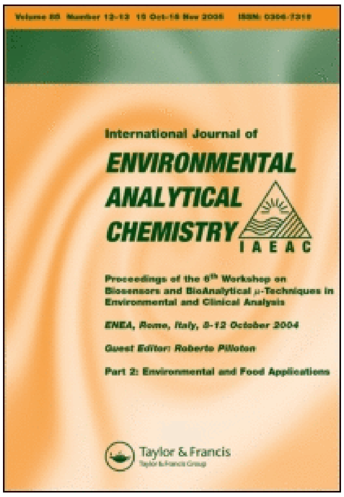

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Yahya S. Al-Degs[a]; Mohammad A. Al-Ghouti[b]
[a] Chemistry Department, The Hashemite University, Zarqa, Jordan [b] Industrial Chemistry Center, Amman, Jordan

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Preconcentration and determination of high leachable pesticides residues in water using solid-phase extraction coupled with high-performance liquid chromatography

Yahya S. Al-Degs[a]* and Mohammad A. Al-Ghouti[b]

[a]*Chemistry Department, The Hashemite University, Zarqa, Jordan;* [b]*Industrial Chemistry Center, Royal Scientific Society, Amman, Jordan*

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A multi-residue procedure was developed for analysis of four common pesticides in water using solid-phase extraction and high-performance liquid chromatography in combination with UV detection at 230 nm. The investigated pesticides (atrazine, dicloran, metazachlor and simazine) are highly leachable and easily migrate within the soil. Multi-walled carbon nanotubes (MWCNTs) adsorbent outperformed C_{18} bonded silica and graphitized carbon black for preconcentration of the pesticides from solution. The optimum experimental conditions for pesticides extraction were carefully studied and optimised. At the optimum preconcentration conditions (sample volume: 700 mL; adsorbent mass: 300 mg; solution pH: 5.0; flow rate: 3.0 mL min^{-1}; and elution medium: methanol), a quantitiative recovery for pesticides was reported and a high preconcentration factor (1400) was attained. The detection limits of the proposed method were found in the range: 5–15 ng L^{-1}. The dynamic range for simazine and atrazine determination was extended from 15 to 1000 ng L^{-1}, while for metazachlor and dicloran the range was within 60–1000 ng L^{-1}. Five replicate determinations of 70 ng of pesticides mixture present in 700 mL solution gave good results with RSD values within the range 2.5 to 4.6%. The present method gave recoveries from 92.7 to 95.3% for determination of 100 ngL^{-1} of pesticides in tap water and recoveries from 85.3 to 87.0 in well water with satisfactory RSD values ($\leq$6%).

Keywords: pesticides; leachability; solid-phase extraction; multi-walled carbon nanotubes; high-performance liquid chromatography

1. Introduction

The pesticides studied have a high impact on the environment and particularly on the terrestrial and hydrosphere compartments. Pesticides are heavily employed in agriculture. Due to their persistence and water solubility, many of them can migrate from soil to reach the groundwater. Accordingly, pesticides have to be considered as a potential risk for marine life as well as for drinking water quality [1]. From the environmental point of view, pesticides with high leachability are highly toxic and should be monitored. Leachability reflects the pesticide's tendency to remain chemically stable while moving to other environments [2]. The groundwater ubiquity score (GUS) value is a standard measure for pesticides leachability. A pesticide is leachable and hence dangerous when its GUS

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*Corresponding author. Fax: +962-5-3826613. Email: aldegs@hotmail.com

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value is higher than 1.8. Such pesticides can easily migrate within the soil to reach the groundwater at the end. Pesticides having GUS values less than 1.8 are not leachable and they are either easily degraded or chemically fixed within the soil [2]. Accordingly, pesticides with higher GUS values should be monitored in the hydrosphere part of the environment.

