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Determination of fungicide carbendazim in water and soil samples using dispersive liquid-liquid microextraction and microvolume UV–vis spectrophotometry

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ABSTRACT

This article presents a new and sensitive method for the determination of trace amounts of fungicide carbendazim by dispersive liquid–liquid microextraction (DLLME) combined with UV–vis spectrophotometry. The method is based on the reduction of Fe(III) to Fe(II) by carbendazim, its reaction with potassium ferricynide to form a blue product and extraction into CCL_4 by DLLME technique using methyltrioctylammonium chloride (Aliquat 336) as a disperser agent. Under the established optimum conditions, the calibration graph was linear in the range of 5–600 ng mL^{-1} of carbendazim with a limit of detection of 2.1 ng mL^{-1}. The relative standard deviations for eight replicate determinations of 50 and 300 ng mL^{-1} of carbendazim were 3.9% and 1.0%, respectively. The proposed method was successfully applied to determination of carbendazim in soil and water samples.

1. Introduction

Carbendazim [methyl benzimidazol-2-ylcarbamate] (Fig. 1) is a broad-spectrum benzimidazole fungicide which is widely used in agriculture for protecting and eradicating of a variety of pathogens affecting fruits, nuts, vegetables, turf, and field crops. It is also used in post-harvest food storage and as a seed pre-planting treatment. Carbendazim is either applied directly to the soil, or sprayed over the crop fields [1,2]. The benzimidazolic ring of this compound is difficult to break and its degradation is slow, consequently it can persist for a long time in the environment. Therefore, determination of trace amount of this residual in water, soil, and various crops has become increasingly important for the environment and health protection [3].

Various methods such as capillary electrophoresis-mass spectrometry [4], fluorescence analysis [5,6], high performance liquid chromatography (HPLC) with different detectors [7–13], voltammetry [14,15] have been used for the determination of carbendazim. The fluorescence and voltammetric measurement techniques are not so expensive as the HPLC or capillary electrophoresis with mass spectrometric, but the instruments are with higher prices than a spectrophotometer.

One of the most important tendencies in analytical chemistry is the miniaturization and simplification of the analytical procedures. Recently, liquid phase microextraction (LPME) has become an attractive alternative for sample preparations because of its simplicity, effectiveness, low cost, minimum use of solvents and extraordinary sample cleanup ability. Different LMPE methodologies such as: single drop microextraction (SDME), hollow fiber-based liquid-phase microextraction (HF-LPME), solidified floating organic drop microextraction (SFODME), and dispersive liquid–liquid microextraction (DLLME) have been developed [16,17]. Among these, DLLME has become a popular sample-preparation technique, because it is inexpensive, consumes low volume of organic solvent, and provides high enrichment factor. DLLME method developed by Rezaee et al. in 2006 is the miniaturized form of liquid–liquid extraction in which acceptor-to-donor phase ratio is greatly reduced compared with other methods [18]. In this method an appropriate mixture of extraction and disperser solvents is injected into the aqueous sample and a cloudy solution is formed. Due to the large surface area of the interface between the two phases, the equilibrium state is achieved quickly and therefore, the extraction time is very short [19]. DLLME has been used for extraction and preconcentration of trace amounts of various organic pollutants and metal ions [20–27].

The aim of the current research is to apply DLLME method to the preconcentration of fungicide carbendazim followed by microvolume UV–vis spectrophotometric determination. Carbendazim reduces Fe(III) to Fe(II) which is then reacted with potassium ferricynide to form a blue product. This compound is extracted into CCL_4 using DLLME technique in the presence of methyltrioctylammonium chloride (Aliquat 336) as a disperser agent.

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2. Experimental

2.1. Apparatus

Recording the spectra and the absorbance measurements was made by a Jenway UV–vis spectrophotometer model 6320 (England) using 350 μL quartz microcells. Metrohm 827 pH-meter (Switzerland) was used to measure pH with a combined glass electrode. A centrifuge model BHG HERMLE (Germany) was used for the phase separation. A Colora (England) thermostat bath maintained at the desired temperature was used for the reaction of blue product.

2.2. Reagents

All chemicals used were of analytical grade and double distilled water was used throughout.

