Research Article

Use of Ionic Liquids for Preconcentration/Separation of Diazinon by In Situ Solvent Formation Microextraction (ISFME) and Measurement by the UV-Vis Spectrophotometer

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ABSTRACT

In the current study, the UV-Vis spectrophotometer has been used for measuring the Diazinon. The extraction and preconcentration of Diazinon was done by the use of In Situ Solvent Formation Microextraction (ISFME) method, and the ionic liquids 1-Hexyl 3-methyl-imidazolium bromide [Hmim] [Br] and lithium (bis-trifluoromethylsulfonyl) -imide [Li (NTF2)] as the opposite ion. Different parameters effective on extraction such as the sample solvent pH, the amount of ionic liquid, the centrifuge duration, the amount of salt, and the amount of the opposite ion (NTF2-) were investigated at the two screening and response levels by the experiment designing software Statgraphic X64, in order to obtain the optimal conditions. Based on the obtained results, the highest rate of extraction was obtained as 95.41% in the pH of -11.77 for 1 ml solvent of 0.5 mg/Lit containing Diazinon, 120 mg of ionic liquid, 1 ml of the opposite ion with a concentration of 0.02 molar, and the duration of 5 minutes in the centrifuge. The limit of detection of this method is 0.42 mg/Lit based on the 3Sb equation and 0.69 mg/Lit based on the 3Sb/m equation. The relative standard deviation is 1.76% and the enrichment factor was calculated as 48.66.

Key words: *Diazinon, preconcentration, UV-Vis spectrophotometer, ionic liquid.*

INTRODUCTION

Separation, identification, and measurement of different materials is the ultimate goal of chemical decomposition science, which has been long considered [1]. Ionic Liquids (ILS) are actually salts in which the ions are coordinated in a weak form, and are liquid in 100 °C temperature or even in the room temperature. They have an organic part which is voluminous, and an ion with unsettled Pi charge which prevents from formation of a stable crystal network. The number of ionic liquids which can be generated today is more than 106 (high variety and different attributes) while the total number of the molecular solvents does not exceed 600 [2, 3]. Today, the ionic liquids are widely used in different sciences and technologies. The most important application of these liquids is to play the role of a green solvent instead of a volatile solvent. Today, the ionic liquids also have other wide cartelistic applications [4, 5].

The newest liquid-liquid homogenous microexraction technique is the ISFME method by the use of ionic liquids. This method is greatly similar to the dispersive liquid-liquid microextraction, however, instead of using the harmful and toxic organic solvents, it uses ionic liquids as the extraction solvent. The main advantage of this method is its capability to be used in measurement of a specified analyte in the samples containing high concentrations of salt. In the ISFME method, there is no borderline between the sample aqueous solution and extraction phases. During the formation of extraction solvent drops, the extraction molecules collect the hydrophobic specimens and the extraction process is completed after the formation of the drops. As a result, the mass transfer from the aqueous phase to the separator phase does not affect the extraction. The ISFME method by the use of ionic liquids as the extracting solvent, has been successfully used for measurement of mineral

specimens in samples containing salt, and extraction and separation of metal ions in sewage and environmental samples. Recently, many of the mineral specimens such as the copper, lead, mercury, cadmium, arsenic, chromium, nickel and zinc, have been successfully studied and measured by the ISFME method. Compared to the other microextraction methods which use heavy metal ions for concentration, the ISFME method is faster and simpler, and can be implemented for solutions with high concentrations of salt [6]. As a new method, the ISFME can be coupled with GC and AAS. This method can be widely used for analysis of heavy metals.

Experimental design is a useful method by the aid of which the data are analyzed to gain objective validity and illation. It includes methods that design experiments for investigation of the effects of different parameters. This design is used with different objectives such as identification of effective parameters, initial estimation parameters effects on the response, identification of interactions between the parameters, and modelling or creation of mathematical equations between the parameters and the responses. Experimental design includes methods that design experiments for investigation of the effects of different parameters on the response [7, 8].

