



## The Dispersive Liquid–Liquid Extraction Method Coupled with HPLC and its Application in Determining S-triazine Group of Herbicides in Soil Samples

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### ABSTRACT

The dispersive liquid-liquid extraction (DLLE) is an environmentally benign process, which is based on simple, sensitive and rapid sample pre-treatment technique, coupled with HPLC-UV. This unique method has been designed for the separation of s-triazine as a herbicide residue in environmental soil samples. The influencing parameters which have been used to optimize the extraction efficiency include type, extraction solvent (ES) volume, dispersive solvents (DS), extraction time (mainly centrifugation time), pH, ionic strength for the addition of different salts. Firstly, tetrachloroethane was taken as extraction solvent (ES) to extract pesticide residues from target samples. Furthermore, acetonitrile acted as dispersive solvent in the DLLE method. The value of linearity that has been reported with concentration range of 0.05-200  $\mu\text{gL}^{-1}$ , and value of correlation coefficient ( $r$ ) lies in between 0.9997. The recovery of the herbicide from three soil samples spiked between 20 and 100  $\mu\text{gL}^{-1}$  were in the recovery in between the range 88.02% to 95.90.0% and the relative standard deviations (RSDs) were 2.7%. Limit of quantitations (LOQs) obtained in this method was 0.09  $\mu\text{gL}^{-1}$ . These results significantly revealed that DLLE is a very accurate and reliable method to estimate the desired pesticide, even at trace amounts, in soil samples.

**Keywords:** Dispersive liquid-liquid extraction, HPLC-UV, Herbicide, Soil.

### INTRODUCTION

Some common agro-chemicals extensively applied in agricultural field for the improvement of production of vegetables, result in great environmental concerns. The spread of problem is serious as over insecticide, fungicide and herbicide applied in the field of agriculture and may found at far distance affecting the non-target species such as air, water, soil and vegetable<sup>1-3</sup>. Development of resistance to pest clean of unwated grass in

the timee of cultivation is another big problem. Now several new pesticides have been generated or greater dose of pesticide is administrated to counteract the pest resistance. In order to protect the lives on earth and to maintain the ecological balance, pesticide application must be regulated on utmost necessary, at least to control misuse. Now, determination of pesticide in water, soil and vegetable matrices proceeds in two-step processes like transfer of solute from parent solution to some desirable phase enrichment of solute to reach the



desired level of detection limit and the analyte was transferred from aqueous phase to highly dense extraction solvent phase followed by its determination.

There are individual common analytical extraction methods like LLE (liquid-liquid extraction)<sup>4,5</sup>, SPE (solid phase extraction)<sup>6</sup> and determination of pesticide occurred generally by chromatographic technique. The analysis mainly performed by liquid or gas chromatographic technique which depends upon nature of the analyte. The gas chromatography (GC)<sup>7-10</sup> along with MSD (Mass Spectrometric Detector)<sup>11-13</sup>, HPLC-UV detector<sup>13-14</sup>, and MSD<sup>15,16</sup> or diode array detector (DAD)<sup>17-18</sup> also used for the identification of plethora of analytes.

Among the different new techniques, liquid-liquid extraction is widely used. This is based on the well-known Nerst distribution law. Liquid phase microextraction (LPME) is modified method of LLE which required mainly high consumption of extraction solvent. The LPME can be classified into different categories like SDME (Single Drop Micro Extraction)<sup>19</sup>, HFLPME (Hollow Fiber Liquid Phase Micro Extraction)<sup>20</sup>, DLLME<sup>21-23</sup> and cloud point extraction (CPE)<sup>24</sup>. Firstly, The DLLME<sup>25,26</sup> was reported by Rezaee *et al.*, in 2006<sup>27</sup>. This DLLME method is operationally very quick, easy, low cost and the enrichment factor is very high. Besides, compared to the reported methods, this method requires very small amount of dispersive as well as extraction solvents, the time required for equilibration is short and the extraction efficiency is significantly high. These factors raise the novelty and greater applicability of the current DLLE method. An important solvent system (ternary component) has been applied in this current method for analysis of trace amount of herbicide in soil. The present study focuses on the assess of DLLE suitability and its application to determine herbicide in environmental soil samples. To conduct these present experimental studies, the samples were collected from different layers near to the Jalangi River at Mayapur, India because the major section of the riverbank is extensively used for agricultural purposes, and the application of plant protecting chemicals i.e pesticides are also very high in amount and excess pesticides are sedimented in the soil through the flow of water. In this way, the quantity of pesticide contaminated soil near the river is also very high. The author believes that this study

discussing about the usages of DLLME method to determine herbicide in the tergate samples is firstly reported. In this report, effects of different experimental factors, for example, variety as well as volume of extraction and dispersive solvents, time of extraction, and effect of salt, have been discussed.