Due to photo and bio-degradation processes, the concentration levels of pesticides and their metabolites in hydrosphere are very low and their direct quantification is a hard task for analytical chemists. To overcome this analytical problem, pesticides should be preconcentrated as large as possible to enable detection by the instrument employed. Liquid-liquid and solid-liquid extraction methods were employed for preconcentration of pesticides before their quantification by high-performance liquid chromatography [3,4] or gas chromatography [5–7]. Unlike liquid-liquid extraction, solid-phase extraction was found more useful because lower solvent use, less operating time and higher concentration factors were achieved [8]. Commercially, many solid-phase extractants have been introduced for preconcentration of pesticides residues from natural waters [9]. An extractant with a high adsorption capacity for a wide range of pesticides is more preferable for the environmental analyses. Recently, multiwalled carbon nanotubes (MWCNTs) adsorbent, a new nanoscale material, has received great attention from analytical chemists. This unique material can be distinguished from existing traditional adsorbents by its particular physical properties as well as by its unique tubular structures of nanometer diameter and their large length-to-diameter ratio, which offers many different applications [10] MWCNTs adsorbent has been employed as a novel extractant for preconcentration of many harmful pesticides [10–12].

Due to their high toxicity, the maximum contamination level, as proposed by the WHO [13], for atrazine and simazine should not exceed $2\,\mathrm{ng\,mL^{-1}}$. Accordingly, very sensitive analytical methods are needed to monitor the presence of these pesticides in water systems [11]. In this work, a practical analytical procedure based on solid phase extraction coupled with high-performance liquid chromatography was developed for determination of high leachable pesticides in different water samples. Three solid-phase extraction media: multi-walled carbon nanotubes, C_{18} bonded silica, and graphitized carbon black were evaluated for their use for pesticide preconcentration. The experimental factors that influence pesticide extraction such as sample volume, eluent type and volume, solution pH, extractant mass, and extraction-elution flow rate were studied and optimised.

2. Method

2.1 *Chemicals, solvents and solutions*

The chemicals and solvents used were of analytical reagent quality unless indicated otherwise. Simazine, atrazine, metazachlor and dicloran of high purity were supplied by Riedel de Häen (Germany). Stock solutions ($100\,\mathrm{mg\,L^{-1}}$) were prepared by dissolving accurately weighed 10 mg of each pesticide in 100 mL of acetonitrile. The solutions were stored at 4.0°C and protected from light exposure; the pesticides solutions were stable for approximately one month. Working solutions were prepared daily by appropriate dilution with acetonitrile. To prevent adsorption of pesticides on the surfaces of employed glassware, all glassware was soaked in 2.0 M HNO_3 and washed with triply distilled water and finally with acetonitrile. Sodium hydroxide (0.4 M) and hydrochloric acid (3.0 M) were used for adjusting the pH solution. The pH measurements were carried out using a WTW-Inolab (Germany) pH-meter using a companied glass electrode. Ultra pure water was obtained using reverse osmosis system (Barnstead Ropure Infinity®).

2.2 *HPLC equipment and chromatographic analysis*

A PerkinElmer instrument (Series 200 Pump, Germany) with UV/V is detector was used for chromatographic analysis of the pesticides. Effect of pH, mobile phase composition, and mobile phase flow rate on pesticide separation were studied and optimised for the current system. The optimised conditions were: Separation on a Merck C_{18} column (5 µm size particle and 15 cm × 4.0 mm), using acetonitrile/water as mobile phase. Analytical separation was achieved at 1.0 mL min^{-1} with a water-acetonitrile gradient. Solvent program was started with 20% acetonitrile, held for 0.5 min, followed by a linear gradient to 50% acetonitrile in 5.0 min, and another linear gradient to 80% acetonitrile in 6 min. Pesticides eluting from the column were detected by UV–spectrophotometer at 230 nm. A 20 µL sample volume was injected in all experiments. Before injection into the HPLC column, all samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size.

