Vortex assisted magnetic ionic liquid based dispersive liquid–liquid microextraction approach for determination of metribuzin in some plant samples with UV–Vis spectrophotometer

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ABSTRACT

A vortex assisted magnetic ionic liquid based dispersive liquid–liquid microextraction (VA-MIL-DLLME) approach was proposed using a tetrachloromanganate-based magnetic ionic liquid (MIL, as extraction solvent) for the determination and extraction of metribuzin in some plant samples by UV–Vis spectrophotometer. The MIL was prepared from a mixture of trihexyl(tetradecyl)phosphonium chloride $[P^+_{6,6,6,14}][Cl^-]$ and manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) in chloroform. Important factors for the VA-MIL-DLLME approach were optimized in detailed. The optimum conditions were: 8.0 of pH, 80 mg of the $[P^+_{6,6,6,14}]_2[MnCl_4^{2-}]$ (extraction solvent), 250 μL of ethanol (as dispersing solvent), 3 min of vortex time and 1.5 mL of 30 % NaCl (w/v) (ionic strength). Calibration graph was linear in the range of 35–800 μg L^{-1} with correlation of determination 0.995. The limit of detection, limit of quantification and enrichment factor were found to be 10.6 μg L^{-1}, 35 μg L^{-1} and 247, respectively. The VA-MIL-DLLME approach was applied for extraction and determination of metribuzin in the samples. The relative standard deviations (RSD) in the samples were less than 2.8 %. Moreover, the recoveries were obtained in the range of 91 ± 2–102 ± 3 %.

1. Introduction

In parallel with the population growth in the world, the need for food increases at the same rate. In order to meet the increasing nutritional needs, it is tried to obtain high yield per unit area in agricultural production. This is mostly possible with the use of chemicals on agricultural lands [1]. Among the most important factors affecting agricultural production are disease, pests and weeds. Pesticides are one of the chemicals used to protect agricultural products from disease, pests and weeds damage [2]. Pesticides are chemicals used to destroy undesirable organisms in agricultural products. It covers all of the chemicals classified as insecticide, herbicide, fungicide, viricide, rodenticide, acaricide, etc. [3].

Among pesticides, herbicides are the most widely used worldwide [4]. Because, crop losses caused by weeds are around 13 % every year in the world [5] and the use of herbicides in weed control has advantages such as being easy to apply, economical and giving fast results [6]. However, as a result of intensive, unconscious and erroneous use of herbicides, which are increasing in use day by day, destructions can

occur on other living things, especially on humans and cultivated plants, and in the natural environment [1]. The destruction caused by herbicides in cultivated plants can occur on the leaves, stems, flowers and fruits of the plants and may cause symptoms such as intervascular chlorosis, spotted chlorosis, yellow spotting, bruising of leaves, necrosis and stem deaths on plants. Due to such reasons caused by herbicide toxicity, the plant remains weak and thus, it is vulnerable to disease factors, pests and adverse environmental conditions, resulting in significant yield losses [7]. In addition, since the duration of action in the natural environment is long, it can take years to degradation and disappear when applied to the soil. This situation poses a threat especially for future generations.

Despite the technological advances in analytical field, most instruments are not yet able to directly analyze in the complex sample matrix. Therefore, sample preparation steps are often required prior to instrumental analysis. The main purpose of sample preparation is to separate the analyte of interest and to convert it into a form suitable for analytical systems while increasing its concentration [8]. Current research focuses on efficiency, inexpensive, and miniaturized sample

preparation methods [9]. Dispersive liquid–liquid microextraction (DLLME) is one of the most widely used sample preparation methods. The DLLME consists of two steps [10]; (1) extraction of a suitable mixture for the aqueous sample containing the analyte and injection of dispersive solvents. In this step, the extraction solvent is well dispersed in the aqueous sample as droplets and the analyte is enriched in it. The extract surface area is obtained large between the reaction solvent and the aqueous sample, the equilibrium state is reached quickly, and the extraction is time-independent. This is the most important advantage of the method. (2) centrifugation of the cloudy solution and determination of the analyte in the precipitated phase after centrifugation with an analytical instrument. The factors affecting the extraction efficiency in DLLME are as follows [11]; (1) suitable extraction solvent, (2) suitable dispersive solvent, (3) volume of extraction solvent, (4) volume of dispersive solvent and (5) pH. The selection of the appropriate extraction solvent is the main parameter in the DLLME process.