## EXPERIMENTAL

### Reagents and standards solutions

The herbicide, atrazine (CAS no 1912-24-9) was obtained from Sigma Aldrich (USA). Solvents used viz. CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>OH and CH<sub>3</sub>COCH<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>O were of HPLC grade (Merck, India), rest of commercially available and highly pure reagents were used to carry out the experiments. 0.01(N) HCl or NaOH were used for maintaining the pH of the solution. The purification of water was processed by using a Milli-Q system (Millipore, Bedford, MA, USA). Solvents were filtered using 0.45 μm membrane filter to filtrate colloidal particles and inorganic elements for HPLC sample preparation. This type of membrane filter was also applied to filtrate supernate i.e acetonitrile extract and an aliquot of that extract was subjected to the DLLE method.

### Preparation of Sample

Samples (soils) used to perform the experiments, were accumulated from the agricultural field near to the bank of the Jalangi river at Mayapur near (latitude: 23.4250146 and longitude 88.3906705), Nadia, West Bengal, India (Fig. 1, marked in pink coloured circle on the map). Mayapur is situated adjacent to Nabadwip West Bengal, at the confluence of two rivers, Jalangi and Bhagirathi.

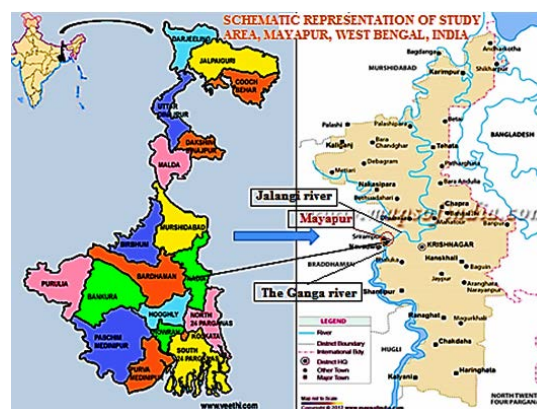


Fig. 1. Schematic representation of study area, Mayapur, Nadia, West Bengal, India.

At first soil were dried under air, pulverized and sieved to sequentially grain size 250  $\mu\text{m}$ . Accurately 1.0 g soil samples were weighed and shaken at 120 rpm for 1 h in a 250 mL conical flask using 200 mL mixture of acetonitrile (1%) and Q-Millipore water. The solutions used in this experiment were centrifuged at the speed of 800 rpm for 15 min and subsequently filtered by using 0.45  $\mu\text{m}$  membrane. Thus, soil samples containing large amounts of small diameter colloidal particles turbidity and leaching concentration of inorganic hazardous elements were filtered during preparation of stock solutions.

### Instrumentation

The chromatographic analysis was performed on Cecil (model CE 4201PC) HPLC coupled with Shimadzu UV-Vis recording spectrophotometer using manual injector having capacity 20  $\mu\text{L}$ . The analytes were separated on Hyper-clone 5  $\mu\text{m}$  ODS (C18), 120A (150 X 4.60m: particle size 5  $\mu\text{m}$ ) fitted with quaternary pump were applied to separate the analytes using acetonitrile: water [(90:10,v/v)] as a mobile phase at flow rate of 1.0  $\text{mL}\cdot\text{min}^{-1}$ . The column temperature and the detector wavelength ( $\lambda_{\text{max}}$ ) were adjusted at 30°C and 220 nm respectively. The volume of the solvent used for injection was 20  $\mu\text{L}$ . Rotofix centrifuge was used for phase separation. A Systronics, India: model no 335 digital pH meters combined with glass electrode was also used.