2.3 *Solid phase extractants and solid phase extraction procedures*

Three commercially available solid-phase media were evaluated for preconcentration of pesticides. The investigated media were: multi-walled carbon nanotubes adsorbent with 1–5 µm length and 40–60 nm external diameter (Shenzhen Nanotechport Co. Ltd., Shenzhen, China), Octadecyl-bonded silica C_{18} cartridge with 300 mg adsorbent and 6 mL tube size (Supelclean ENVI-18, Supelco, USA), and graphitized carbon cartridge with 300 mg adsorbent and 6 mL tube size (Supelco, Bellafonte, USA). Prior to the extraction experiments, MWCNTs adsorbent was washed many times with pure water and then dried at 70°C for 24 hrs. Exactly weighted 300 mg of the adsorbent was properly placed in a typical 6 mL polyethylene extraction tube. Prior to extraction of pesticides, the extractants were conditioned by washing with 10 mL of acetonitrile followed by 10 mL of triply distilled water. The conditioning solutions were forced through the extractants at flow rate of 0.5 mL min^{-1} to ensure removing all adsorbed impurities and activate the adsorbents for pesticides extraction. Typically, 700 mL of water sample were spiked with pesticides and pumped through the extractant at a flow rate of 3.0 mL min^{-1}. All extraction experiments were carried out with the aid of a Visiprep-12-port vacuum manifold (Supelco, USA) under a controlled pressure using an appropriate vacuum pump (Knf Neuberger D-7800, Germany). After the extraction step, the extractant was washed with pure water at high flow rate (20 mL min^{-1}) to remove any weakly co-adsorbed substances. The trapped solutes were eluted with 8.0 mL of methanol, and the final solution was evaporated to dryness using a rotavapor (Heidolph Laborata 4001, Germany) under a moderate vacuum (Rotavac valve control). The remaining residue was dissolved in 500 µL of methanol and the pesticides content in the mixture was quantified using the proposed HPLC method.

2.4 *Sampling and sample preparation*

Natural water samples including tap and well waters were collected from different local locations. Tap water samples were obtained after flowing for 15 min from various water taps in our department in different days. The collected samples were combined together and treated as a representative sample. The representative sample for well water was generated by mixing water samples collected from three different wells on different days. The wells, that were used for irrigation purposes, were located within the Al-Zarqa area. Water samples were stored in polyethylene bottles at 10 C. Prior to spiking with pesticides, the samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size to remove any suspended matter. Furthermore, the pH of water samples was adjusted to 5.0 (±0.5). Finally, the content of pesticides in natural samples was determined according to the general procedure outlined in section 2.3. The occurrence of the target pesticides in natural water samples before spiking was investigated.

3. Results and discussion

3.1 *Leachability of pesticides*

To determine the leachability of pesticides, groundwater ubiquity score (GUS) values were estimated from Equation (1) [2]:

$$\mathrm{GUS} = \mathrm{Log}(t_{1/2}) \times [4 - \mathrm{Log}(K_{oc})] \tag{1}$$

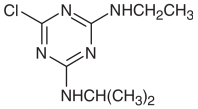
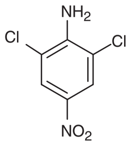
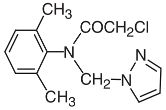
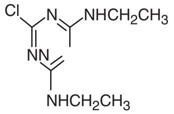
where $t_{1/2}$ and K_{oc} are the half-life time (in days) and the water/organic carbon distribution coefficient (L/kg) of the pesticide. Both $t_{1/2}$ and K_{oc} values are given in Table 1. The estimated GUS values for dicloran, simazine, atrazine, and metazachlor were 1.9, 3.4, 3.8, and 4.3, respectively. An average value of K_{oc} was used to estimate GUS values from Equation (1). All pesticides were leachable because GUS values were all higher than 1.8 [2]. The high mobility of pesticides was also indicated from the lower values of K_{ow}. Pesticides of low K_{ow} usually exhibited a high migration though the soil and have a weak adsorption on the soil [14]. To be fixed in the soil, K_{ow} value should be very high ($\sim 10^6$) which is the case for aldrin and DDT pesticides which remain in the soil for a long time [15].

3.2 *Pesticides analysis using HPLC*

The chromatographic separation of pesticides was carried out using a conventional C_{18} column. For better chromatographic separation, both isocratic and gradient elution modes were investigated. The other experimental variables that influence solute separation, including mobile phase composition, pH and detection wavelength were also studied and optimised. Separation of pesticide at the optimum experimental conditions was carried out using a gradient elution from 20% to 80% acetonitrile. Identification of pesticides was based on their retention times from the column. Table 2 summarises the analytical results for pesticides analysis directly by HPLC without any preconcentration step. Calibration curves (peak area against pesticide concentration) were obtained from triplicate determination using five standard samples in appropriate concentration range for each individual pesticide. As shown in Table 2, good linearities were found between the repose of the chromatographic method and the studied concentration range, the obtained regression coefficients (R^2) were in the range 0.9965 to 0.9999. The limits of detection (LODs) of pesticides were estimated on the basis of a signal-to-noise ratio of 3 (3 S/N method) and results are given in Table 2. LOD values were within the range 7 to 20 $\mu g\,L^{-1}$.