A stock solution of 100 μg mL^{-1} of carbendazim was prepared by dissolving 0.010 g of carbendazim (Merck, Germany) in 20 mL of 0.001 mol L^{-1} hydrochloric acid (Merck) and diluting to 100 mL in a volumetric flask with water. Working standard solutions were prepared daily by successive dilutions of this stock solution. 0.010 mol L^{-1} solution of potassium ferricynide was prepared by dissolving 0.3293 g of $K_3[Fe(CN)_6]$ (Merck) and diluting to 100 mL. 100 mg L^{-1} solution of Fe(III) was prepared by dissolving 0.029 g of $FeCl_3$ (Merck) and diluting to 100 mL. A formate buffer (pH 3.0) was prepared by adding 0.1 mol L^{-1} of sodium hydroxide (Merck) to 0.1 mol L^{-1} of formic acid (Merck) solution and adjusting the pH to 3.0 using a pH meter. A phosphoric acid solution (1.0 mol L^{-1}), was prepared by diluting 6.8 mL of concentrated H_3PO_4 (Fluka, 85%, d = 1.7 g mL^{-1}) to 100 mL in a volumetric flask. 0.67% (w/v) solution of (Aliquat 336) (Merck) was prepared by dissolving 0.067 g of Aliquat 336 in carbon tetrachloride and diluting to 10 mL.

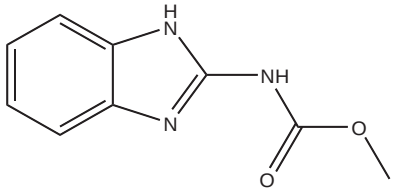

Fig. 1. Chemical structure of carbendazim.

2.3. Dispersive liquid–liquid microextraction procedure

An aliquot of the carbendazim solution (to provide a final concentration of 5–600 ng mL^{-1}), 0.5 mL of 10 mg L^{-1} of Fe(III), 0.4 mL of 4×10^{-4} mol L^{-1} of $K_3[Fe(CN)_6]$ and 0.5 mL of format buffer (pH 3.0) were added to a glass test tube with a conical bottom and placed in a thermostat bath at 50 °C for 2 min. After this period, the solution was placed in a cool water bath, then 1.0 mL of H_3PO_4 (0.1 mol L^{-1}) was added, diluted to 10 mL with water and mixed. Afterward 180 μL of carbon tetrachloride containing Aliquat 336 (0.67% (w/v)) was rapidly injected into the solution by a microsyringe to induce the formation of cloudy solution and the mixture was shaken for several seconds manually. The mixture was then centrifuged at 5000 rpm for 5 min. The dispersed fine droplets of the extraction phase were settled at the bottom of the conical test tube (175 ± 5 μL) as a blue phase. After elimination of the aqueous phase, the settled phase was removed using a microsyringe, placed into the quartz microcell and its absorbance was measured at 685 nm against the blank. A blank solution was also run under the same procedure without adding any carbendazim. The schematic presentation for this DLLME procedure is shown in Fig. 2.

2.4. Collection and preparation of samples

The water samples were collected from Dez and Karun River (Iran) and filtered before use. An aliquot of water samples was treated under the recommended procedure.

The extraction of carbendazim from soil samples (collected from agriculture fields in Khuzestan, Iran) before DLLME was carried out according to the following procedure [28]. Soil sample 1 was collected from a tomato farm which has been treated with carbendazim and soils 2 and 3 from an untreated land field. The samples were air-dried at room temperature, powdered and passed through 250-μm sieve.

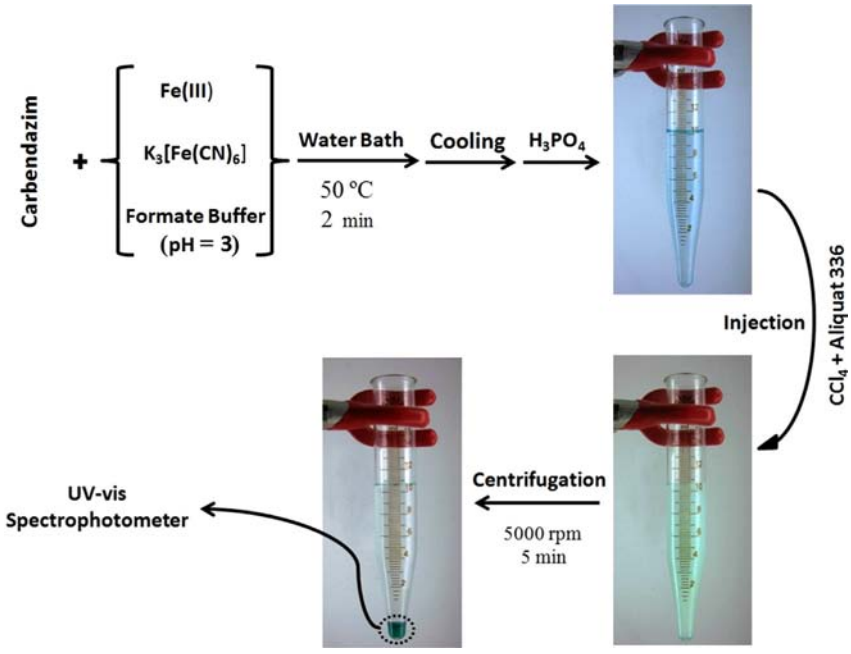

Fig. 2. Schematic procedure for the LLME method.