### Procedure of Dispersive Liquid-Liquid Extraction

5.0 mL of aqueous sample was transferred into a 10 mL glass test tube with screw cap and having conical bottom. To obtain the best extraction result, dispersive solvent (DS) acetonitrile (0.1 mL) was used, which was homogenised with a 0.9 mL of tetrachloroethane as extraction solvent (ES) and this aliquot was quickly added to the sample solution using a dispovan medical syringe. On gentle shaking, a hazy solution appeared first forming fine droplets. To obtain the extreme extraction, this mixture was centrifuged at the speed of 4000 rpm for 5 minutes. The fine droplets were allowed to settle, and the upper phase was withdrawn using a micro syringe. The sediment phase diluted with acetonitrile, was run through HPLC-UV for solute characterization and subsequent spectrophotometric determination.

### Mathematical Representation: Enrichment Factor (EF) and Recovery Percent (RP)

To explain the effects of experimental parameters, enrichment factor (EF) and extraction recovery (EP) the following equations were used;

$$\text{Enrichment factor (EF)} = C_{\text{sed}}/C_o \quad (1)$$

$$\text{Recovery percentage (RP)} = (W_{\text{sed}}/o) \times 100 = (C_{\text{sed}} V_{\text{sed}}/C_o V_o) \times 100 \quad (2)$$

Where,  $C_{\text{sed}}$ ,  $V_{\text{sed}}$  &  $W_{\text{sed}}$  are concentration, volume and amount of solute in sediment phase,  $C_o$ ,  $V_o$  &  $W_o$  represent concentration, volume and solute amount in aqueous phase. The equation (3) was obtained by combining equations (1) and (2), where EF and RP can be related as.

$$\text{RP} = \text{EF} \times (V_{\text{sed}}/V_o) \times 100 \quad (3)$$

## RESULTS AND DISCUSSION

DLLE miniaturized form of liquid-liquid extraction where milliliter volumes of extraction solvent (more dense solvent) were used for extraction of target analytes from solution. The Distribution coefficient (K) was stated as the ratio of the analyte concentrations in extraction solvent and sample solution respectively. This DLLE method was suitable for analytes having moderate to high lipophilic character and not suitable for neutral highly hydrophobic analytes. A very crucial point to be noted here that the distribution coefficient of acidic and alkaline analytes were enhanced by maintaining pH of that analytes whereas analytes remained in nonionic form. In DLLE, solute remains in water solution. A couple of dispersive solvent and extraction solvent were injected with a dispovan syringe to the sample solution. The cloudy appearance (aqueous/DS/ES) was seen and finally this dispersed droplets of ES sedimented at the bottom of the tube, were used for chromatographic detection. The extraction efficiency significantly depended on the types as well as volumes of extraction and dispersive solvents, the extraction time, pH and ionic strength of the sample solution. This study focused on the assess of DLLE suitability to determine pesticide as well as herbicide concentrations specially atrazine concentrations in soil samples. The parameters affecting the extraction efficiency were also optimized.

### Choice of extraction solvent

In this efficient method, choice of extraction solvent was very important factor. The extraction solvent must have higher density than water, good chromatographic nature and extremely well to extract analytes. Based on these criteria, in this study four chlorinated solvents viz.  $\text{CCl}_4$  ( $1.59 \text{ gmL}^{-1}$ ),  $\text{CH}_2\text{Cl}_2$  ( $1.33 \text{ gmL}^{-1}$ ),  $\text{CHCl}_3$  ( $1.47 \text{ gmL}^{-1}$ ) and  $\text{C}_2\text{H}_2\text{Cl}_4$  ( $1.60 \text{ gmL}^{-1}$ ) were examined and  $\text{CCl}_4$  acted as non polar extraction solvent. In each experiment, 0.3 mL of DS and 0.7 mL of ES were injected. The effect of the extraction solvents on the recoveries using different combination dispersive solvents was shown in Fig. 2. It was observed that  $\text{C}_2\text{H}_2\text{Cl}_4$  in combination with acetonitrile provided the highest extraction efficiency. Therefore,  $\text{C}_2\text{H}_2\text{Cl}_4$  was selected as an extraction solvent