According to the European legislation for pesticides in drinking water, the minimum allowable concentration of a certain pesticide is 100 $ng\,L^{-1}$ and 500 $ng\,L^{-1}$ as a total

Table 1. Some chemical information for the studied pesticides[1]

Pesticide (type)	Class	Structural formula	K_{ow}[2]	K_{oc}[3]	$t_{1/2}$[4]	Solubility (in mg L^{-1}) at 25°C				
						Water	Methanol	Acetone	Toluene	Ethyl acetate
Atrazine (herbicide)	Triazine		320	70–140	86	33	15	31	4.0	24
Dicloran (Fungicide)	chlorophenyl		630	760–1062	60	6.3	–	34	–	19
Metazachlor (herbicide)	chloroacetamide		135	50[5]	77	430	200	1000	–	590
Simazine (herbicide)	Triazine		144	100–280	96	6.2	570	1500	130	–

Notes: [1] The given data were collected from Tomlin[14]; [2] K_{ow}: *n*–octanol/water distribution coefficient estimated at 25°C; [3] K_{oc}: water/organic carbon distribution coefficient (L/kg); [4] pesticide half-life time (in days); [5] Estimated from the equation: $\mathrm{LogK_{oc}} = 0.69\mathrm{LogK_{ow}} + 0.22$ (Girard).[15]

Table 2. Analytical parameters for pesticides analysis directly by HPLC (UV-detection at 230 nm).

Pesticide	t_R (min)	R^2	Precision (RSD)	LOD ($\mathrm{mg\,L^{-1}}$)	Linearity range ($\mathrm{mg\,L^{-1}}$)
Simazine	4.1	0.9999	3.5	0.007	0.02–2.0
Atrazine	5.3	0.9985	4.1	0.008	0.02–2.0
Dicloran	7.1	0.9965	5.1	0.02	0.08–2.0
Metazachlor	9.3	0.9972	4.8	0.02	0.08–2.0

concentration for the mixture of pesticides [16]. Therefore, direct determination of pesticides at a concentration range of 100 to 500 $\mathrm{ng\,L^{-1}}$ using the outlined method is not possible because the instrument detection limits were much higher than the demanded concentration range. To overcome this analytical problem, two options could be followed: (a) applying instruments of higher sensitivity for pesticides analysis like GC-MS; and (b) preconcentration of pesticides in water samples to be detectable by HPLC. Due to its simplicity and lower operational costs, the second option was adopted in this work.

3.3 *Optimised conditions for extraction of pesticides using MWCNTs*

To ensure high preconcentration levels of pesticides, the process of extraction by MWCNTs was optimised beforehand. After optimisation of SPE process, the characteristics of the developed analytical method could be generalised and applied for real samples containing the harmful pesticides. Sample flow rate, eluent type and volume, sample volume, and solution pH are the main factors that influence the adsorption of pesticides by MWCNTs.

In SPE procedure, it is necessary to elute all the adsorbed analytes on the adsorbent surface to obtain the highest recovery. Different elution efficiency would be obtained when different eluting solvents are used because of the physical and chemical properties of the involved organic solvents and the characteristics of the extractant. Four common solvents including methanol, acetone, toluene, and ethyl acetate were tested as elution media for pesticide desorption. The solvents were carefully selected due to the good solubility of the pesticides in these solvents as indicated in Table 1. Results of studying the effect of type of eluting solvent, under appropriate experimental conditions, are presented in Figure 1. The experimental results indicate that methanol and acetone were the best elution media, however, methanol was selected as eluent in all subsequent experiments due to its lower cost and availability in our laboratory.