20.0 g of the soil sample was accurately weighed and placed into a 100 mL beaker, to which 40.0 mL 0.1 mol L^{-1} HCl was added. The resultant sample mixture was stirred for 60 min, then filtrated and the pH of the filtrate was adjusted to 7.0 by diluted sodium hydroxide. 5.0 mL of each soil sample solution was under the DLLME procedure.

3. Results and discussion

Fe(III) is reduced by carbendazim to Fe(II) and upon its reaction with potassium ferricynide a precipitate known as Turnbull 's Blue is produced [29,30]. This product is soluble in acid and in the presence of methyltrioctylammonium ion as an ion pair is extracted into carbon tetrachloride. The developed spectrophotometric method here is based on the extraction of this color product into carbon tetrachloride in the presence of Aliquat 336. Aliquat 336 also plays the role of disperser agent which is injected along with extraction solvent to aqueous solution. In order to find the appropriate conditions for DLLME, different experimental parameters were studied and optimized using a carbendazim solution with a concentration of 500 ng mL^{-1}.

3.1. Wavelength selection

In order to perform UV–Vis spectrophotometry for the determination of carbendazim, maximum absorption wavelength was established. In the preliminary experiment, the sample solution containing different concentrations of carbendazim was examined according to the recommended procedure for DLLME and the corresponding spectra of sedimented phase was recorded in the range of 500–850 nm. The absorption spectra are shown in Fig. 3. The results showed that maximum absorption occurs at 685 nm for the sedimanted phase and the absorbance at this wavelength is increased upon increasing of carbendazim concentration. Therefore, 685 nm was selected for measuring the absorbance of the extracted phase throughout this study.

3.2. Effect of pH

The pH of the sample solution is an important factor affecting the absorbance of the sedimented phase. Thus DLLME procedure for carbendazim was performed in the solutions with different pH values ranging from 1.0 to 7.0. The results shown in Fig. 4 indicated that the signal intensity of the phase was nearly constant at pH values between 2.0 and 4.0 and decreased at higher pH values. Thus, pH 3.0 was chosen for DLLME of carbendazim in the further experiments and 0.5 mL of formate buffer pH 3.0 was added to the solutions to maintain this value.

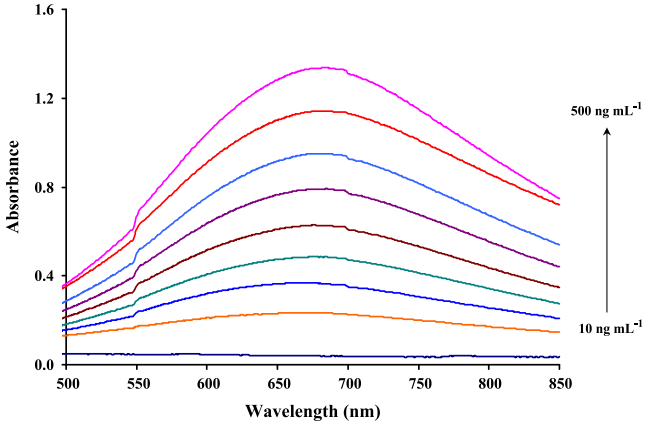

Fig. 3. UV-Visible absorbance spectra of sedimented phase in the presence of different concentration of carbendazim.

3.3. Effect of Fe(III) concentration

The effect of Fe(III) concentration on the formation of blue product was investigated. As can be seen in Fig. 5, maximum absorbance for the sedimented phase was obtained when Fe(III) concentration was 0.5 mg L^{-1} in the final solution. Therefore this concentration was chosen as optimum for further experiments.

3.4. Effect of $K_3[Fe(CN)_6]$ concentration

The influence of potassium ferricynide concentration on the resultant product and hence the absorbance of sedimented phase after DLLME procedure was studied. The obtained results showed that the absorbance is increased by increasing the concentration of potassium ferricynide up to 16 μmol L^{-1} and above this value it is decreased again. Therefore, 16 μmol L^{-1} of potassium ferricynide was selected as optimum concentration.