### Choice of dispersive solvent

The solvents like  $\text{CH}_3\text{CN}$  ( $786.00 \text{ kgm}^{-3}$ ),  $\text{CH}_3\text{OH}$  ( $791.80 \text{ kgm}^{-3}$ ),  $\text{CH}_3\text{COCH}_3$  ( $791.00 \text{ kgm}^{-3}$ ) and  $\text{C}_4\text{H}_8\text{O}$  ( $889.20 \text{ kgm}^{-3}$ ) are capable of miscible with water and ES and DS are very important factor for improvement of extraction. Combinations of ES ( $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_2\text{H}_2\text{Cl}_4$ ) and DS ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{COCH}_3$  and  $\text{C}_4\text{H}_8\text{O}$ ) were tested. The 0.3 mL of DS containing 0.7 mL of ES was dispersed to the sample solution. For each dispersive solvent, all four extraction solvents were combined and examined. The result indicated that  $\text{CH}_3\text{CN}$  showed the best performance than other DS. Finally, the  $\text{C}_2\text{H}_2\text{Cl}_4$ - $\text{CH}_3\text{CN}$  selected as the best ES-DS combination for the extraction of herbicide (atrazine) by DLLLE method which is shown in Fig. 2. The combination of extraction solvents with dispersive solvents produced a two-phase system and this effect on extraction recovery was shown in Fig. 2. It was noticed that, acetonitrile gave the best extraction efficiency and therefore, acetonitrile was opted as the dispersive solvent for subsequent studies.

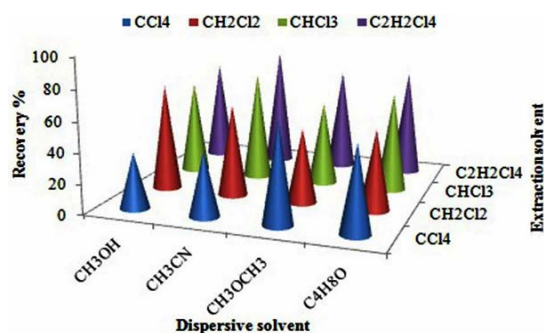


Fig. 2. Selection of different kinds of extraction-dispersive solvents combination for recovery of atrazine where 0.3 mL of dispersive solvent containing 0.7 mL extraction solvent used for selection. Sample volume 5.0 mL each case

### Influence of extraction solvent volume

In this study, volume of extraction solvent varied from 0.1 mL to 1.5 mL. When less than 0.1 mL volume of  $\text{C}_2\text{H}_2\text{Cl}_4$  was used no sediment appeared. Analyte must have better extractability in ES, compared to the water i.e., ES must be hydrophobic in nature. The ternary phase formation is an important parameter for selection of ES. To observe the effect of ES volume on recovery of analyte, the volume varied in the range 0.1 mL to 1.5 mL for a fixed volume of acetonitrile (0.1 mL) as DS which was shown in Fig. 3. Recovery percentage increased with increase of ES volume for at fixed volume of DS. After reaching the maxima, the recovery percent decreased with the increase of ES volume.

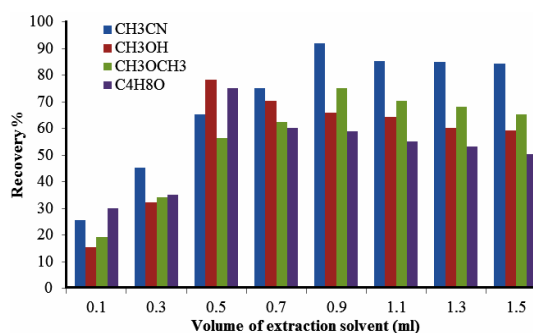
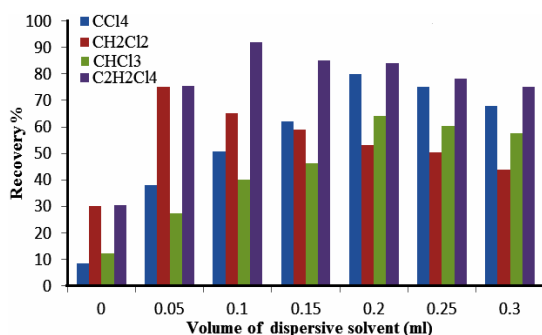