The eluent volume is an important factor for pesticide preconcentration and was investigated through a series of experiments. The results are given in Table 3. A volume of 8.0 mL methanol could completely satisfy the requirements for analysis, so 8.0 mL methanol was selected as the optimum elution volume in the following experiments. The influence of the extraction flow rate and elution rate on preconcentration was studied over different values. Up to an extraction flow rate of 3.0 $\mathrm{mL\,min^{-1}}$ and an elution flow rate of 1.5 $\mathrm{mL\,min^{-1}}$, quantitiative recoveries for all pesticides were achieved. Accordingly, 3.0 and 1.5 $\mathrm{mL\,min^{-1}}$ were chosen as the optimum extraction and elution flow rates.

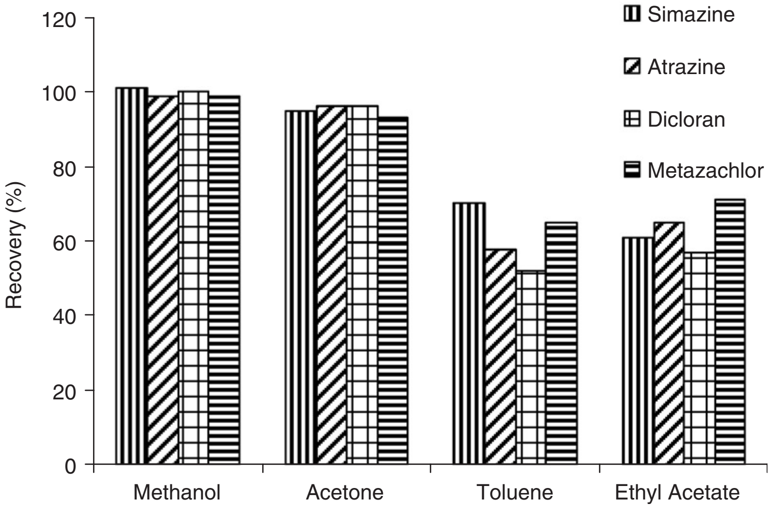


Figure 1 Effect of type of eluting solvent on recovery of pesticides.
Notes: Mass of MWCNTs: 300 mg, individual pesticide concentration 100 ng L^{-1}, eluent volume: 8.0 mL, extraction rate: 3.0 mL min^{-1}, elution rate: 1.0 mL min^{-1}, pH: 5.0, sample volume: 700 mL.

The sample volume also has a high influence on the extraction performance and preconcentration factor [17]. In the current study it was varied over a wide range: 700–1300 mL and the results were given in Table 3. As can be seen, MWCNTs extractant exhibited outstanding enrichment capacity for all pesticides. Quantitative recoveries for pesticides were obtained for all studied sample volumes. In order to reduce the analysis time and obtain a high enrichment factor, the 700 mL sample volume was selected as the optimum one. High preconcentration factors were obtained for pesticides in this study. The preconcentration factor (*PF*) for the solute can be estimated from the initial (V_i) and final (V_f) volumes as follows [17]:

$$\text{Preconcentration Factor } (PF) = \frac{V_i}{V_f} \tag{2}$$

where V_i and V_f are the initial sample volume (volume before preconcentration) and the final volume obtained after preconcentration. It is important to mention that Equation (2) only applied when the extraction recovery for the solute is very high (>99). For lower extraction recoveries, the *PF* value for the solute can be calculated as:

$$\text{Preconcentration Factor } (PF) = \frac{V_i}{V_f} \times \text{extraction recovery} \tag{3}$$

In the current extraction system, V_i varied from 700 to 1300 mL while V_f was always constant (500 µL). As indicated in Table 3, quantitative recoveries ($>99\%$) for all pesticides were obtained at the studied sample volumes. Accordingly, *PF* values of 1400, 1800, 2200, and 2600 were obtained for sample volumes of 700, 900, 1100, and 1300 mL, respectively, as calculated from Equation (2). In fact, the high *PF* reflected the excellent extraction efficiency of MWCNTs for pesticides. The pH of the solution has an important effect on the extraction of pesticides because this variable determines the ionization degree of analytes and

Table 3. Influence of various parameters on the preconcentration recovery of 100 ng L^{-1} of pesticides using MWCNTs.

