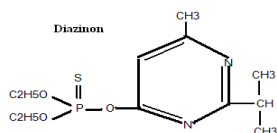
A shimadzu-160 double beam UV- spectrophotometer was used for the determination and analysis of diazinon samples using 1 cm quartz cells.

### Materials

All compounds were of high purity purchased and obtained from Fluka and BDH and no further purification was need. Diazinon commercially available were of technical purity (table-1). All glassware was cleaned with detergent and water, rinsed with distilled water, dried and rinsed with chloroform or dichloromethane several time before use.

### Preparation of samples

Samples of different standard concentrations of diazinon were prepared by transferred accurately weighted amount of liquid standard diazinon pesticide into appropriate volumetric flasks and added distill water or organic solvents.



Phosphorothioic acid o,o-diethyl-o-(6-methyl-2-(1-methyl ethyl)-4-pyrimidinyl) ester

### Extraction

The apparatus used for the continuous solvent extraction-steam distillation of diazinon in water by heavier solvents, chloroform or dichloromethane (table-2) is shown in ( fig.1).

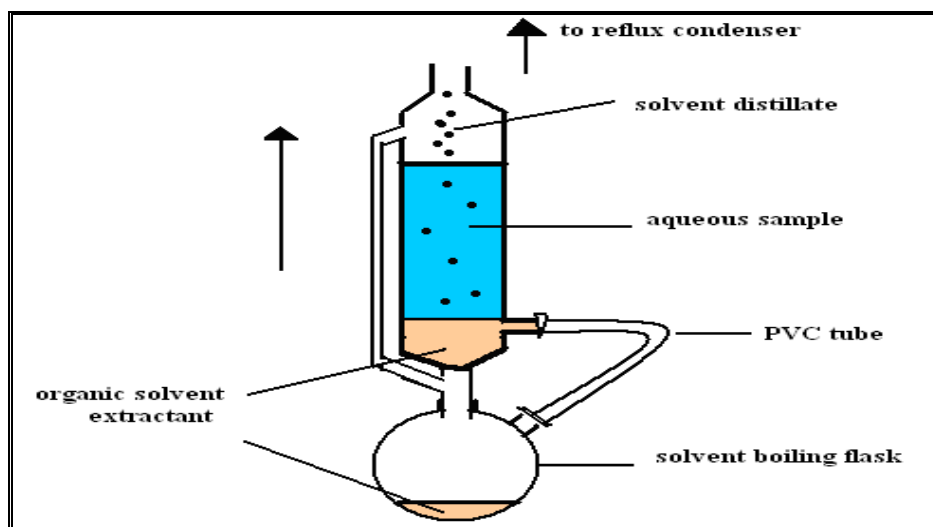


Fig. -1: Continuous solvent extraction apparatus for solvent heavier than water

Diazinon in chloroform or dichloromethane exhibit two maximum absorption peaks at 250, 270 nm, (fig-2) the absorption peak ( $\lambda_{max}$ ) at 250 nm having the highest absorption intensity, was selected for the determination of diazinon, construction of standard calibration graph, and %extraction using 1 cm quartz cells in acidic (pH=1.5-2) and basic (pH=12-13)aqueous samples using hydrochloric acid and sodium hydroxide to adjusted pH, and phase ratio organic to aqueous layer was 1:5 and 1:10 at extraction time 2 and 5 minutes .

Table-1: Physical and chemical properties of diazinon pesticide

Compound	M.Wt	Empirical Formula	LD50 mg/ kg	Solubility in water mg/L	Liquid density, gm/ml	B. P. ° C	TLV, g/m <sup>3</sup>
Diazinon	304.34	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	250m,285f	40	1.116-1.118	120	0.1

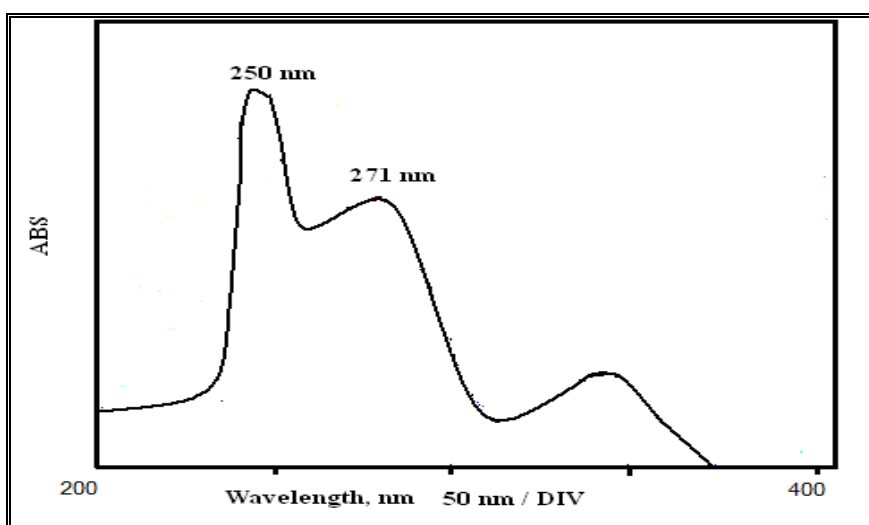


Fig. -2: UV-Spectrum of Diazinon in chloroform or dichloromethane

Table-2: Physical and chemical properties of organic solvents

Organic solvent	Chemical formula	density	B. p °C	Dielectric constant	Solubility in water, g/l
dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	1.144	40.1	9.1	20
Chloroform	CHCl <sub>3</sub>	1.498	61.62	4.8	10

A 100 ml volume of dichloromethane was placed in 250 ml round bottom flask and a boiling chips was added. The extractor containing 50 ml of dichloromethane was placed above the flask. The aqueous sample, 500 ml was adjusted to pH=1.5-2.0 with hydrochloric acid and

poured into the extractor to form a layer above the dichloromethane which distilled and condensed and fell as small drops through the water column and returned to the boiling flask. The diazinon were continuously extracted with fresh portions of solvent. After 5 hour the extraction-steam distillation is finished, the extract was collected and dried with sodium sulfate . The sample was ready for analysis by UV-spectrophotometer.