Fig. 3. Influence of ES volume on the RP of atrazine with variation of dispersive solvent, when  $\text{C}_2\text{H}_2\text{Cl}_4$  act as an extraction solvent optimum volume at 0.9 mL for its fixed volume of dispersive solvent 0.1 mL. Sample volume 5.0 mL

### Influence of dispersive solvent volume

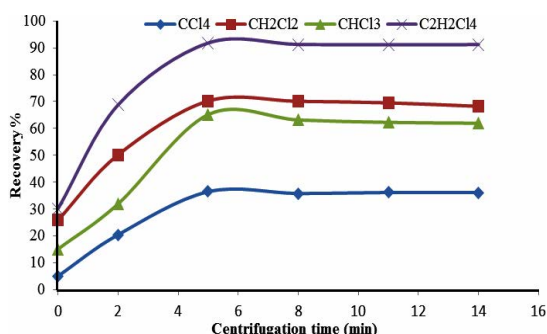
It was minutely observed that when the volume of acetonitrile changed from 0.0 to 0.3 mL, the trend of recovery increased upto 0.1 mL then decreased Fig. 4. Therefore, it is definite that the minimum volume of DS for highest recovery is 0.1 mL for atrazine extraction. Such difference of extraction-dispersive volume for pesticide recovery may be explained from the difference in extractability arises due to solubility, dispersibility and cloud formation ability. At fixed volume of ES, percent recovery of pesticide was lower and at higher volume of DS, it was found lower recovery percent. Without DS, the analyte could not disperse into ES properly and inhibited the formation of the cloudy solution resulting incomplete or poor extraction. At higher volume of DS, however, due to dilution effect extraction becomes less. Thus, the optimum volume of ES 0.9 mL and DS for atrazine extraction were 0.9 mL and 0.1 mL respectively.



**Fig. 4.** Influence of DS volume on RP of atrazine with variation of ES volume (0.9 mL) when CH<sub>3</sub>CN act as dispersive solvent. Sample volume, 5.0 mL

### Influence of extraction time

Extraction time referred to the time interim between injecting the DS and ES before starting to centrifuge. The extraction time was in the range upto 50.0 minute. Result showed that extraction time has minimum influence on extraction efficiency of DLLE. The effect of extraction time was studied over the time range between 1.0 and 15.0 min at an 2.0 min interval at an centrifugation speed 4000 rotation per min (rpm). These present results indicated that the extraction time was very short and equilibrium state attained quickly. Thus the extraction time has no impact on the extraction recoveries. The optimum extraction time i.e., centrifugation time (CT) was 5.0 min shown in Fig. 5. To accelerate the phase separation process, a centrifuge was used, and this process consumed less time. Unwanted long centrifugation was avoided because this might disturb the phase separation due to heat generation and might dissolve the analyte.

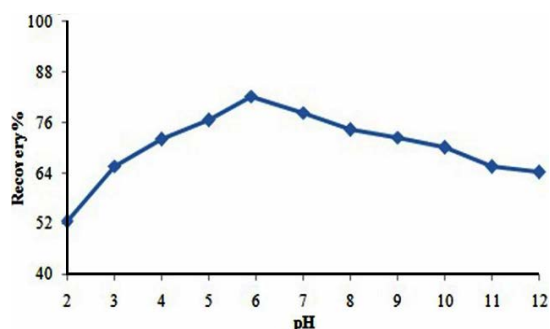


**Fig. 5.** Influence of centrifugation time (CT) with recovery percent of atrazine residue with variation of different extraction solvent, when acetonitrile act as DS volume (0.1 mL) and ES volume (0.9 mL) in each case. Sample volume 5.0 mL centrifugation speed 4000 rpm

### Influence of pH on extraction

pH of experimental solution is a very

significant factor in this extraction process containing acidic or basic analytes. To investigate the effect of pH on the extraction efficiency of DLLE, we took a limit range 2 to 12 in one pH interval. The sample solution was adjusted to such a pH that analytes extraction was very effective. The pH was adjusted with dropwise addition of 0.01(N) NaOH and HCl. It demonstrated that the proposed method significantly improved the detection sensitivity compared with other techniques were shown in Fig. 6. Results showed that the recovery of atrazine increases by increasing pH from 2 to 6.1, when mixture of CH<sub>3</sub>CN acts as disperser and C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> extraction solvent give best performance. However, subsequent increase in pH led to a decrease in extraction efficiency. It was observed that pH of the solution was 6.1 and which was optimum for extraction.