Since the use of organic solvents (extraction solvents) in DLLME studies is not environmentally friendly, the synthesis and use of new and green extraction solvents such as magnetic ionic liquid (MIL) and deep eutectic solvent has gained importance in recent years [12,13]. The MILs are an interesting alternative to organic solvents because their unique physicochemical properties depend on the nature and size of their cationic and anionic components [14]. The main advantages of MILs include negligible vapor pressures, good thermal stability, incandescent viscosities, miscibility with water and organic solvents [10]. Therefore, they are useful as extraction solvents for the DLLME technique.

In this study, a simple, fast and low cost vortex assisted magnetic ionic liquid based dispersive liquid–liquid microextraction (VA-MIL-DLLME) combined with UV–Vis spectrophotometer was proposed for the determination and extraction of metribuzin in various plant samples. Plant samples with metribuzin added were prepared artificially in our research greenhouses. The $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ was prepared with a mixture of trihexyl(tetradecyl)phosphonium chloride and manganese (II) chloride tetrahydrate in chloroform. In the VA-MIL-DLLME procedure, metribuzin in sample solution were extracted into the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ by forming a metribuzin-Ni(II) complex with Ni(II) ion. The magnetic ionic liquid was then separated from the aqueous solution with the help of a magnet. The mixture was diluted with ethanol and determined in UV–Vis spectrophotometer.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade and purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA). Stock solution of metribuzin [4-amino-6-*tert*-butyl-3-(methylthio)-1,2,4-triazine-5-one, chemical formula is $C_8H_{14}N_4OS$, molar mass is 214,29 g mol^{-1}, density is 1.31 g cm^{-1} and appearance is colorless, crystalline soil] (1000 mg L^{-1}) was prepared by dissolving its proper amount in the water. Working and calibration solutions were freshly prepared by sequential dilution of the stock solutions in the water. pH of the sample solutions was adjusted using 1 mol/L NaOH and 1 mol/L HCl solutions. Trihexyl(tetradecyl)phosphonium chloride $[P_{6,6,6,14}^+][Cl^-]$ and manganese(II) chloride tetrahydrate (MnCl$_2$·4H$_2$O) were used to prepare the magnetic ionic liquid (MIL). Acetonitrile, ethanol, acetone, and methanol were used as disperser solvents. Sodium chloride was used as the salt solution.

2.2. Instrumentation

Spectrophotometric analysis were performed using an UV-1800 Shimadzu dual-beam spectrophotometer (Tokyo, Japan) equipped with 10 mm quartz microcells. Ultrapure water (18.2 MΩ cm) was obtained by a Milli-Q water purification system (Millipore, Bedford, MA, USA) and used for the preparation of all solutions. A vortex mixer

(IKA®-Werke GmbH & Co. KG, Staufen, Deutschland, Germany), digital pH meter (Selecta 2001 Sartorius, North America), centrifuge (A Hettich Universal-320 model, London, England) and rotary evaporator (BUCHI R-200, Labortechnik AG, Flawil, Switzerland) were used to mix the solution, adjusting the pH of all solutions, accelerate the phase separation and to prepare the MIL, respectively. A neodymium magnet (1.17 T magnetic field) was used in the separation step.

2.3. Sampling and sample preparation

The research was established in 3 replications in plastic pots with a capacity of 3 kg under greenhouse conditions. Lettuce, green onion, sunflower, chickpea, red cabbage, okra and bean plants were used as test plants. Initially, 150 mg N kg^{-1}, 100 mg P kg^{-1} and 125 mg K kg^{-1} were applied to each pot as basic fertilization (in the form of CaNO$_3$·4H$_2$O, KH$_2$PO$_4$, respectively). After the plants germinated, weed pesticide application containing 70 % (w/w) metribuzin was applied 3 times at one-week intervals. In addition, a control group that did not apply any herbicide to the same plants was formed. All plants were sowed on 17 May 2021 and harvested on 05 July 2021 by cutting 1 cm above the soil surface.