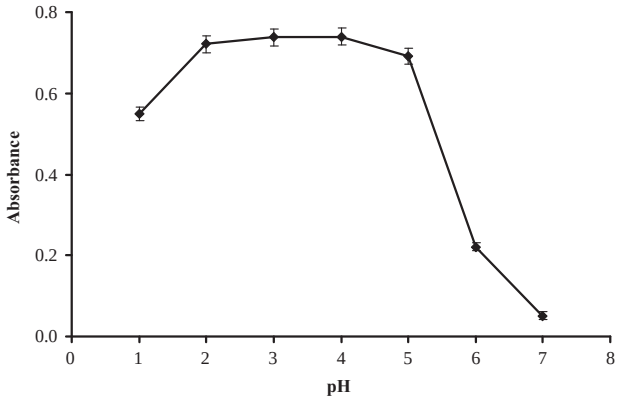

Fig. 4. Effect of pH on DLLME of carbendazim. Extraction conditions: aqueous sample volume, 10 mL; carbendazim concentration, 500 ng mL^{-1}; Fe(III) concentration, 0.5 mg L^{-1}; $K_3[Fe(CN)_6]$ concentration, 16 μmol L^{-1}; time and temperature equilibration, 50 °C for 2 min; H_3PO_4 concentration, 0.01 mol L^{-1}; volume of CCl_4-Aliquat 336, 180 μL; centrifugation time, 5 min. Each number is average of three determinations.

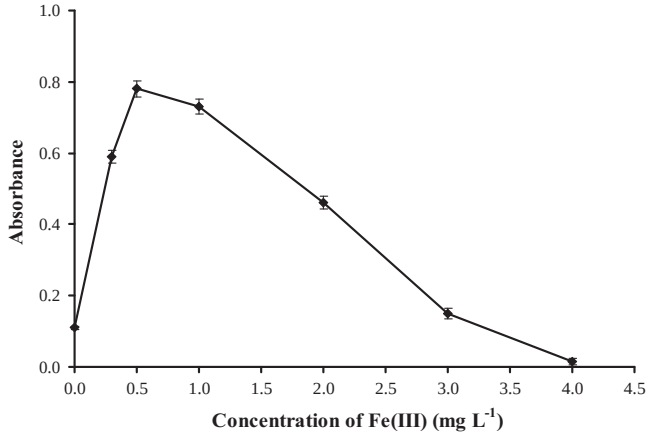

Fig. 5. Effect of Fe(III) concentration in DLLME of carbendazim. Extraction conditions: sample volume, 10 mL; carbendazim concentration, 500 ng mL^{-1}; $K_3[Fe(CN)_6]$ concentration, 16 μmol L^{-1}; pH of solution, 3; time and temperature equilibration, 50 °C for 2 min; H_3PO_4 concentration, 0.01 mol L^{-1}; volume of CCl_4-Aliquat, 180 μL; centrifugation time, 5 min. Each number is average of three determinations.

3.5. Effects of equilibration temperature and time

Optimization of incubation time and equilibration temperature is necessary for completion of the reaction. However, in the analytical procedure using the lowest equilibration temperature and shortest equilibration time is desired. Therefore the effects of equilibration temperature and incubation time on DLLME of carbendazim were evaluated in the range of 10–80 °C and 0.5–5.0 min, respectively. The results revealed that the rate of reaction is increased by increasing the temperature to 50 °C and it was almost constant above this value. Thus, an equilibration temperature of 50 °C was selected. The investigation of incubation time also indicated that the maximum absorbance signal was obtained at 2 min. Therefore, an incubation time of 2 min was chosen for the next experiments.

3.6. Effects of H_3PO_4 concentration

The preliminary experiments showed that the solubility of blue product in the organic solvent is very poor and in the absence of phosphoric acid, its extraction to the droplets of extractant solvent does not occur. For this purpose a series of experiments was carried out using different concentration of phosphoric acid in the range of 0.0–20.0 mmol L^{-1} in the final aqueous solution. The experimental results showed that the absorbance signal increased up to 10.0 mmol L^{-1} of H_3PO_4 and then remained constant. Thus, 10.0 mmol L^{-1} of H_3PO_4 was chosen for the purpose of this study.

3.7. Nature of the extraction solvent and disperser solvent

The extraction solvent in DLLME has to meet several characteristics, including low volatility, low water solubility, higher density than water, and high capability for extracting target compound. Based on these requirements, carbon tetrachloride, trichloromethane, and dichloromethane were chosen as extraction solvent. Therefore, studies were conducted using different volumes of these extraction solvents containing a constant amount of Aliquat 336. The cloudy solution and two-phase system appeared by applying carbon tetrachloride and trichloromethane whereas this event was not observed using dichloromethane. However, carbon tetrachloride was chosen, because in this case the highest and more reproducible signal was observed and smaller volume of extraction solvent was required in the injection step.

