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ARTICLES

Ion Pair-Dispersive Liquid–Liquid Microextraction Combined with Spectrophotometry for Carbamazepine Determination in Pharmaceutical Formulations and Biological Samples

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Abstract—A simple, economical and selective method employing ion pair dispersive liquid–liquid microextraction (**DLLME**) coupled with spectrophotometric determination of carbamazepine (**CBZ**) in pharmaceutical preparations and biological samples was developed. The method is based on reduction of Mo(VI) to Mo(V) using a combination of ammonium thiocyanate and ascorbic acid in acidic medium to form a red binary Mo(V) thiocyanate complex. After addition of CBZ to the complex, extraction of the formed CBZ–Mo(V)–$(SCN)_6$ was performed using a mixture of methylene chloride and methanol. Then, the measurement of target complex was performed at the wavelength of 470 nm. The important extraction parameters affecting the efficiency of DLLME were studied and optimized in detail. At the optimum conditions, the linear range was 0.02–0.2 μg/mL. Moreover, the limits of detection and quantification were 0.01 and 0.04 μg/mL, respectively. High enrichment factor was obtained (118). Good recoveries at 0.06, 0.15 and 0.2 μg/mL ranging from 93 to 102% were achieved. The proposed method was successfully applied to the determination of CBZ in pharmaceutical formulations and biological samples.

Keywords: carbamazepine, ion pair, dispersive liquid–liquid microextraction, biological sample, pharmaceutical formulation

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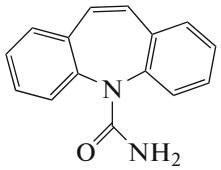
The antiepileptic agent carbamazepine chemically known as [5H-dibenz[b,f]azepine-5-carboxamide], is tricyclic with a white to off white color almost odorless crystalline powder with pK_a 13.9 (Scheme 1). Carbamazepine is soluble in alcohol and acetonitrile but it is slightly soluble in aqueous media [1]. It is most frequently prescribed for the treatment of epilepsy, trigeminal neuralgia and bipolar disorders. Mostly, CBZ metabolizes in the liver into various metabolites, it is considered as a strong inducer of microsomal enzymes in the liver (cytochrome P450 in the liver) able to accelerate its own metabolism. Therefore, polytherapy may be related to drug interaction and undesired toxicity [2, 3]. After long-term treatment with CBZ, $t_{1/2}$ of plasma decreases from 36 to 21 h that supports the assumption that there is an autoinduction [4].

In the literature, various analytical techniques, such HPLC [5], liquid chromatography–tandem mass spectrometry [6], gas chromatography [7], micellar electrokinetic capillary chromatography [8], flow injection analysis [9], chemiluminescence [10], spectrophotometry [1, 11], flow injection-fluorimetry [12], have been published for the quantification of CBZ.



Scheme 1. Chemical structure of carbamazepine.

One of the most important tendencies in analytical chemistry is simplification and miniaturization of the analytical procedure especially for the determination of low concentrations. Therefore, development of a simple, economic and rapid method for the separation, preconcentration and estimation of the selected drug in biological samples and pharmaceutical formulations is of great importance.

Microextraction techniques have been developed to overcome the drawbacks of traditional sample preparation techniques.

A powerful preconcentration method named dispersive liquid–liquid microextraction was introduced by Rezaee et al. in 2006 [13]. The main advantage of this method is short reaction time because of the infinitely large surface area between the extraction solvent and aqueous sample resulting in a quick achieve-

ment of the equilibrium state. Other advantages are high enrichment factor, rapidity, simplicity of operation, low cost and environmental benignity [14]. DLLME has been developed for the preconcentration and determination of pesticides [15], drugs and ions [16–21].

UV-visible spectrophotometric methods are most commonly used and widely popular techniques. The availability of the instruments, analytical procedure simplicity and low operation cost make the spectrophotometric technique attractive. Therefore, this study describes a combination of DLLME with UV-visible spectrophotometry for the preconcentration and determination of CBZ trace levels in pure and real samples. The performance of the suggested method for the analysis of a pharmaceutical preparation and a real sample was tested. To the best of our knowledge, this is the first study on the combination of DLLME with UV-Vis for CBZ determination.

EXPERIMENTAL

Apparatus. A Shimadzu 1800 UV-Vis spectrophotometer (Germany) with 1-cm quartz microcells was used in the wavelength range of 190–1100 nm. Phase separation process acceleration was performed using a HERMLE centrifuge (Z-200A) (Germany) with 10-mL centrifuge tubes.