The plant materials, which were dried at room temperature in the shade, were ground into powder in a laboratory-type grinder. Then, 1 g of each plant sample was weighed and 10 mL distilled water (1:10 ratio) was added to it and left to maceration on the shaker at 150 rpm for 24 h. After the maceration, filtration was done with the help of Whatman filter paper (blue band) and dry extracts were obtained by evaporating the distilled water with a rotary evaporator at 40 °C [15].

2.4. Preparation of MIL

The $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ was prepared according to the method reported with minor modifications [16,17]. The experimental steps were listed below. First, 0.75 mol/L equivalent of MnCl$_2$·4H$_2$O was carefully added to a methanolic solution of $[P_{6,6,6,14}^+][Cl^-]$ in conical tube including chloroform. Second, the tube was stirred for 24 h at room temperature so that the reaction between the added chemicals could take place. Three, the solvent was removed by rotary evaporation. Four, the obtained product $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ was dried in a vacuum oven at 50 °C.

2.5. VA-MIL-DLLME procedure

The VA-MIL-DLLME procedure was carried out as follows. First, 10 mL sample solution including 60 μg of metribuzin was spiked in 15 mL-centrifuge tube including 700 μL of Ni(II) ions (50 mmol/L). Second, the pH of the sample solution was adjusted to pH 8.0 using 1.0 mol/L NaOH solution. At this stage, chelate formation was achieved between Ni(II) ions and metribuzin. Three, 80 mg of the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL with 250 μL of ethanol (as dispersing solvent) were added to the resulting solution. Four, 1.5 mL of 30 % NaCl (w/v) solution was pipetted into the resulting solution to increase the ionic strength of the solution. Five, the tubes were vortexed for 3 min. Six, a neodymium magnet was used to collect the MIL microdroplets from the sample solution, and then the aqueous solution was drained by decantation. Seven, the collected MIL was dissolved in 250 μL of ethanol and subjected to UV–VIS spectrophotometric analysis (308 nm). All experimental were performed against aqueous standards and blank solutions.

3. Results and discussion

3.1. Optimization of the VA-MIL-DLLME procedure

Important factors for the VA-MIL-DLLME procedure including pH, mass of MIL, disperser solvent type and amount, vortex time, and the ionic strength of the sample solution were optimized in detailed.

3.1.1. Effect of pH

In the VA-MIL-DLLME, pH value of sample solution plays an important role in the extraction of analyte. Hence, the effect of pH values on the recoveries of metribuzin was tested in the range of 3.0–10.0. According to the results in Fig. 1a, metribuzin was quantitatively extracted at pH 7.0–9.0, whereas the recovery of metribuzin was not quantitative at especially below pH 6.0. The reason for the facts is that at the corresponding pH values, metribuzin can react with Ni(II) ions to form the stable and hydrophobicity complexes, which were extracted by $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$. However, Ni(II) ions fails to chelate metribuzin at especially below pH 6.0, resulting in a very low recovery. Therefore, pH 8.0 was utilized for extracting metribuzin by the VA-MIL-DLLME procedure.

3.1.2. Effect of amount of Ni(II) ions

In the VA-MIL-DLLME, it is very important to be able to form a hydrophobic complex containing metribuzin in order to achieve quantitative extraction. In this context, Ni(II) ions were used to chelate with metribuzin (Kumar et al.,2018). The effective chelate formation depends on the amount of Ni(II) ions. Therefore, the effect of the volume of 50 mmol/L Ni(II) ions on the recovery of metribuzin was investigated in the range of 200–800 μL. According to the results in Fig. 1b, recovery of metribuzin was improved by enhancing the volume from 500 μL to 700 μL and then remained almost constant. In addition, at volumes less than 500 μL, the reproducibility of the VA-MIL-DLLME procedure was not acceptable as the final step was extremely difficult to process. Therefore, 700 μL of Ni(II) ions was utilized for extracting metribuzin by the VA-MIL-DLLME procedure.