Pesticides are synthetic or natural compounds widely used to control or eliminate pests. Indeed, the viruses, bacteria, and other microorganisms living in the human or other creatures' bodies are exceptional [9, 10]. Diazinon is a relatively volatile phosphorus pesticide used extensively to kill flies and fleas, especially the Argacidae Flea. This pesticide is also absorbed through the skin, therefore, touching it must be prevented. This pesticide, with having the capability to permeate the waxy layers of the plant tissues, can be successfully used in controlling the pests (Cosmopolites sordidus and Phyllocnistis citrella). Diazinon is one of the highly used organophosphorus pesticides which plays an important role in chemically controlling the pests through controlling a wide range of pests such as sucking and gnawing pests in the farms and gardens [11].

The current study has aimed at investigation of the use of ionic liquids for concentration/separation of some of the pollutants such as the insecticides, pesticides, and drugs, by ISFME method, and measurement by the UV-Vis spectrophotometer.

METHODS AND MATERIALS

In order to measure the intended analyte, the double beam UV-Vis spectrophotometer with the model Thermo spectonic Helios Alpha Spectrometer was used. For synthesis, the raw material of the ionic liquid [P(mim)$_2$][Cl][Br], with the molar ratios of 1 to 2 from 1-bromo-3-chloropropane and methyl imidazole are poured into a round-bottom balloon, and are synthesized for 24 hours under a temperature of 70 °C. After this duration is passed, a milky and rigid solid is produced. The information on the peak zone and the chemical transmission of the synthesized ionic liquid are provided in the table 1.

Table 1: the H^{1}NMR information of the [P(mim)$_2$][Cl][Br] ionic liquid

H1, H7	3.869
H2, H6	8.775
H3, H5	4.296
H4	2.497
H8, H11	7.439
H9, H10	7.496
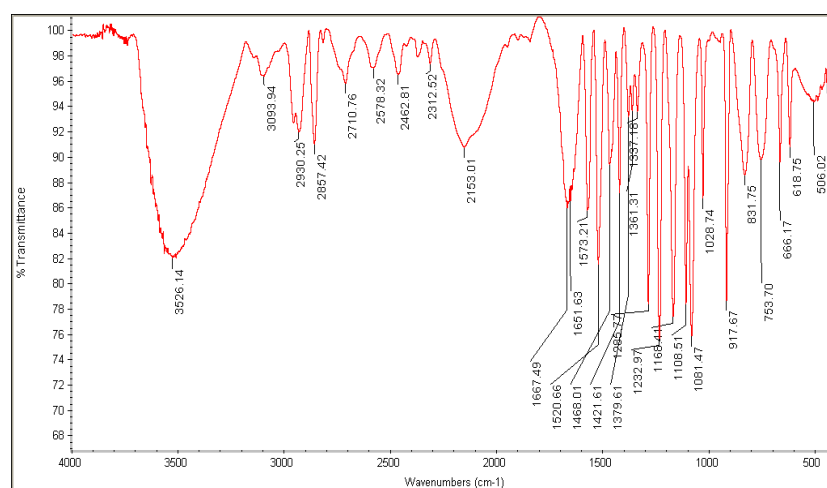
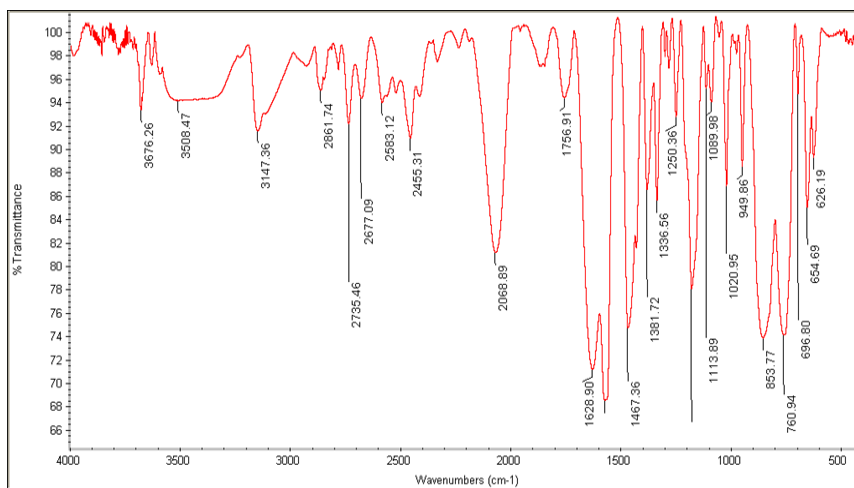**Figure 1:** the FT-IR spectrum of [P (mim) $_2$] [Cl] [Br] ionic liquid