**Fig. 6.** Role of pH on recovery of atrazine when sample volume 5.0 mL; extraction solvent, 0.9 mL C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (ES); 0.1 mL CH<sub>3</sub>CN (DS)

### Influence of salt addition

Addition of salt often ameliorates extraction in conventional LLE, because of the salting out effect. To evaluate the possibility of the salting out effect, extraction recovery of herbicide by DLLE was studied range of 0-12.5% (w/v) of salt. It was found that recovery increases in the order, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>>KNO<sub>3</sub>>KCl>NaCl. In this study, all experiments were performed repeatedly. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> shows better performance than other. Increasing (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> amount more than 2.5%w/v causes a small decrease in the extraction recovery of atrazine shown in Fig. 7. Therefore, 2.5% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>(w/v) was optimum concentration used in this experiment. Each case the sample volume is 5.0 mL.

### Quantitative analysis

The important parameters obtained from the experimental results, implied for the validity of this method. For test of efficiency of herbicide extraction

a series of working solution were prepared. Each concentration level was repeatedly used in this extraction procedure. The linearity was range of 0.05-200 $\mu\text{gL}^{-1}$ . The correlation coefficient symbolized by 'r' = 0.9997. The observed LOD of this method was 0.03 $\mu\text{gL}^{-1}$ , the enrichment factors ranged above 600, with RSDs was from 2.7% and the recoveries ranged from 93.25% to 98.59% Table 1.

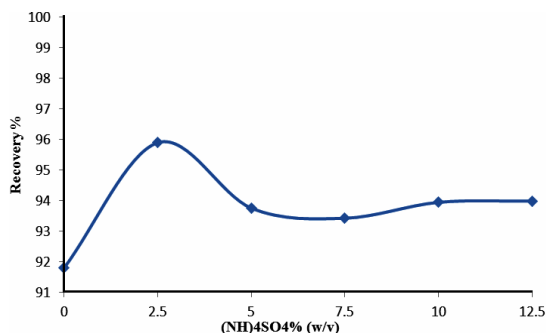


Fig. 7. Influence of ionic strength of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>%(w/v) on recovery of atrazine. When sample volume 5.0 mL; 0.9 mL C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (ES); 0.1 mL CH<sub>3</sub>CN (DS)

**Real sample analysis**

Three soil samples were collected from three different layers near to the Jalangi River at Mayapur. The source of this river is Padma (Jalangi) and mouth is Bagirati (Mayapur) near about 250 km. It flows over the district Murshidabad and Nadia. The

results of these recovery results obtained from soil samples were given in Table 2. The recovery values obtained were very satisfactory. HPLC-UV detection, CH<sub>3</sub>CN: H<sub>2</sub>O [90:10(v/v)] used as mobile phase, passed with flow rate of 1.0 mLmin<sup>-1</sup> for 3.0 minute. The detector set at wave length ( $\lambda_{\text{max}} = 220$ ), injection volume: 20 $\mu\text{L}$ , retention time 01:25.3 (mm:ss), 01:27.3 (mm:ss) where starting time 01:22.2 (mm:ss), 01:26.1(mm:ss) and end time 01:26.1 (mm:ss), 01:29.0(mm:ss) where peak area 6.4 (mAs), 5.9(mAs) and peak height 3.2(mA), 3.2(mA) respectively for acetonitrile. It was also observed that to investigate the analyte in solution showed sharp peak at retention time 01:47.7 (mm:ss), where starting time 01:42.2 (mm:ss) to ending time 01:55.8 (mm:ss). In experimental conditions, the peak height 13.4 (mA) and peak area are 77.8 (mAs) respectively for the determination of chromatogram of atrazine. The soil sample was spiked at concentration of 20, 50 and 100  $\mu\text{gL}^{-1}$ . The results were shown in Table 2. The method provides good repeatability and high relative recoveries of herbicide from environmental samples (soil samples) were above 88.0%. The Fig. 8. showed the chromatograms of atrazine in. The chromatographic analysis was performed on Cecil (model CE 4201PC) HPLC coupled with Shimadzu UV-Vis recording spectrophotometer.