	Preconcentration recovery (%)*			
Parameter	Atrazine	Dicloran	Metazachlor	Simazine
Eluent volume (mL)[1]				
2.0	45.0	59.0	63.0	72.0
4.0	76.0	72.0	78.0	90.0
6.0	94.0	90.0	92.0	96.0
8.0	> 99.0	> 99.0	> 99.0	> 99.0
10.0	> 99.0	> 99.0	> 99.0	> 99.0
Extraction flow rate (mL min^{-1})[2]				
1.0	> 99.0	> 99.0	> 99.0	> 99.0
3.0	> 99.0	> 99.0	> 99.0	> 99.0
5.0	92.0	89.0	91.0	95.0
7.0	83.0	79.0	84.0	86.0
9.0	77.0	69.0	73.0	64.0
Elution flow rate (mL min^{-1})[3]				
0.5	> 99	> 99	> 99	> 99
1.0	> 99	> 99	> 99	> 99
1.5	> 99	> 99	> 99	> 99
2.0	96.0	92.0	90.0	90.0
Sample volume (mL)[4]				
700	> 99.0	> 99.0	> 99.0	> 99.0
900	> 99.0	> 99.0	> 99.0	> 99.0
1100	> 99.0	> 99.0	> 99.0	> 99.0
1300	> 99.0	> 99.0	> 99.0	> 99.0
Solution pH[5]				
3.0	> 99.0	> 99.0	> 99.0	> 99.0
5.0	> 99.0	> 99.0	> 99.0	> 99.0
7.0	> 99.0	> 99.0	> 99.0	96.3
9.0	79.0	82.0	84.0	67.0
10.0	62.0	68.0	73.0	52.0
Mass of MWCNTs (mg)[6]				
100	50.0	66.0	67.0	79.0
200	88.0	89.0	84.0	94.0
300	> 99.0	> 99.0	> 99.0	> 99.0
400	> 99.0	> 99.0	> 99.0	> 99.0

Notes: [1] Mass of MWCNTs: 300 mg, extraction rate: 3.0 mL min^{-1}, elution rate: 1.0 mL min^{-1}, pH: 5.0, sample volume: 700 mL; [2] Mass of MWCNTs: 300 mg, eluent volume: 8.0 mL, elution rate: 1.0 mL min^{-1}, pH: 5.0, sample volume: 700 mL; [3] Mass of MWCNTs: 300 mg, eluent volume: 8.0 mL, extraction rate: 3.0 mL min^{-1}, pH: 5.0, sample volume: 700 mL; [4] Mass of MWCNTs: 300 mg, eluent volume: 8.0 mL, extraction rate: 3.0 mL min^{-1}, elution rate: 1.0 mL min^{-1}, pH: 5.0; [5] Mass of MWCNTs: 300 mg, eluent volume: 8.0 mL, extraction rate: 3.0 mL min^{-1}, elution rate: 1.0 mL min^{-1}, sample volume: 700 mL; [6] Eluent volume: 8.0 mL, extraction rate: 3.0 mL min^{-1}, elution rate: 1.0 mL min^{-1}, pH: 5, sample volume: 700 mL; *Values reported were average of triplicate measurements (RSD: 4–8 %).

accordingly their extent of extraction. In the current study, the effect of pH was investigated over a wide range: 3–10. The results in Table 3 indicate that there was no significant influence of pH on enrichment of pesticides within the pH range: 3–7. Modest recoveries were obtained at pH > 7, and this was obvious for simazine where the reported recovery at pH 10 was only 52 %. The poor recoveries of pesticides at pH > 9 were attributed to the instability of these pesticides at basic conditions. In fact, at these conditions the studied pesticides undergo hydrolysis [14]. In order to achieve the maximum enrichment efficiency for pesticides, sample pH was adjusted to pH 5.0 in the extraction experiments. The effect of amount of adsorbent on pesticides extraction was examined in the range 100 to 400 mg. The results in Table 3 indicate quantitative recoveries of pesticides in the range of .300 to 400 mg. Hence, 300 mg of MWCNTs adsorbent was selected as the optimum mass of extraction.