In order to synthesize the [Hmim] [Br] ionic liquid, firstly equal molar ratios of Methyl Imidazole and 1-Bromohexane are mixed with each other and treated under the temperature of 70 °C for 72 hours. After this time period is passed, the product was obtained as a viscous liquid, which was washed by 3 milliliters of Ethyl acetate for three times, in the next phase. Finally, in order to remove the extra Ethyl Acetate, the experiment container was treated by a 90 °C heat, and a brownish liquid with a high viscosity was obtained, which was the same 1-hexyl 3-methyl-imidazolium bromide. Figure 2 shows the H^1NMR spectrum of the [Hmim] [Br] ionic liquid.
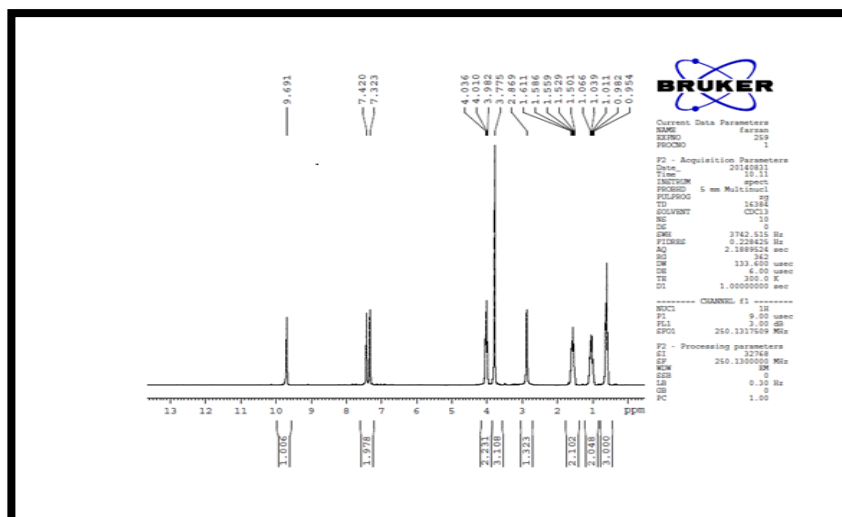
Figure 2: the H^1NMR spectrum of the [Hmim] [Br] ionic liquid

Table 2: the H^1NMR of the [Hmim] [Br] ionic liquid

| H1	3.7
H2	9.69
H3	4.036
H4	2.869
H5	1.066
H6	1.039
H7	1.55
H8	0.982
H9	7.323
H10	7.420

Figure 3: the FT-IR spectrum of the [Hmim] [Br] ionic liquid

In order to determine the Diazinon peak zone in UV-Vis spectroscopy, solutions with different concentrations of Diazonin were prepared and then, they were identified by the UV-Vis device, for the Diazonin peak zones to be specified. Then, for the sake of efficiency of the ISFME method in extraction of Diazinon, its extraction was done in the default conditions.

For preparation of the samples, the almonds and apricot leaves were collected from one of the gardens in the city of Buin Zahra, Qazvin province, and then the soil sample (the same soil at the root of the almond and apricot trees in the same garden) was prepared. For preparation of the urine samples, firstly 40 ml of water was added to 10 ml of urine (in order to dilute it), and after that, for purification of the solution, it was treated by the Minisart 40µm filter, and this purified solution was used for the experiment.