3.1.3. Effect of mass of MIL

The amount of extraction solvent was an important factor that could change the efficiency of the VA-MIL-DLLME procedure. Increasing the amount of extraction solvent provides many active sites for the extraction of the analytes, thus increasing the efficiency of the method. However, due to the increase in the amount of extraction solvent, the problem of not being able to distribute the sample solution to all parts may arise. Therefore, it is not preferred to use large amounts of extraction solvent. To carry out the quantitative extraction of metribuzin, the effect of mass of $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ on recovery was investigated within the mass range of 10–120 mg. As shown in Fig. 1c, 80 mg of the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ was sufficient for the quantitative recovery of metribuzin (>90 %). The extraction efficiency was almost constant above the mass. Therefore, 80 mg of the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ was employed for further experiments.

3.1.4. Effect of dispersing solvent type and amount

In VA-MIL-DLLME studies, a dispersing solvent was often used to effectively disperse the extraction solvent into the sample solution. In this context, the type of dispersing solvent can affect the separation
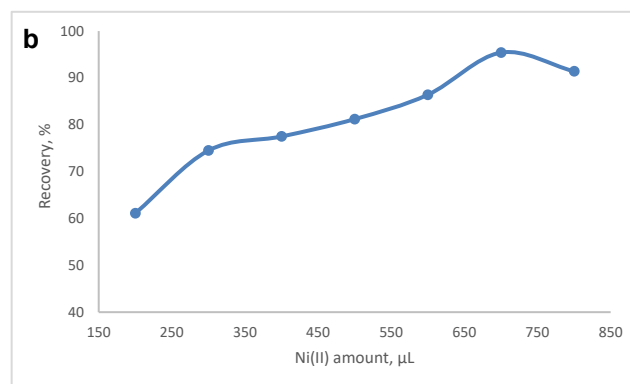
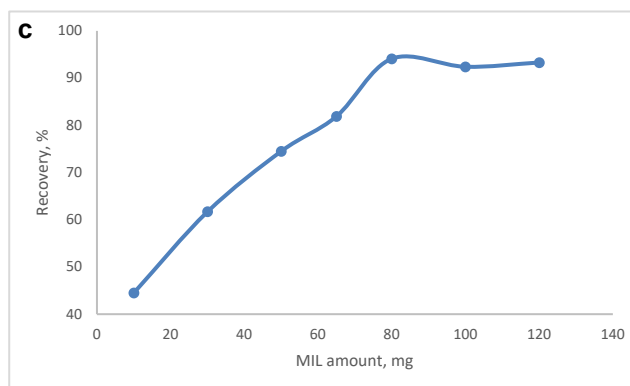**Fig. 1b.** Effect of Ni(II) amount on recovery of metribuzin.

Fig. 1c. Effect of MIL amount on recovery of metribuzin.

efficiency of the analyte. In the light of these facts, the effect of five different dispersing solvents including ethanol, methanol, acetone, THF and acetonitrile on the recovery of metribuzin was investigated. An equal volume of all dispersing solvents was used. According to the results in Fig. 1d, the best recovery was obtained in the presence of ethanol. Therefore, ethanol was selected as dispersing solvent for further experiments.

Volume of the dispersing solvent (ethanol) was another key factor that should be optimized. The volume of ethanol can change the amount of metribuzin carried from the sample solution to the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ and their solubility in the aqueous phase used in the VA-MIL-DLLME step. For this purpose, effect of ethanol volume on the recovery of metribuzin was investigated in the range of 100–600 μL. In all experiments whole of the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ was removed, mixed with ethanol and used in VA-MIL-DLLME step. According to the
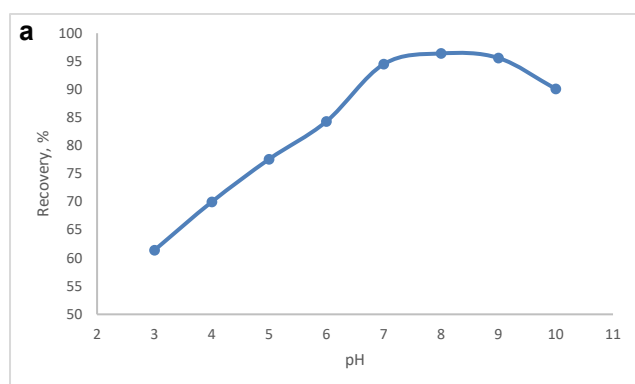
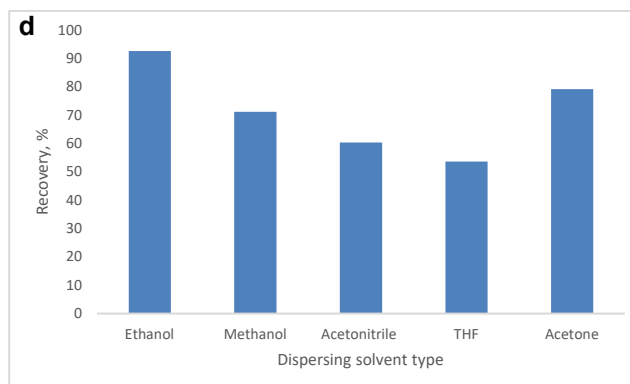**Fig. 1a.** Effect of pH of sample solution on recovery of metribuzin.