Materials and solutions. All chemicals and reagents used were of analytical reagent grade. Acetonitrile, methanol, ascorbic acid, ammonium thiocyanate and ammonium molybdate were supplied from BDH (England). HCl and methylene chloride were purchased from Fluka (Germany) and GCC (UK), respectively. A 1000 μg/mL stock solution of carbamazepine (Samarra Drug Industry) was prepared by dissolving 0.100 g of CBZ standard in acetonitrile and diluting to 100 mL using this solvent. A series of working solutions (100, 10 μg/mL) were prepared in acetonitrile. Solutions of ascorbic acid, ammonium thiocyanate and ammonium molybdate (20, 25 and 0.12%, w/v, respectively) were prepared by dissolving accurate weights of each substance in 100 mL of distilled water. A 5 M HCl solution was prepared by accurate dilution of concentrated hydrochloric acid.

Dispersive liquid–liquid microextraction procedure. 3 mL of 0.12% (w/v) ammonium molybdate, 0.75 mL of 5 M HCl, 1.75 mL of 20% (w/v) ascorbic acid and 0.75 mL of 25% (w/v) ammonium thiocyanate were placed in a 15 mL centrifuge tube and mixed. The mixture was then left for 5 min at room temperature to complete binary complex formation. After that, different volumes (20–200 μL) of CBZ (10 μg/mL) were added to the mixture and diluted with distilled water up to 10 mL to form CBZ–Mo(V)–$(SCN)_6$ (ion-pair). 1100 μL of methanol containing 300 μL of methylene chloride was rapidly injected into the solution using a microsyringe to induce cloudy solution formation. 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 tube as an orange red complex. After elimination of the aqueous phase, the organic layer was removed using a microsyringe, placed into the 1 cm quartz microcell and its absorbance was measured at the wavelength of 470 nm against blank. A blank solution was prepared under the same conditions without CBZ addition. Figure 1 summarizes the steps of the suggested DLLME procedure.

Procedure for the preparation of tablets. 10 tablets of Tegral (each tablet contained 200 mg of CBZ) were weighed, powdered and mixed. 100 mg of the drug powder was dissolved in distilled water, filtered through a Whatman no. 1 filter paper, transferred to a 100 mL volumetric flask and then diluted to the mark with distilled water. This solution was 1000 times diluted to prepare a working tablet sample solution. An aliquot of the solution equivalent to 50 μL was taken and subjected to analysis by the recommended DLLME procedure.

Procedure for real sample preparation. Biological samples were collected from five heathy volunteers living in Baghdad, Iraq. For human serum preparation, 1 mL of serum sample was transferred into a 100 mL volumetric flask after its separation from blood by centrifugation at 3000 rpm for 10 min. Then, the sample was diluted to the mark with distilled water and stored in a refrigerator until used. To prepare human urine sample, 1 mL of urine was transferred into a 100 mL volumetric flask and diluted to the mark with distilled water. Serum and urine samples were fortified with CBZ working solution to achieve different concentration levels before analysis. Then, 50 μL aliquots of the spiked serum and urine samples were separately subjected to the DLLME procedure as described above.

RESULTS AND DISCUSSION

In acidic media and in the presence of ascorbic acid and/or thiocyanate, Mo(VI) is reduced to Mo(V) to form a red Mo(V)–$(SCN)_6^-$ binary complex and then it reacts with protonated CBZ^+ to form orange–red ion-pair complex in same concentration of acid solution [22]. Scheme 2 shows that ion pair formation occurs via protonated nitrogen atom (i.e., tertiary amine group of CBZ) with Mo(V)–thiocyanate negative complex via electrostatic attraction [23].