FINDINGS:

In order to investigate the effects of the salt type on Diazinon extraction, the two types of salt as NaCl and NaNO$_3$ were used. The results are shown in the figure (4). Based on the chart in figure (3), the NaNO$_3$ has a significant effect on the Diazinon extraction. Therefore, this type of salt is effective on the rate of extraction, and it is used for the experiments.
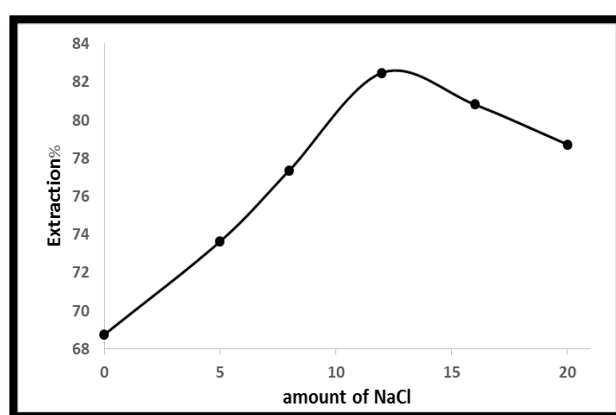
(a)
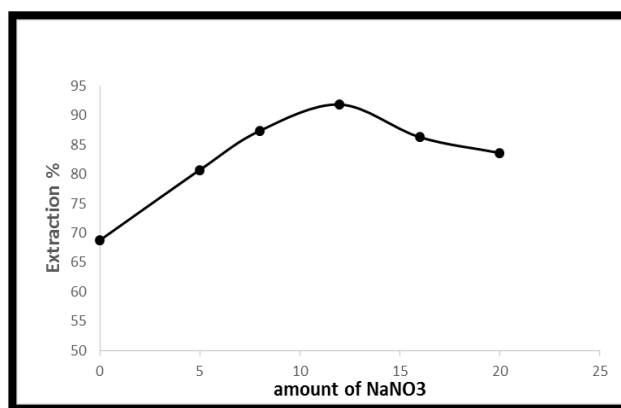
(b)

**Figure 4:** NaCl effect (a), NaNO$_3$ effect (b)

In the current study, parameters such as the ionic liquid, pH amount, salt amount, the opposite ion concentration, the centrifuge duration, and the mixing time have been used for screening. In fact, by the use of the software Statgraphics X64, one phase of screening by the use of Full Factorial and Center Point Iteration equal to 3, and 38 iterations of experiment (number of blocks× number of center points+2^{n-1}-nuber of experiments, n the number of parameters), was designed and the parameters with the highest effects on the Diazinon extraction were determined. Also, the parameters effective on the extraction process were defined and input to the software in the two high and low levels of the data, and then, in the Box-Behnken Design and center point equal to 3, 27 experiments were designed (N= 2^K + 2K+ C$_P$), K is the number of parameters, and C$_P$ is the

number of the center points. The high and low levels, and the parameters units are provided in table (3), and the experiment results are shown in table (4).

Table 3: the unit and level of parameters in screening and optimization

Parameter	Symbol		Unit		Low level		High level	
	Screening	Optimization	Screening	Optimization	Screening	Optimization	Screening	Optimization
pH	A	D	-	-	4	4	12	12
Salt amount	B	C	Weight-volume percentage	Weight-volume percentage	0	0	20	20
Mixing time	C		Minute		1		4	
Centrifugr duration	D		Minute		5		10	
The amount of opposite ion NTF$_2$)(	E	B	Molar	Molar	0/02	0/02	0/07	0/07
The amount of ionic liquid	F	A	mg	mg	30	30	120	120