Fig. 1d. Effect of dispersing solvent type on recovery of metribuzin.

obtained results in Fig. 1e, recovery of metribuzin increase up to 250 µL of ethanol and then decrease gradually. Therefore, 250 µL of ethanol was employed for further experiments.

3.1.5. Effect of ionic strength

Generally, the ionic strength facilitates the phase separation in the VA-MIL-DLLME studies. A 30 % (w/w) NaCl solution was used to evaluate the effect of adding salt to the sample solution in the extraction step. In this context, the effect of NaCl solution volume on phase separation was investigated in the range of 0–2 mL. The results obtained were presented in Fig. 1f. While the recovery of metribuzin was 75 % in the absence of NaCI solution, it was observed that the recovery increased with the addition of NaCl and reached the highest level at 94.9 % when 1.5 mL NaCl solution was used. Therefore, 1.5 mL of 30 % (w/w) NaCl solution was used for further studies to ensure efficacy and easy phase separation.

3.1.6. Effect of vortex time

The extraction solvent must be completely dispersed in the sample solution to obtain both phase separation and quantitative analytical results. If the extraction solvent ($[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$) is effectively dispersed in the sample solution, its interaction with the complex formed (Ni-metribuzin) increases and accordingly extraction becomes easier. Thus, the effect of vortex time was investigated in the range of 1–10 min (see Fig. 1g). The results showed that the recoveries of metribuzin increased with the increase of vortex time, and then reached a plateau after 3 min. No significant change was observed in the recovery of metribuzin at vortex applications over 3 min. Therefore, 3 min vortex was utilized as the extraction time.

3.2. Analytical figures of merit

The VA-MIL-DLLME procedure for determining metribuzin in some plant samples using UV–Vis spectrophotometer was validated based on the key analytical validation parameters: working range, limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD), enrichment factor (EF), precision, extraction recovery and selectivity. The figures of merit were given in Table 1. Calibration graph was linear in the range of 35–800 µg L^{-1} with correlation of determination 0.995. Linearity result confirmed by analysis of variance showed good linear regression and no significant deviation in linearity (p less than 0.05). The LOD (10.6 µg L^{-1}) and LOQ (35 µg L^{-1}) were calculated according to 3S$_b$/m and 10S$_b$/m, respectively (S$_b$ and m were standard deviation of the ten blank measurements, and slope of a calibration graph, respectively). The EF (2 4 7) was calculated from the ratio of the slopes of the calibration graph obtained before and after the VA-MIL-DLLME procedure. The relative standard deviations (RSD%) and extraction recovery of 50 and 200 µg/L of metribuzin for five replicated measurements were in the range of 1.9–2.7 % and 95.7–98.1 %,