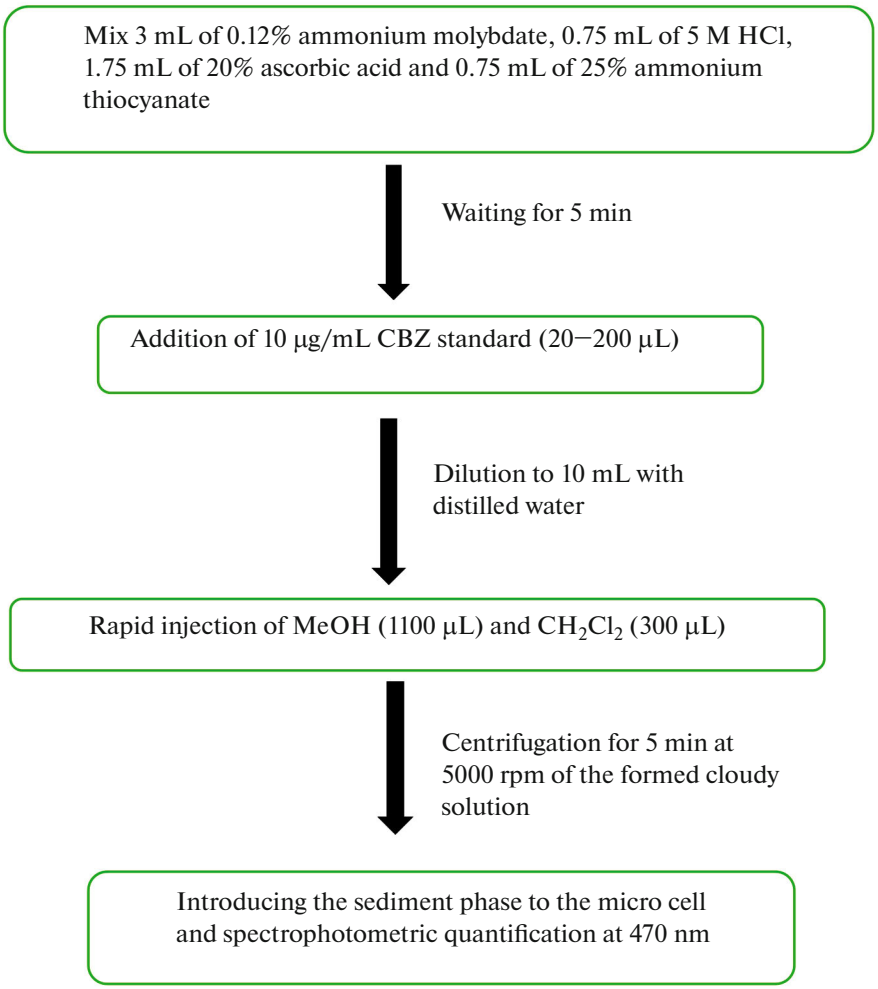
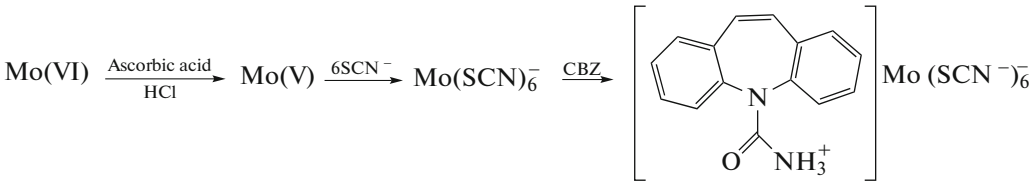


Fig. 1. Dispersive liquid–liquid microextraction procedure for carbamazepine determination.



CBZ–Mo(V)

Scheme 2. Suggested structure of formed ion pair carbamazepine Mo(V).

The colored product of ion pair is soluble in methylene chloride while Mo–thiocyanate binary complex is insoluble. Therefore, in this paper, the spectrophotometric method based on this colored product extraction using methylene chloride in the presence of methanol was developed. The absorbance spectra of the sedimented phase after DLLME showed that the maximum band was at 470 nm. Therefore, all the absorbance measurements were performed at 470 nm (Fig. 2).

Optimization of the reaction variables for the formation of ion pair. *Effect of ascorbic acid and ammonium thiocyanate concentrations.* As we mentioned earlier, reduction of Mo(VI) to Mo(V) occurs in the presence of ascorbic acid and ammonium thiocyanate combination. In addition to ascorbic acid functioning in the