The results of the responses normalized by the mentioned software are interpreted and finally, they are evaluated through the Pareto charts and the main effect chart. As it is seen from the results of the Pareto chart in figure 5, the pH, the ionic liquid amount, the amount of salt, and the opposite ion's concentration had positive effects while the centrifuge duration and the mixing time had negative effects.
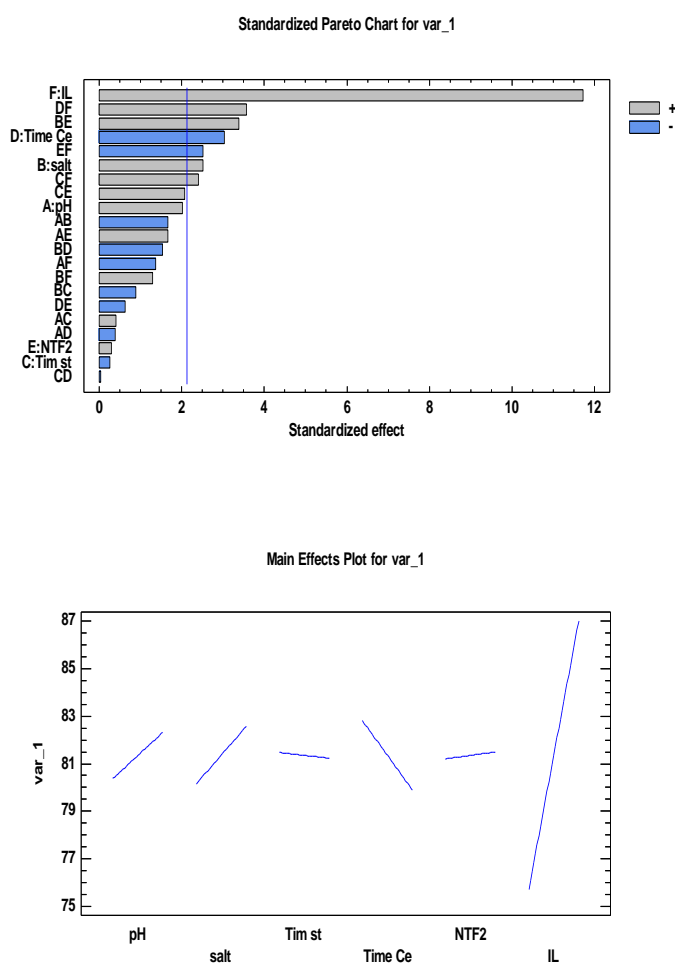
Figure 5: the Pareto chart and main effects of chart in Diazinon extraction

Table 4: the optimal values

Optimal amount	High level	Low level	Parameter
119/99	120	30	Ionic liquid
0/02	0/07	0/02	Opposite ion NTF_2
12/103	20	0	Salt
11/7	12	4	pH

The closeness of the experimental and estimated results, which were determined by the software, is indicative of the high efficiency of this method for Diazinon extraction. Table 5 shows the obtained results.

Table 5: the results of Diazonin extraction in the optimal conditions

Experimental percentage 95/4142	Estimated percentage 95/3056	parameters			
		pH 11/77	Ionic liquid amount (mg) 99/119	Opposite ion concentration (molar) 02/0	Salt amount (weight-volume percentage 12

Table 6: the method's fitness values

The linear range of method (µg/L) 7-1500	Relative standard deviation (%) 1/76%	Limit of detection (µg/L) 3Sb=0/42 3Sb/m=0.69	Enrichment factor 48/66

In order to investigate efficiency of the method for the real samples, three samples including the almond tree leaves, apricot tree leaves, and the soil were prepared and the initial concentration of Diazinon existing in them, was measured by the above-mentioned method and in optimal conditions. Then, by adding different amounts of Diazinon concentration, the method validity and credibility in extraction of Diazinon were investigated. The obtained results are provided in table 8.

Table 7: the results of Diazinon extraction from the real samples

Recovery (%)	The read Diazinon amounts (mg/L)	The added diazonin amounts(mg/L)	
-	0	0	
%87	0/0435	0/05	Sample
%89	0/179	0/2	Almond tree leaf
-	0	0	Apricot tree leaf
%88	0/044	0/05	
%91	0/1821	0/2	Soil
-	0	0	
%91	0/0455	0/05	
%93	0/186	0/2	

CONCLUSION:

The ISFME method have advantages such as simplicity, high speed, safety, and resistance against high concentrations of salt, instant extraction time, high concentration factor, cheapness, and low consumption of organic solvents. Recent studies show that replacement of a solvent with an ionic liquid leads to a significant improvement in the chemical processes. In the current study, ionic liquids with unique attributes such as being liquid in a wide range of temperatures, low steam pressure, and non-volatility, were used. The ionic liquids used are able to solve a wide range of organic and mineral compounds in them. The extraction of two types of Diazinon by the use of ionic liquids had a high efficiency. The opposite ion in the extraction process, is used as a helper agent in separation of the aqueous and organic phases. In the current study, firstly we have the 1-Hexyl-3-methylimidazolium ([Hmim] [Br]) ionic liquid in the reaction environment, which is fully mixable in the aqueous phase. Thus, it can easily interact and mix with the aqueous and organic phases in a highly effective manner, and this attribute leads to the organic analyte type (Diazinon in the current study) to easily react with the organic phase, and mix with it. After this process is finished, in order to separate the aqueous and organic phases, a voluminous anion such as lithium (Trifluoromethyl sulfonyl) imide (NTF_2^-) is used, which replaces Br

in the [Hmim][Br] compound, and leads to the formation of hydrophobic ionic liquid [Hmim][NTF$_2$] , which can be easily separated, also isolating the Diazinon from aqueous phase with it. In case the voluminous anion is not used, the two phases would not be separated or they would be separated partially, in which case, a large amount of Diazinon and [Hmim] [Br] would remain in the aqueous phase, and it is even possible that the extraction would not occur.

Among the other aspect of the current study, beside the separation, is the preconcentration. In the preconcentration tasks, the lower the amount and volume of organic phase, the higher the concentration factor will be. Therefore, the lower the amount and the volume of organic phase, the higher the preconcentration factor value will be. The preconcentration factor enables the method to measure the specific analyte concentration in dilute solution. By the increase in ionic liquid as the organic phase, the rate of extraction is significantly increased, so that the full extraction of Diazinon would be realized. In fact, the volume of ionic liquid should be such that it include whole Diazinon. Thus, volumes higher or lower than this volume would disrupt the Diazinon extraction process. In order to investigate the durability of ISFME method in extraction Diazinon in environments with concentrations different from the electrolyte salts, the effects of NaNO$_3$ salt were investigated and studied. To the extent an extraction method can extract the analyte in solutions with high-concentration of salt or a high ionic power efficiently, the efficiency of that method, especially for analysis of the real samples which usually have a high ionic power, would be highly significant, and the method would have a better performance. In extraction of Diazinon by the use of ISFME method, the increase in salt leads to the increase in solution's ionic power, and the Diazinon enters the organic phase, leading to the increase in extraction efficiency. However, the amount of salt up to a specific level leads to the increase in extraction percentage and after that, due to the increase in the density of aqueous phase and closeness of the densities of the two phases, their separation is done with difficulty and the extraction percentage is reduced.

Synthetically, the higher the speed of reaction between the analyte and organic phase, the higher becomes the touching surface, and as a result, in terms of decomposition, the extraction duration is reduced. In the current study, regarding the fact that the material and type of the ionic liquid [Hmim][Br] is fully mixable in aqueous phase prior to adding the opposite ion, due to the high mixability of the two phases in each other, the extraction is done in the shortest time possible. In the current study, it was observed by the unarmed eye that instantly after addition of the opposite ion, a mixture in the form of a suspension is formed. Therefore, the extraction is done momentary. It is indicative of the quick synthetization of the extraction process. The reason behind the use of centrifuge in the current study was to separate the aqueous and organic phases from each other, better and more completely. In fact, after the opposite ion (NTF$_2^-$) is added to the mixture, it leads the organic phase to become hydrophobic, however, this preparation is not complete. Therefore, the lower the time needed in centrifuge, the higher the mixability of the two phases is, which, in terms of decomposition, is privilege for this method; in the current study, the optimal centrifuge duration has been considered to be 5 minutes. By the increase in this duration, the turbulence is made in the solution and the separation of the two phases would not be done completely. The method's fitness values which are mentioned in the decomposition works, include the limit of detection, linear range, concentration factor, and the relative standard deviation. These fitness values are studied and measured in order to evaluate the decompositional efficiency of a method, since it is important that from the decompositional aspect, the method proposed for a specific and particular application, has specified and significant attributes so that it can be introduced to the scientific centers.

It should be noted that using experiment design method in ISFME method is very useful due to the reduction in the number of experiments, saving time, saving the chemicals consumption, and considering the effects of different factors, simultaneously.

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