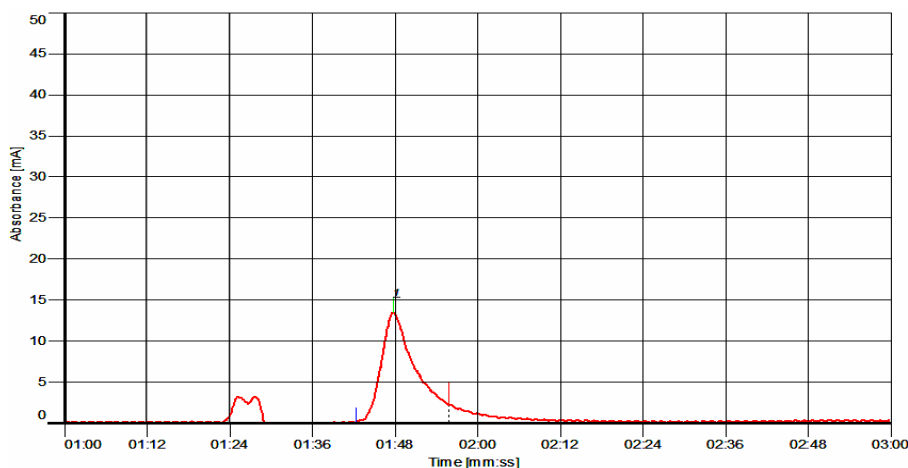


Fig. 8. HPLC Chromatogram of the atrazine, CH<sub>3</sub>CN: H<sub>2</sub>O [90:10 (v/v)] passed with flow rate of 1.0 mLmin<sup>-1</sup> for 3.0 minute. The detector set at wavelength ( $\lambda_{\text{max}} = 220$ ), injection volume: 20  $\mu\text{L}$

**Table 1: Linear range, correlation coefficient (r) recovery percent, precision and LOQ and LOD of this proposed method**

| Herbicide | LR* ( $\mu\text{gL}^{-1}$ ) | CR#(r) | Recovery(%) | Precision (RSD, %, n = 3) | LOQ ( $\mu\text{gL}^{-1}$ ) | LOD ( $\mu\text{gL}^{-1}$ ) |
|-----------|-----------------------------|--------|-------------|---------------------------|-----------------------------|-----------------------------|
| atrazie   | 0.05-200                    | 0.9997 | 95.90       | 2.7                       | 0.09                        | 0.03                        |

\*Linear range, # correlation coefficient

**Table 2: Recovery of the atrazine in DLLE from different spiked soil samples**

| Herbicide | Environmental samples (Soil) | Added ( $\mu\text{g L}^{-1}$ ) | Extraction ( $\mu\text{g L}^{-1}$ ) | Recovery percent |
|-----------|------------------------------|--------------------------------|-------------------------------------|------------------|
| Atrazine  | S <sub>1</sub>               | 20                             | 18.25 $\pm$ 0.04                    | 91.25 $\pm$ 0.04 |
|           |                              | 50                             | 44.53 $\pm$ 0.02                    | 89.06 $\pm$ 0.05 |
|           |                              | 100                            | 90.10 $\pm$ 0.01                    | 90.10 $\pm$ 0.02 |
|           | S <sub>2</sub>               | 20                             | 18.14 $\pm$ 0.15                    | 90.7 $\pm$ 0.07  |
|           |                              | 50                             | 45.72 $\pm$ 0.04                    | 91.44 $\pm$ 0.05 |
|           |                              | 100                            | 91.25 $\pm$ 0.24                    | 91.49 $\pm$ 0.02 |
|           | S <sub>3</sub>               | 20                             | 18.01 $\pm$ 0.02                    | 90.05 $\pm$ 0.06 |
|           |                              | 50                             | 44.01 $\pm$ 0.01                    | 88.02 $\pm$ 0.01 |
|           |                              | 100                            | 91.22 $\pm$ 0.05                    | 91.28 $\pm$ 0.03 |