Our preliminary observation showed that Aliquat 336 acts as a disperser by accelerating the formation of fine droplets of the extraction solvent in aqueous sample as well as forming an ion pair with the blue product. Despite this the influence of several conventional disperser solvents such as methanol, ethanol, acetonitrile and acetone was also investigated. For this purpose, supplementary experiments were performed through injection of a mixture containing appropriate amount of CCl_4, Aliquat 336 and mentioned disperser solvents. The results showed that carbon tetrachloride is partially dissolved in the disperser solvent and migrates into aqueous phase and the dissolved carbon tetrachloride is not sedimented down well and the extraction efficiency is decreased. Therefore, the suggested method was carried out by injecting the extraction solvent (without any disperser solvent) and only containing appropriate amount of Aliquat 336 to the sample solutions. Unlike using conventional disperser solvents, very small volume of CCl_4 is dissolved in aqueous solutions in the presence of Aliquat 336, and the volume of sedimented phase was almost equal to the volume of injected CCl_4, which is an advantage for the proposed method.

3.8. Effect of methyltrioctylammonium chloride amount

The injection of the Aliquat 336 along with extraction solvent made a stable cloudy solution. Consequently, the fast equilibrium was achieved due to the formation of very fine solvent droplets, which greatly increased the contact area between the extraction solvent and aqueous phase the analyte was rapidly transferred from aqueous phase to extraction solvent. Therefore, the amount of Aliquat 336 on the extraction of carbendazim is very important. For this purpose, 180 μL of carbon tetrachloride containing different amounts of the Aliquat 336 (0.00–1.17% (w/v)) was injected into the sample solutions. The experimental results showed that the absorbance signal increased up to the concentration of 0.67% (w/v) of Aliquat 336 and then remained constant. Thus, 0.67% (w/v) of Aliquat 336 in CCl_4 was chosen as the disperser-solvent mixture.

3.9. Effect of CCl_4 volume

The volume of extraction solvent is another crucial parameter that could affect the extraction efficiency, enrichment factor, and sensitivity, due to its effect on the volume of the sedimented phase. In order to examine the effect of this parameter, different volumes of CCl_4 (180–500 μL) containing Aliquat 336 (0.67% w/v) were subjected to the same DLLME procedure. The obtained results in Fig. 6 show that the absorbance of organic phase is decreased by increasing the volume. Due to the dilution effect which decreases the concentration of the extracted colored product in the sedimented phase. Thus, in order to achieve high enrichment factor and low detection limit, 180 μL of CCl_4 containing 0.67% (w/v) of Aliquat 336 was selected as the optimum volume. Using injection volumes less than 180 μL of the solution, low volume of organic phase was obtained, so that the absorption signal could not be measured by spectrophotometer even fitted with micro-cells.

3.10. Effect of time

The extraction time is an affecting parameter in DLLME experiments. Therefore, the effect of extraction time was studied over the range of 1–5 min. The results indicated that the extraction process is time-independent and very fast due to the large surface of contact between the extraction solvent and the aqueous phase. This is the most important advantage of the DLLME technique. The influence of centrifugation time was also studied. The results indicated that for a

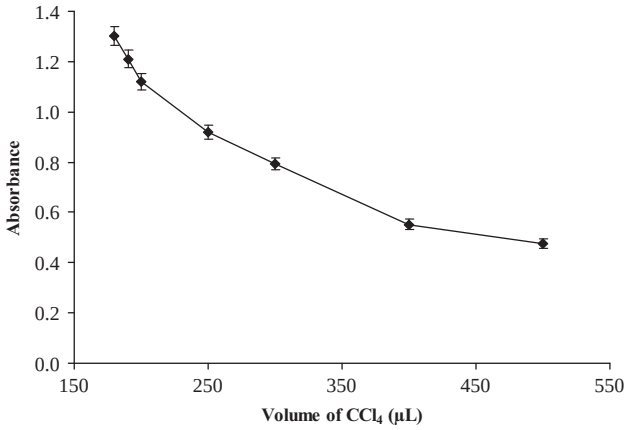

Fig. 6. Effect of volume of CCl_4-Aliquat 336 in DLLME of carbendazim. Extraction conditions: sample volume, 10 mL; carbendazim concentration, 500 ng mL^{-1}; Fe(III) concentration, 0.5 mg L^{-1}; $K_3[Fe(CN)_6]$ concentration, 16 μmol L^{-1}; pH of solution, 3; time and temperature equilibration, 50 °C for 2 min; H_3PO_4 concentration, 0.01 mol L^{-1}; centrifugation time, 5 min. Each number is average of three determinations.

complete separation of organic and aqueous phase the mixture should be centrifuged for 5 min at 5000 rpm.