3.4 *Comparison between MWCNTs and other common pesticides extractants*

The enrichment power of MWCNTs toward pesticides was compared with other popular extractants that are frequently employed for pesticides extraction. In fact, few comparison studies have been carried out on the extraction efficiency of common pesticides extractants. The tested extractants were C_{18} bonded silica (Isolute-SPE C_{18}) and graphitized carbon black (Superclean-Envicarb). Both extractants were investigated for enrichment of many common pesticides prior to their analysis by HPLC/UV [9,16–18]. The extraction recoveries for pesticides as obtained from triplicate determinations are presented in Figure 2. Relatively speaking, MWCNTs and C_{18} exhibited high enrichment capacities for the studied pesticides, however, MWCNTs can be considered as an outstanding extractant because quantitiative recoveries were obtained for all pesticides. The reported results agreed with the results reported by Zhou and coworkers [10,11,19]. The previous authors showed that MWCNTs have an outstanding capacity for preconcentration of many pesticides and their metabolites from pure and real water

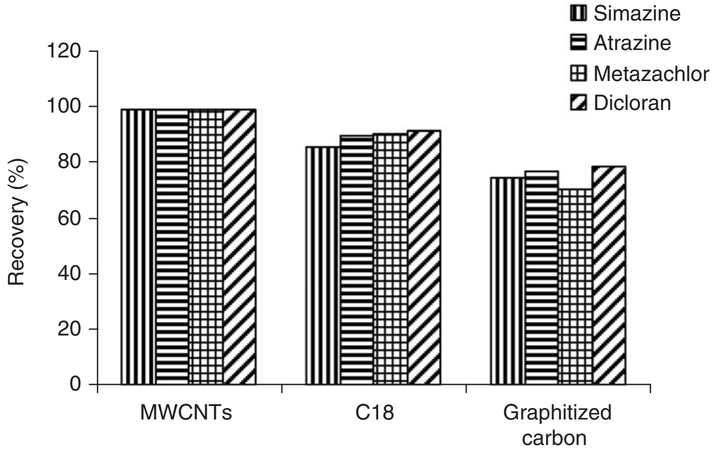


Figure 2 Recovery of pesticides using different extractants.
Notes: Mass of extractant: 300 mg, flow rate: 3.0 mL min^{-1}, elution medium: methanol, elution flow rate: 1.0 mL min^{-1}, pH: 5.0, sample volume: 700 mL, and individual pesticide concentration 100 ng L^{-1}. Values reported were average of triplicate measurements (RSD: 2–5%).

Table 4. Analytical parameters for SPE-HPLC analytical method developed for trace analysis of pesticides.

Pesticide	r^2	Precision (RSD, $n = 5$)	LOD (ng L^{-1})	Liner range (ng L^{-1})
Simazine	0.9982	2.5	5.0	15–1000
Atrazine	0.9932	3.3	6.0	15–1000
Metazachlor	0.9945	2.7	15.0	60–1000
Dicloran	0.9994	4.6	15.0	60–1000

samples. In fact, graphitized carbon black is not recommended for extraction of the studied pesticides because the obtained recoveries were modest (70.2–78.5%).

3.5 *Analytical parameters for pesticides analysis using SPE-HPLC method*

A number of experiments were carefully carried out for determining the important values, such as limits of detection, precision and linear ranges. The obtained results are given in Table 4. The detection limits of pesticides (estimated on the basis of a signal-to-noise ratio of 3) were within the range 5–15 ng L^{-1}. The results indicated that MWCNTs adsorbent has an outstanding enrichment efficiency for pesticides where analysis can go beyond the limit proposed by the European legislation (100–500 ng L^{-1}). The experimental results also indicate an excellent linear relationship over the concentration range of 15–1000 ng L^{-1} for simazine and atrazine and from 60 to 1000 ng L^{-1} for metazachlor and dicloran. The obtained correlation coefficients were in the range 0.9932 to 0.9994. The reported detection limits of atrazine and simazine were 40 times lower than those reported using heat-treated diatomaceous earth [13]. Precision was determined by performing five identical determinations of pesticides mixture containing 100 ng L^{-1} under the optimum extraction conditions. The RSD values for simazine, atrazine, metazachlor, and dicloran were 2.5, 3.3, 2.7, and 4.6, respectively. Statistical analysis showed that the proposed method has a high stability and can be adopted for determination of these four pesticides at trace levels in real water matrixes.