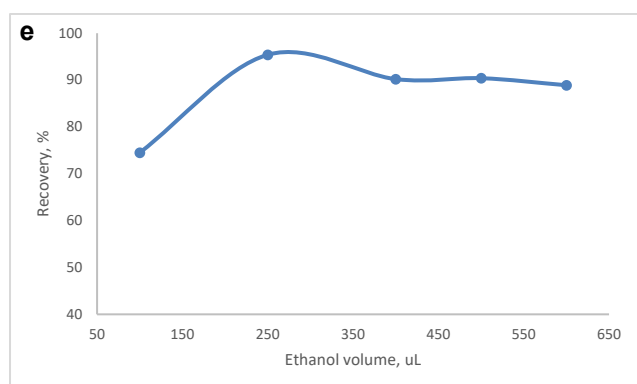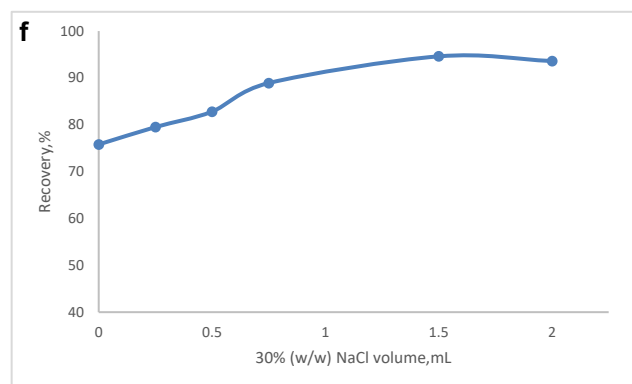**Fig. 1f.** Effect of ionic strength on recovery of metribuzin.
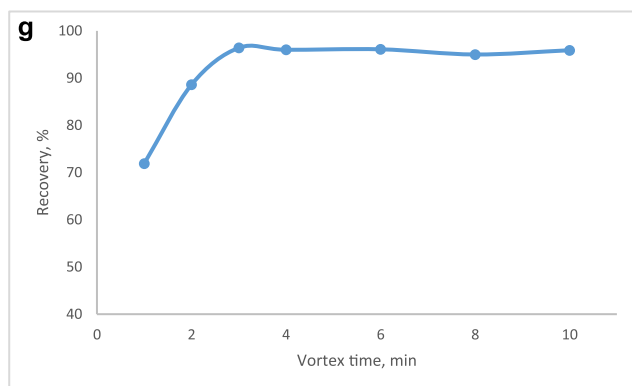
Fig. 1g. Effect of vortex time on recovery of metribuzin.

Table 1
Analytical performance of the VA-MIL-DLLME procedure.

Analytical parameters	Obtained values
Regression equation A=(a ± SD$_a$) c + (b ± SD$_b$)	A=(0.4725 ± 0.0019)C+(0.2504 ± 0.09576)
Working range, µg L^{-1}	35–800
R^2	0.995
LOD, µg L^{-1}	10.6
LOQ, µg L^{-1}	35
RSD for 50 and 200 µg/L of metribuzin	1.9 and 2.7
ER for 50 and 200 µg/L of metribuzin	95.7 and 98.1
EF	247

A, absorbance of metribuzin; c, metribuzin concentration in plant samples (µg L^{-1}); a, slope; b, intercept; SD$_a$ and SD$_b$, standard deviations of slope and intercept, respectively.
R^2: Determination coefficient.
LOD: Limit of detection.
LOQ: Limit of quantification.
RSD: Relative standard deviation.
EF: enrichment factor.
ER: Extraction recovery.

respectively.

3.3. Selectivity

Evaluation of the resulting calibration curve is one of the important strategies for detecting possible interferences in the development of the method. Residues of organic/inorganic substances from samples extracted with extraction solvents or analytes used in experimental studies may be present in the final composition of the measurement phase and cause a matrix effect. Therefore, the selectivity of the VA-MIL-

Fig. 1e. Effect of ethanol volume on recovery of metribuzin.

DLLME procedure was tested by the following study. The matrix ions in Table 2 were spiked to the model solutions at different amounts. The VA-MIL-DLLME procedure was then applied to the resulting mixture. Tolerable limit, extraction recovery and RSD% were determined for matrix ions. The tolerance limit of the matrix ions does not cause deviation of more that ± 5 % in analytical signal. The obtained extraction recovery and RSD% in Table 2 confirm that the samples matrix effect is negligible.

3.4. Precision and accuracy

The intra-day and inter-day precision were investigated by carried out five replicate extractions and analysis of three different amounts of metribuzin solution to selected plants in a day (intra-day) and five replicates in five succeeding days (inter-day). The spiked metribuzin amounts were selected as low (50 µg L^{-1}), middle (100 µg L^{-1}) and high (300 µg L^{-1}) concentrations for the working range obtained. Intra and inter-day precisions were found to be excellent within the range of 1.5–2.2 % and 2.3–2.9 %, respectively. The accuracy of the VA-MIL-DLLME procedure was tested by the standard addition method (three levels of metribuzin concentrations). The characteristic concentrations were (50 µg L^{-1}), middle (100 µg L^{-1}) and high (300 µg L^{-1}). As a result of the application, recovery values for intra-day and inter-day studies were in range of 93.6–98.5 % and 91.4–97.8 %, respectively. Obtained results were given in Table 3.