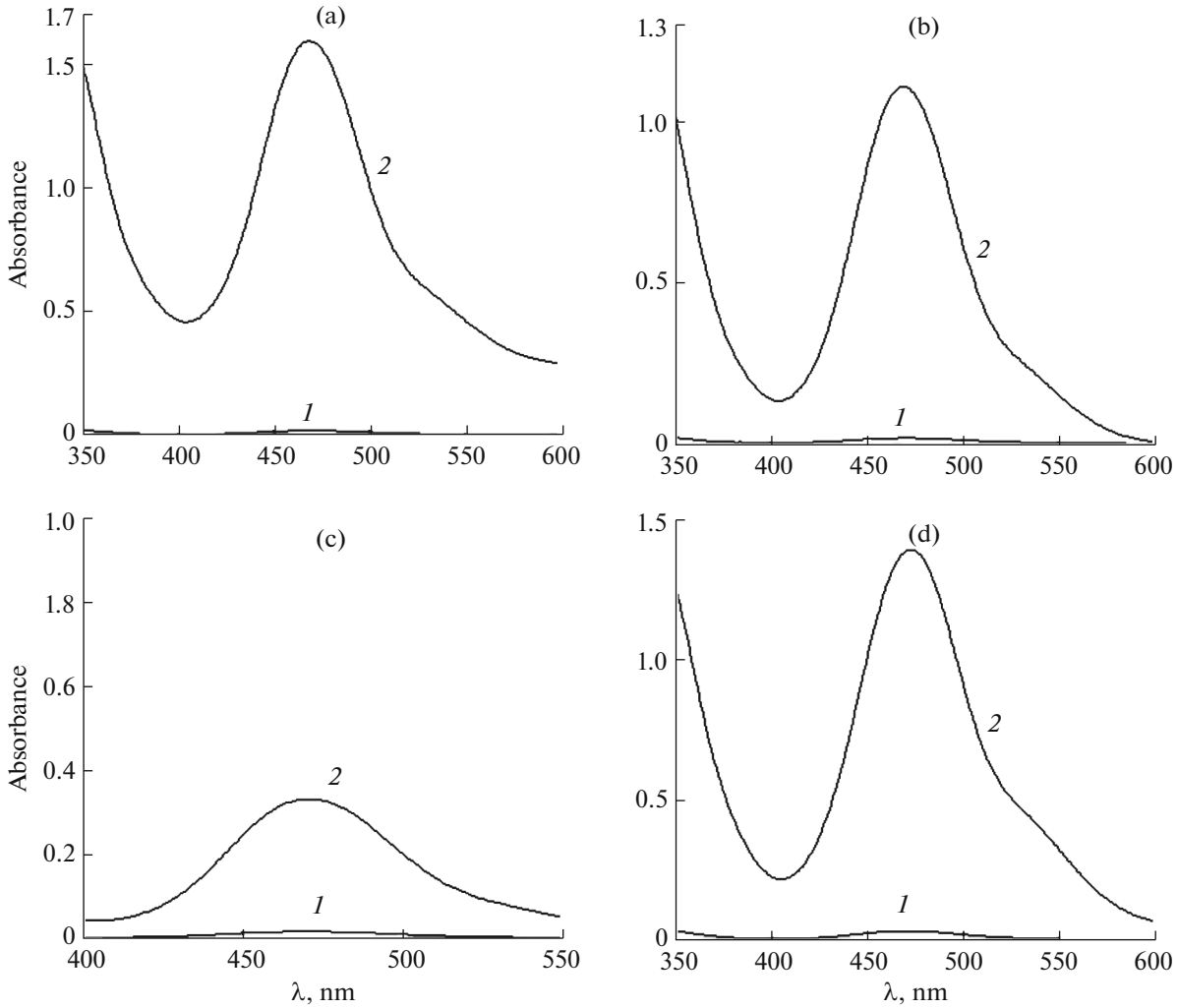


Fig. 2. Absorption spectra of extracted organic phase of 0.1 μg/mL carbamazepine before (*1*) and after dispersive liquid-liquid microextraction (*2*) for standard (a), drug (b), urine (c) and serum (d).

reduction process of Mo(VI), it plays an important role in the formation of the ion-pair as it enhances the sensitivity and stability of the binary Mo(V)–SCN complex, gives reproducible values and masks many interfering ions [24]. Therefore, the influence of ascorbic acid and thiocyanate concentrations was investigated in the range between 5–25% (w/v). The data showed that higher absorbance was obtained with 20 and 25% (w/v) of ascorbic acid and thiocyanate, respectively. Therefore, 20 and 25% (w/v) were adopted for the subsequent study.

Effect of ammonium molybdate concentration. To study the effect of ammonium molybdate concentration on the ion-pair formation, a series of experiments were conducted in which the concentration was studied in the range of 0.02–0.12% (w/v). 0.12% (w/v) of ammonium molybdate gave maximum absorbance, consequently, this value was chosen for further experiments.

Effect of hydrochloric acid concentration. The effect of HCl concentration on the reduction of ammonium molybdate was investigated in the range of 1–6 M. Based on the results obtained from Fig. 3a, absorbance increased gradually till 5 M hydrochloric acid concentration and then it decreased. Hence, 5 M HCl concentration was chosen as optimum.

Effect of temperature and time. Generally, in the analytical analysis, employing experimental conditions at lowest temperature and shortest reaction time is preferred [25]. The effects of temperature and reaction time were investigated in the ranges of 25–50°C and 5–30 min, respectively. The results revealed that the maximum reaction rate was obtained at room temperature within 5 min.