**CONCLUSION**

In this work, the application of DLLE coupled with HPLC-UV was successfully discussed and applied for the extraction and determination of atrazine herbicide from soil samples. This simple and versatile method provides good enrichment factors and efficient separation and recoveries for the target analyte. In comparison to solvent extraction, it is much safer, since only a small volume of the solvent is used. Finally, experimental results clearly indicate that the DLLE method gave a swift and economical procedure for recovery of herbicide

**Table 3: Comparison of experimental results with other methods applied for atrazine herbicide determination in different matrices**

| Preconcentration technique | DSA type, volume (mL)     | ESb type, volume (mL)                               | Centrifugation Time (min) | Speed (rpm) | Linear range                   | Recovery%  | LOD <sup>c</sup>                | RSD <sup>d</sup> | Application           | Reference No. <sup>e</sup> |
|----------------------------|---------------------------|---|---------------------------|-------------|--------------------------------|------------|---------------------------------|------------------|-----------------------|----------------------------|
| DLLME-SFO-HPLC-UV          | Acetone (1.0)             | C <sub>6</sub> H <sub>5</sub> Cl (0.12)             | 5                         | 6000        | 0.2-200 $\mu\text{g L}^{-1}$   | 85.2-90.2  | 0.021-0.12 $\mu\text{g L}^{-1}$ | 1.36-8.67        | water                 | 29                         |
| DLLME-HPLC                 | CH <sub>3</sub> OH (5.50) | CH <sub>3</sub> OH (0.6)                            | 2                         | 5000        | 0.5-50 $\mu\text{g L}^{-1}$    | 69-89.8    | 0.1 $\mu\text{g L}^{-1}$        | 6.4              | Water                 | 30                         |
| DLLME-HPLC-DAD             | CH <sub>3</sub> OH (1.0)  | [C <sub>6</sub> MIM][PF <sub>6</sub> ] (0.6)        | 10                        | 3800        | 5-200 $\mu\text{g L}^{-1}$     | 67.0       | 0.46-0.89 $\mu\text{g L}^{-1}$  | 6.80-10.78       | Water                 | 31                         |
| DLLME-GC-MS                | CH <sub>3</sub> CN (1.0)  | CHCl <sub>3</sub> (1.0)                             | 5                         | 3500        | 0.5-200 ng mL <sup>-1</sup>    | 83.8-98    | 0.1 ng mL <sup>-1</sup>         | 2.9-5.6          | Water                 | 32                         |
| QuiChERS-DLLME-GC-MS       | CH <sub>3</sub> CN (1.0)  | CCl <sub>4</sub> (1.0)                              | 5                         | 5000        | 0.025-2 $\mu\text{g L}^{-1}$   | 89-114     | 19 $\mu\text{g L}^{-1}$         | 4-5              | Maize                 | 33                         |
| DLLME-SFO-GC-MS            | CH <sub>3</sub> CN (1.0)  | 1-undecanol (0.1)                                   | 5                         | 4000        | 0.01-100 ppb                   | 97.7-108.5 | 0.008 $\mu\text{g L}^{-1}$      | 0.03-5.1         | Water sugarcane water | 34                         |
| DLLME-SFO-HPLC-UV          | Acetone (1.0)             | 1-undecanol (0.3)                                   | 4                         | 5000        | 0.2-200 $\mu\text{g L}^{-1}$   | 99         | 0.05 $\mu\text{g L}^{-1}$       | 4.2              | Soil                  | 35                         |
| DLLME-HPLC-UV              | CH <sub>3</sub> CN (0.1)  | C <sub>2</sub> H <sub>5</sub> Cl <sub>4</sub> (0.9) | 5                         | 4000        | 0.05-200 $\mu\text{g mL}^{-1}$ | 95.90      | 0.03 $\mu\text{g mL}^{-1}$      | 2.7              | Soil work             | This work                  |

<sup>a</sup> Dispersive solvent, <sup>b</sup> Extraction solvent, <sup>c</sup> Detection limit, <sup>d</sup> Relative standard deviation (RSD), <sup>e</sup> reference number

from environmental sample. The recovery greater than 91% compared with other methods shown Table. 3. Finally, this developed method was successfully applied for the recovery of pesticide from different matrices.

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**Conflict of interest**

There is no conflict of interests.

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