3.5. Applications

Various plants including lettuce, green onion, sunflower, chickpea, red cabbage, okra and bean plants were analyzed using the VA-MIL-DLLME procedure to evaluate its feasibility in determination and extraction of metribuzin in real samples. Relative recoveries of metribuzin were investigated to assess the effect of the samples matrix on efficiency of the VA-MIL-DLLME procedure. Relative recoveries were calculated at three concentration of 100, 200 and 300 µg L^{-1} according to the following equation:

$$Relative\ recoveries = \left(A_{sample}/A_{ultrapure\ water}\right) \times 100$$

where A$_{sample}$ was absorbance of metribuzin in the added plant samples and A$_{ultrapure\ water}$ is absorbance of metribuzin in the ultra-pure water which added at the same level. The relative recoveries (see Table 4) were in the range of 91 ± 2–102 ± 3 %. As can be seen from the results, the VA-MIL-DLLME procedure can be applied on the samples examined with negligible matrix effect. In addition, the RSD obtained (1.7–2.8 %) were acceptable for the analysis of real samples.

Table 2
Selectivity study results for metribuzin of the VA-MIL-DLLME procedure (n = 3).

Matrix ions	Tolerable limit	RSD (%)	Recovery (%)
Mg(II)	3000	1.9	98 ± 2
Ca(II)	3000	1.8	99 ± 3
K(I)	3000	2.0	98 ± 2
Co(II)	2000	2.2	97 ± 2
SO$_4$(II)	2000	1.7	98 ± 4
C$_2$O$_4$(II)	2000	2.0	97 ± 3
Pb(II)	2000	2.1	99 ± 5
Cu(II)	2000	2.3	98 ± 4
Fe(II)	1000	2.4	97 ± 2
Simazine	1000	2.3	97 ± 3
Prometryn	1000	2.2	98 ± 3
Dimethenamid	500	2.0	97 ± 4
Clomazone	500	1.8	96 ± 4
Acetochlor	500	2.3	95 ± 2
Fluroxypyr	250	2.4	95 ± 3
Oxyfluorfen	250	2.5	94 ± 4

Table 3
Intraday and interday studies for the determination of metribuzin in spiked selected plant samples.

Spiked caoncentration	Intraday (n = 5)			Interday (n = 5 × 5)		
	Found	Recovery (%)	RSD (%)	Found	Recovery (%)	RSD (%)
Low (50 µg L^{-1}),	46.8	93.6	1.5	45.7	91.4	2.3
Middle (100 µg L^{-1})	95.2	95.2	1.7	94.2	94.2	2.7
High (300 µg L^{-1})	295.5	98.5	2.2	293.4	97.8	2.9

Table 4
Determination and extraction of metribuzin in selected plant samples using VA-MIL-DLLME procedure (n = 3).

Plant samples	Spiked (µg L^{-1})	Found ± SD[a] (µg L^{-1})	Recovery ± SD[a] (%)	RSD (%)
Green onion	100	95 ± 4	95 ± 3	2.4
	200	194 ± 7	97 ± 4	2.7
	300	276 ± 11	92 ± 3	2.8
Lettuce	100	91 ± 5	91 ± 2	2.0
	200	186 ± 8	93 ± 3	2.3
	300	288 ± 10	96 ± 4	2.5
Sunflower	100	102 ± 5	102 ± 3	1.7
	200	202 ± 9	101 ± 2	1.8
	300	303 ± 13	101 ± 2	2.1
Chickpea	100	94 ± 3	94 ± 4	2.0
	200	192 ± 8	96 ± 2	2.2
	300	294 ± 11	98 ± 3	2.1
Red cabbage	100	92 ± 3	92 ± 4	2.4
	200	190 ± 7	95 ± 4	2.5
	300	291 ± 12	97 ± 3	2.7
Okra	100	102 ± 4	102 ± 3	1.9
	200	204 ± 7	102 ± 2	2.1
	300	303 ± 10	101 ± 2	2.4
Bean	100	95 ± 5	95 ± 4	1.9
	200	194 ± 8	97 ± 2	2.2
	300	294 ± 12	98 ± 3	2.3

[a] Standard deviation (n = 4, 95 % confidence interval).