3.6 *Determination of the pesticides in real water samples*

Obviously, the next step was to determine how well the proposed analytical method will do when applied to the analysis of the pesticides in natural water samples. Blanks of tap and well waters were subjected to the proposed analytical method and the results revealed the absence of the pesticides in samples. 700 mL of each water sample was spiked with 100 ng L^{-1} of each individual pesticide and subjected to the extraction method and finally analysed by the proposed HPLC method. Figure 3, shows the chromatographic results obtained from analysis of well water before and after spiking with pesticides. The obtained recoveries of pesticides from natural water samples were given in Table 5. As indicated, the obtained recoveries for pesticides were from 93 to 95 % in tap water and from 85 to 87% in well water. RSD values for both systems were satisfactory ($\leq 6\%$). The proposed method has a good validity for simultaneous determination of simazine, atrazine, metazachlor, and dicloran in complex water samples. Relatively speaking, the obtained recoveries

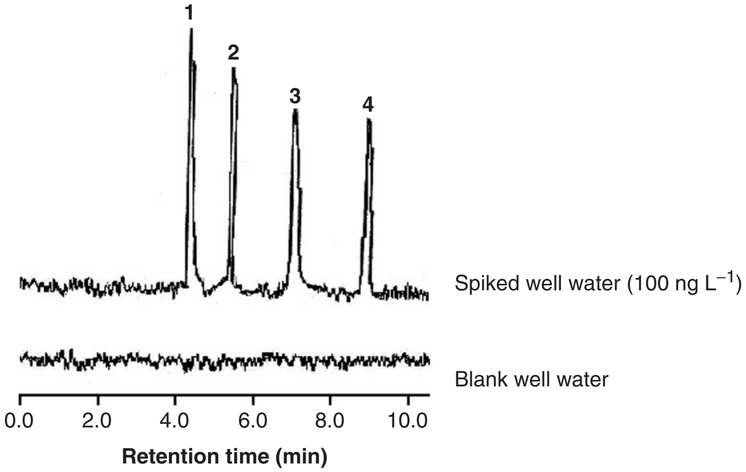


Figure 3 Chromatograms obtained from analysis of well water before and after spiking with pesticides.

Notes: Preconcentration conditions: Spiked level 100 ng L^{-1}; sample volume: 700 mL; eluent volume: 8.0 mL; flow rate: 3.0 mL min^{-1}; elution flow rate: 1.0 mLmin^{-1}; pH: 5.0. (1) simazine, (2) atrazine, (3) dicloran, (4) metazachlo.

Table 5. Obtained recoveries of pesticides from different water samples using MWCNTs[1].

		Tap water		Well water	
Mixture	Added (ng L^{-1})	Found (ng L^{-1})	Recovery (RSD)[2]	Found (ng L^{-1})	Recovery (RSD)[2]
Simazine	100	94.7	94.7(4.1)	84.7	84.7(3.8)
Atrazine	100	93.3	93.3(3.8)	85.3	85.3(5.1)
Metazachlor	100	92.7	92.7(2.9)	87.0	87.0(5.6)
Dicloran	100	95.3	95.3(4.5)	86.2	86.2(6.0)

Notes: [1] Added concentration: 100 ngL^{-1}, sample volume: 700 mL, eluent volume: 8.0 mL, flow rate: 3.0 mL min^{-1}, elution flow rate: 1.0 mLmin^{-1}, and pH: 5.0; [2] Average of three trials.

of pesticides in well water was lower compared to those obtained for tap water which was attributed to the high complexity of the well water sample.

4. Conclusions

A sensitive analytical procedure was developed for trace analysis of four common pesticides in water using solid-phase extraction coupled with HPLC. The results proved that multi-walled carbon nanotubes adsorbent has an outstanding ability for preconcentration of the pesticides at trace levels from solution. A preconcentration factor of 1400 was obtained at the optimum extraction conditions. Higher preconcentration factors (up to 2600) were obtained at larger sample volumes; however, the time of analysis increased significantly. The proposed analytical method achieved detection limits in the range 5–15 ng L^{-1}. A successful extraction of 100 ng L^{-1} of the pesticides from natural waters was reported with recoveries from 93 to 95% for tap water and from 85 to 87% for well water.

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