### Analysis

A 10 – 35  $\mu\text{L}$  volumes of the diazinon solutions were diluted with appropriate solvent and analysis using UV-spectrophotometer. A standard calibration graph for diazinon ( fig. -3 ) in the concentration range 0.5 to  $20 \text{ mg.L}^{-1}$  were prepared and used to determine the amounts of diazinon using the Method of Least Squares (M.L.S )(19).

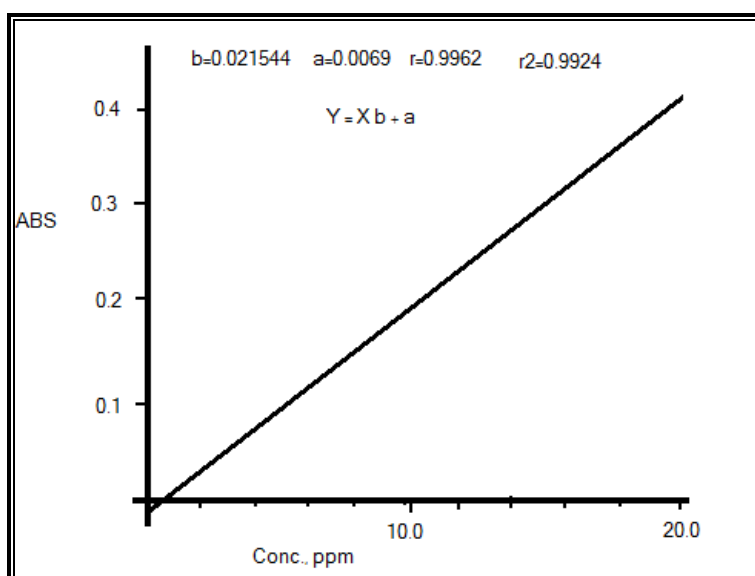


Fig.- 3: Standard calibration graph for diazinon at  $\lambda_{\text{max}} = 250 \text{ nm}$

The regression equation  $\{ Y = Xb \pm a \}$ , where Y is the sample absorbance, X is the calculated unknown concentration, b is the slope  $= 0.021544$ , a is the intercept  $= 0.0069$ , r is the correlation coefficient  $= 0.9962$  were utilized for the calculation of unknown concentration in polluted aqueous samples.

## RESULTS AND DISCUSSION

In this paper describe a method for the determination of diazinon based on continuous solvent extraction-steam distillation. The method has been successfully applied to aqueous samples.

Dichloromethane was the solvent of choice because of its moderate polarity, higher density compared with water, lower tendency to form emulsion and ease to distillation (table-2). The extraction in acidic

aqueous samples give best results compared with basic which give emulsion. One extraction with small volumes of chloroform or dichloromethane, diazinon could be recovered to the extent of 70-78% in the range 1-10 mg.L<sup>-1</sup>. The results showed that 2 minutes extraction time is sufficient to do and obtain higher extraction with phase ratio 1:5 or 1:10 organic to aqueous layer (table-3) .

Using a continuous solvent extraction-steam distillation apparatus, for an aqueous sample 500 ml with 150 ml of dichloromethane as extractor the diazinon were continuously extracted with fresh portions of solvent, after 3.5 hour the extraction-steam distillation is finished, the extract was collected and dried with sodium sulfate The recovery for a concentration about 10 mg.L<sup>-1</sup> approaches to 100% using acidification of the water sample (pH=1.5-2). The sample was analysis by UV-spectrophotometer by measured the absorbance at  $\lambda_{max} = 25 \cdot \text{nm}$  using 1 cm quartz cells. The validity of the regression equation was tested by analyzing standard samples of diazinon. Beers law is valid within the concentration ranges of diazinon. The results are summarized in(table-4) for standard samples , with chloroform or dichloromethane as extractor.

The accuracy and precision of the method were determined by preparing laboratory samples of diazinon , the results showed relative error ranging from  $\pm 0.2$  to 4.8 % and the Relative standard deviation did not exceed 8.19 %. This method proved to be simple and could be implemented with relatively low-coast equipment which is already available in chemical laboratories and it may be applicable to a wide range of aqueous samples .

Table-3: %Extraction of diazinon from acidic and basic aqueous samples using chloroform or dichloromethane

Organic solvent	pH aqueous layer	Phase Ratio Organic : Aqueous	% Extraction $\pm 3$
Dichloromethane	1.5-2.0	1:5	73
Dichloromethane	1.5-2.0	1:10	73
Dichloromethane	12-13	1:5	21
Dichloromethane	12-13	1:10	22
chloroform	1.5-2.0	1:5	75
chloroform	1.5-2.0	1:10	75
chloroform	12-13	1:5	20
chloroform	12-13	1:10	18

Table-4: Analysis of standard diazinon samples

Sample No.	ABS	Diazinon Conc.,mg.L <sup>-1</sup>	Absolute Error	Relative Error %	Average Conc. mg.L <sup>-1</sup>	Standard Deviation	%Relative Standard Deviation
1	0.104	5.147	+0.147	2.94	5.025	0.412	8.19
2	0.106	5.24	+0.24	4.8			
3	0.101	5.01	+0.01	0.2			
4	0.103	5.10	+0.10	2.0			
5	0.098	4.87	-0.13	2.6			
6	0.096	4.78	-0.22	4.4			

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