3.11. Interference studies

The potential interference from other species on the determination of carbendazim was investigated. The effect of different cations and anions possibly existing in natural samples was studied. In this experiment, solutions containing 200 ng mL^{-1} of carbendazim and various amounts of interfering ions were treated according to the recommended procedure. An error of $\pm 5\%$ in the absorbance reading was considered tolerable. The results summarized in Table 1, show good selectivity of the procedure toward these ions.

3.12. Analytical features of the method

Under the optimized experimental conditions, the analytical parameters were investigated. The calibration graph was linear in the range of 5–600 ng mL^{-1} of carbendazim with a correlation coefficient (r) of 0.9996. The limit of detection (LOD) calculated based on 3 S_b was 1.2 ng mL^{-1} and limit of quantification (LOQ) based on 10 S_b was 4.0 ng mL^{-1}. The preconcentration factor, defined as the volume ratio of the aqueous sample solution (10 mL) and sedimented phase (0.18 mL), was 55.5. The intra-day and inter day precision calculated as the relative standard deviations (RSD) for eight replicate determinations of 50 ng mL^{-1} of carbendazim were 3.9% and 4.1%, respectively.

3.13. Application to environmental samples

3.13.1. Water sample analysis

Two water samples were analyzed by the proposed DLLME procedure combined with microvolume UV–Vis spectrophotometry. These samples were spiked with 25 and 75 μg L^{-1} of carbendazim solution and subjected to the DLLME procedure. The results shown in Table 2 demonstrate that the waters matrices have no significant effect on the proposed method and recoveries in the range of 95.2–105.2 were obtained.

Table 1
Tolerance limit of interfering ions on determination of 200 ng mL^{-1} carbendazim using DLLME.

Interfering ions	Tolerance ratio (w/w)
Na^+, NH_4^+, NO_3^-, SO_4^{2-}, Ca^{2+}, I^-	1000
Pb^{2+}, Ni^{2+}, CO_3^{2-}, Mg^{2+}, Ag^+, Cl^-	500
Cu^{2+}, Cd^{2+}, Hg^{2+}	100
Co^{2+}, Cr^{3+}, Mn^{2+}	50
Al^{3+}, $C_2O_4^{2-}$	5

Table 2
Determination of carbendazim in water samples by proposed method.

Sample	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)
River water (Karun)	0	N. D [b]	–
	25	23.8 ± 0.9	95.2
	75	74.1 ± 2.8	98.8
River water (Dez)	0	N.D	–
	25	26.3 ± 1.0	105.2
	75	78.0 ± 3.0	104.0

[a] Mean ± standard deviation (n=3).
[b] Not detected.

3.13.2. Soil sample analysis

The developed method was also applied to the determination of carbendazim in soil samples under the optimum conditions. The results (Table 3) revealed that there are no residues of carbendazim in soil samples No. 2 and 3 but for No. 1 soil sample, carbendazim was found to be 0.218 μg g^{-1}. The spectra of soil sample with and without carbendazim are presented as Fig. 7.

The recovery tests for the soil samples were also performed by spiking the soil samples with carbendazim concentrations of 50 and 100 ng mL^{-1}. The analyzed results are shown in Table 3, as can be seen, the recoveries were ranged from 95.4 to 104.6%. Also, in order to investigate of the accuracy of the suggested method, the obtained result from No.1 soil sample was compared with HPLC using Sylvaine et. al method [31] for sample preparation. The results are presented in Table 4. According to the Student's t-test

Table 3
Determination of carbendazim in soil samples by proposed method.

Sample No.	Added (ng mL^{-1})	Found [a] (ng mL^{-1})	Recovery (%)
1[b]	0	43.7 ± 1.7	–
	50	92.1 ± 3.5	96.8
	100	142.1 ± 5.5	98.4
2	0	N. D[c]	–
	50	47.7 ± 1.8	95.4
	100	103.2 ± 3.9	103.2
3	0	N. D	-
	50	52.3 ± 2.0	104.6
	100	101.8 ± 3.9	101.8

[a] Mean ± standard deviation (n=3).
[b] Amount of carbendazim was 0.218 μg g^{-1}.
[c] Not detected.