3.6. Comparison of the method with the previously published methods

The efficiency of the VA-MIL-DLLME procedure was compared with the other analytical methods performed on real samples for the determination and extraction of metribuzin. In this context, the LOD, LOQ, working range, extraction time and RSD values of these methods were given in Table 5. The LODs of the VA-MIL-DLLME procedure were comparable to the analytical methods outlined in Table 5. In addition, the precision of the method was good and the RSD values were lower than the RSD values of other analytical methods. Compared to other reported spectrophotometric methods, the VA-MIL-DLLME procedure uses a short extraction time and few mL of sample solution. In addition, the wide working range was another advantage of this study. One of the most important advantages of the VA-MIL-DLLME procedure compared to the compared methods is that it does not require heating and centrifugation steps. This makes the VA-MIL-DLLME procedure more attractive in terms of cost. Furthermore, the analytical parameters obtained with the VA-MIL-DLLME procedure were comparable to techniques (GC–MS, HPLC-UV and GC-ECD) that are particularly expensive

Table 5

Comparison of the presented method with other methods used in extraction and determination of the metribuzin.

Extraction procedure	Technique	Working range ($\mu g \, L^{-1}$)	LOD ($\mu g \, L^{-1}$)	RSD (%)	EF	Extraction time (min)	References
DES-USAEME	HPLC-UV	5–500	0.8	≤ 7.6	100	12	[18]
D-μ-SPE	GC-ECD	25–1000	10	≤ 6.3	–	5	[19]
MISPE	HPLC-UV	20–200	12.48	≤ 4.8	–	7	[20]
MA-DES-DLLME	GC–MS	–	7.7	≤ 6.1	345	4	[21]
	UV–vis spectrophotometry	2000–24000	66	≤ 5	–	2	[22]
VA-MIL-DLLM	UV–vis spectrophotometry	35–800	10.6	≤ 2.7	247	3	Current study

DES-USAEME: Deep eutectic solvent based on ultrasound-assisted emulsified microextraction.
HPLC-UV: High-performance liquid chromatography UV detector.
D-μ-SPE: Dispersive-micro-solid phase extraction.
GC-ECD: Gas chromatograph electron capture detector.
MISPE: Molecularly imprinted solid-phase extraction.
MA-DES-DLLME: Microwave-assisted–deep eutectic solvent based dispersive liquid–liquid microextraction.
GC–MS: Gas chromatography–mass spectrometry.

and require skilled users. This showed us that the selected chemicals have high selectivity for the metribuzin.

4. Conclusions

In this study, the VA-MIL-DLLME approach was proposed using a tetrachloromanganate-based the MIL as extraction solvent for the determination and extraction of metribuzin in some plant samples by UV–VIS spectrophotometer. The MIL was prepared from a mixture of trihexyl(tetradecyl)phosphonium chloride $[P_{6,6,6,14}^{+}][Cl^{-}]$ and $MnCl_2 \cdot 4H_2O$ in chloroform. Based on the outcomes, low LOD (10.6 μg L^{-1}), wide working range (35–800 μg L^{-1}), good precision (RSDs $\leq$ 2.8 %), high EF (2 4 7) and quantitative relative recoveries (97–101 %) were obtained using the VA-MIL-DLLME procedure. According to the results obtained, the VA-MIL-DLLME procedure was a sensitive, fast and reproducible approach. Therefore, this method can be a beneficial, reliable, and easy to operate technique for the extraction and determination of metribuzin in selected plant samples. With these points in mind, the proposed approach can be reliably used for the determination of metribuzin in these samples at the μg L^{-1} level.

CRediT authorship contribution statement

Adil Elik: Supervision, Writing – review & editing. **Handan Sarac:** . **Hasan Durukan:** . **Ahmet Demirbas:** Investigation, Supervision. **Nail Altunay:** Investigation, Validation, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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