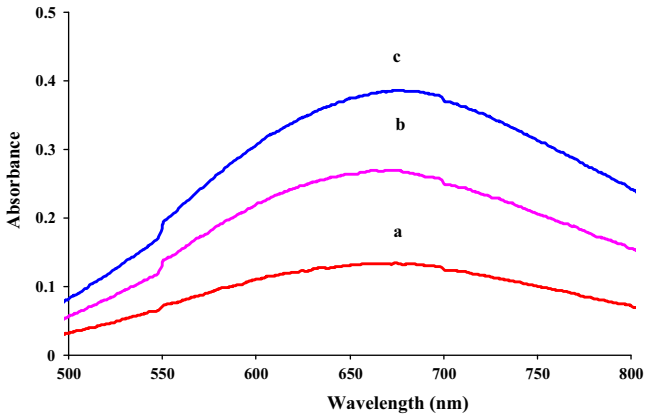

Fig. 7. The spectra of sedimented carbendazim from soil sample 1 (a) soil sample alone (b) soil sample spiked with 50 ng mL^{-1} and (c) soil sample spiked with 100 ng $mL^{-1}$of carbendazim, conditions: sample volume, 10 mL; carbendazim concentration, 500 ng mL^{-1}; Fe(III) concentration, 0.5 mg L^{-1}; $K_3[Fe(CN)_6]$ concentration, 16 μmol L^{-1}; pH of solution, 3; time and temperature equilibration, 50 °C for 2 min; H_3PO_4 concentration, 0.01 mol L^{-1}; centrifugation time, 5 min.

Table 4
Comparison of determination of carbendazim in soil sample by DLLME method and HPLC.

	Carbendazim found (μg g^{-1}) [a]			
Sample	DLLME method	HPLC method	t-test [b]	F-test [c]
No. 1 soil sample	0.218 ± 0.008	0.231 ± 0.007	2.13	1.3

[a] Mean ± standard deviation (n=3).
[b] Tabulated t-value for four degrees of freedom at 95% confidence level is 2.78.
[c] Tabulated F-value for (2,2) degrees of freedom at 95% confidence level is 39.

Table 5
Comparison of the proposed DLLME method with other methods for determination of carbendazim.

Procedure	Determination technique	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	RSD (%)	Ref.
DLLME[a]	HPLC	5–800	0.5	3.5	[28]
SPE[b]	HPLC	–	20	2.9	[12]
IC[c]	FD[d]	200–15000	67	3.9	[2]
Modified-Elect.	St.Vol.[e]	10–500	10	2.9	[32]
MWCNT–GCE[f]	St.Vol.	49–595	10.5	–	[14]
HPLC-HPLC	MS[g]	25–100	25	4.5	[33]
HPLC-HPLC	DAD[h]	75–100	75	16	[33]
IL[i]-DLLME	HPLC	5–500	5.0	1.9–4.8	[34]
DLLME	UV-vis	5–600	2.1	1.0–3.9	This work

[a] Dispersive liquid–liquid microextraction.
[b] Solid phase extraction.
[c] Ion chromatography.
[d] Fluorescence detector.
[e] Stripping voltammetry.
[f] Multiwalled carbon nanotubes-glassy carbon electrode.
[g] Mass.
[h] Diod array detector.
[i] Ionic liquid.

and F-test, there was no significant difference between the results obtained by both methods at 95% confidence level.

4. Conclusions

A new DLLME method with UV–Vis spectrophotometric detection was developed for the preconcentration and determination of trace amount of carbendazim in water and soil samples. The suggested DLLME method provides advantages such as simplicity, rapidity, low operation cost and solvent volume, employment of usual laboratory equipment, high preconcentration factor, and short extraction time. Although various analytical methods have been reported for the determination of carbendazim in different crop matrices and environmental samples, to the best of our knowledge this is the first combined preconcentration and spectrophotometric method for carbendazim. Spectrophotometric detection has merits of simplicity, cheapness, and portability. In addition, in this method there is no need for conventional dispersive solvents because the Aliquat 336 used for assisting the extraction of blue product by forming an ion pair, also acted as a disperser. A comparison between the present DLLME- UV–Vis spectrophotometry method and other sample preparation techniques from the viewpoint of linearity, LOD, % RSD, and EF are shown in Table 5. As can be seen in the table the LOD, enrichment factor and RSD % of the suggested method is better or comparable to some of the reported techniques and especially the extraction time for this method is much shorter since the extraction equilibrium is reached quickly due to the large surface area between the organic droplets and the aqueous sample solution.

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References

[1] K.A. Bean, J.D. Henion, J. Chromatogr. A. 791 (1997) (119–12).
[2] Q. Subhani, Z.h. Huang, Z. Zhu, Y. Zhu, Talanta 116 (2013) 127–132.
[3] Y. Guo, S.h. Guo, J. Li, E. Wang, S.h. Dong, Talanta 84 (2011) 60–64.
[4] J. Dominguez-Alvarez, M. Mateos-Vivas, D. Garcia-Gomez, E. Rodriguez-Gonzalo, R. Carabias-Martinez, J. Chromatogr. A. 1278 (2013) 166–174.
[5] J.F. Garcia Reyes, P. Ortega Barrales, A. Molina Diaz, Anal. Chim. Acta 493 (2003) 35–45.
[6] M.J. Rodriguez-Cuesta, R. Boque, F.X. Rius, D. Picon Zamora, M. Martinez Galera, A. Garrido Frenich, Anal. Chim. Acta 491 (2003) 47–56.
[7] B. Gilbert-Lopez, J.F. Garcia-Reyes, A. Molina-Diaz, Food Chem. 135 (2012) 780–786.
[8] M. Radisic, S. Grujic, T. Vasiljevic, M. Lausevic, Food Chem. 113 (2009) 712–719.
[9] P. Jovanov, V. Guzsvány, M. Franko, S. Lazic, M. Sakac, B. Saric, V. Banjac, Talanta 111 (2013) 125–133.
[10] A. Veneziano, G. Vacca, S. Arana, F. De Simone, L. Rastrelli, Food Chem. 87 (2004) 383–386.
[11] Y. Wena, J. Li, F. Yang, W. Zhang, W. Li, C.h. Liao, L. Chen, Talanta 106 (2013) 119–126.
[12] M. Michel, B. Buszewski, J. Sep. Sci. 26 (2003) 1269–1272.
[13] M. Michel, B. Buszewski, J. Chromatogr. B. 800 (2004) 309–314.
[14] W.F. Ribeiro, T.h.M. Guimaraes Selva, I. Campelo Lopes, E.C.S. Coelho, S.h.G. Lemos, F.C. de Abreu, V.B. do Nascimento, M.C.U. de Araujo, Anal. Methods 3 (2011) 1202–1206.
[15] A.M. Ashrafi, J. Đordevic, V. Guzsvány, I. Švancara, T. Trtic-Petrovic, M. Purenovic, K. Vytras, Inter. J. Electrochem. Sci 7 (2012) 9717–9731.
[16] F. Pena-Pereira, I. Lavilla, C. Bendicho, Anal. Chim. Acta 669 (2010) 1–16.
[17] A.A. Nuhu, C.h. Basheer, B. Saad, J. Chromatogr. B. 879 (2011) 1180–1188.
[18] M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A. 1116 (2006) 1–9.
[19] A.N. Anthemidis, K.G. Ioannou, A. Rev. Talanta 80 (2009) 413–421.
[20] Q. Zhoua, N. Zhao, G. Xie, J. Hazard. Mater. 189 (2011) 48–53.
[21] S. Rastegarzadeh, N. Pourreza, A. Larki, Spectrochim. Acta, Part A 114 (2013) 46–50.
[22] J. Skrlikova, V. Andruch, I.S. Balogh, L. Kocurova, L. Nagy, Y. Baze, Microchem. J. 99 (2011) 40–45.
[23] X. Wen, Q. Yang, Z.h. Yan, Q. Deng, Microchem. J. 97 (2011) 249–254.
[24] J.A. Baig, A. Hol, A. Akdogan, A.A. Kartal, U. Divrikli, T.G. Kazi, L. Elci, J. Anal. At. Spectrom 27 (2012) 1509–1517.
[25] G. Chen, Q. Li, J. Agric. Food Chem. 61 (2013) 98–102.
[26] A.C.H. Alves, M.M. Pontes, B. Goncalves, M.M.S. Bernardo, B.S. Mendes, J. Sep. Sci. 35 (2012) 2653–2658.
[27] M. Asensio-Ramos, J. Hernandez-Borges, L.M. Ravelo-Perez, M.M. Afonso, J.A. Palenzuela, M.A. Rodriguez-Delgado, Electrophoresis 33 (2012) 1449–1457.
[28] Q. Wu, Y. Li, C.h. Wang, Z.h. Liu, X. Zang, X. Zhou, Z.h. Wang, Anal. Chim. Acta 638 (2009) 139–145.
[29] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, third ed., Interscience Publishing, New York, USA, 1974.
[30] A. Vogel, A Textbook of Macro and Semimicro Qualitative Inorganic Analysis, fourth ed., Longman, UK, 1974.
[31] S.D. Regis-Rolle, G.M. Bauville, Pestic. Sci. 37 (1993) 273–282.
[32] P. Manisankar, G. Selvanathan, C. Vedhi, Talanta 68 (2006) 686–692.
[33] D.H. Thomas, V. Lopez-Avila, L.D. Betowski, J. Van Emon, J. Chromatogr. A. 724 (1996) 207–217.
[34] M. Asensio-Ramos, J. Hernandez-Borges, T.M. Borges-Miquel, M. Angel Rodriguez-Delgado, J. Chromatogr. A. 1218 (2011) 4808–4816.