Optimization of dispersive liquid–liquid microextraction procedure. *Selection of extraction and disperser solvents.* Selection of extraction and disperser solvents is an important factor to get efficient extraction. An

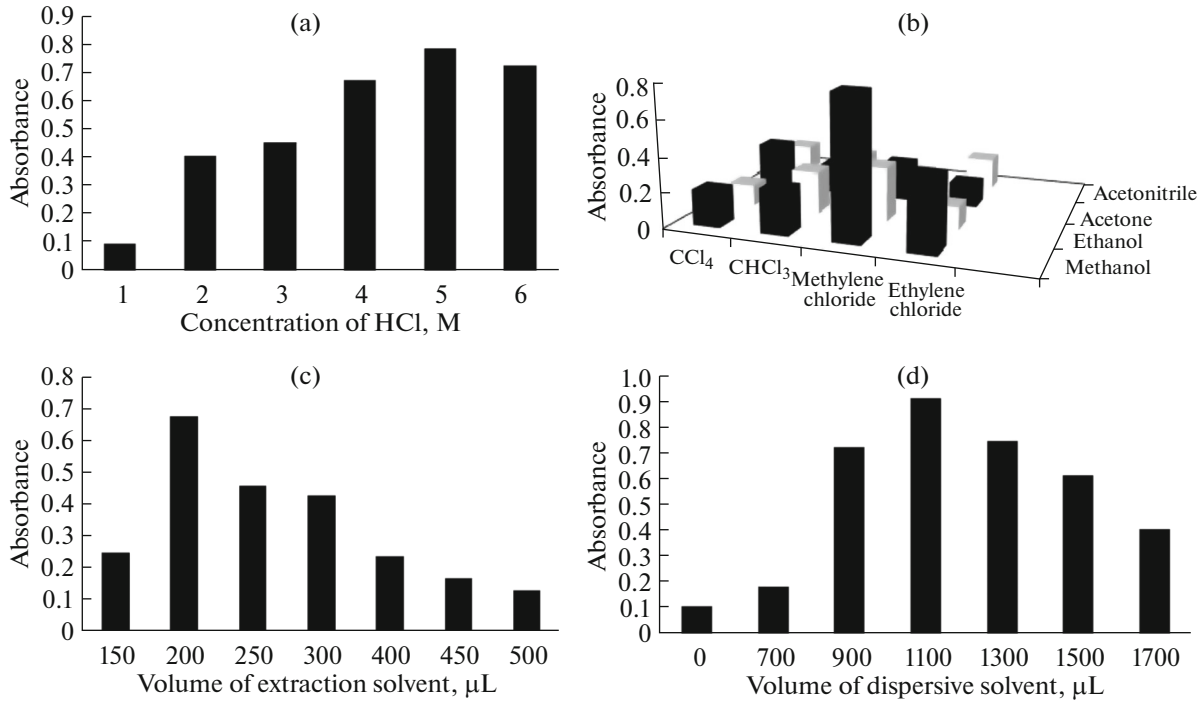


Fig. 3. Effects of hydrochloric acid concentration (a), types of extraction and dispersive solvents (b), extraction solvent volume (c) and disperser solvent volume (d).

efficient extraction solvent should have high extraction capability of target compounds, higher density than water, lower solubility in water and ability to form tiny droplets in the presence of a dispersive solvent [26]. For this purpose, halogenated hydrocarbons, such CCl_4, $CHCl_3$, benzene, methylene chloride and ethylene chloride, were tested as extraction solvents. The key factor of dispersive solvent selection is the miscibility of a dispersive solvent with both organic and aqueous phases. Therefore, selection of dispersive solvents is limited to some solvents such as acetonitrile, ethanol, acetone and methanol [27]. Combinations of selected extraction and disperser solvents were tested. As show in Fig. 3b, a stable two-phase system and higher signal were observed with a mixture of methylene chloride and methanol. Thus, methylene chloride and methanol were chosen as a suitable mixture for CBZ extraction.

Effect of extraction solvent volume. Another parameter greatly affecting the extraction efficiency, enrichment factor and sensitivity is the sediment phase volume [25]. CH_2Cl_2 volume was studied in the range of 200–500 μL. The results in Fig. 3c show that the absorbance increases by increasing the volume of CH_2Cl_2 up to 300 μL but decreases thereafter. The decrease in the absorbance is due to the dilution effect that decreases the amount of extracted colored complex in the organic layer [25]. Therefore, 300 μL was selected for the rest of the study.

Effect of disperser solvent volume. The volume of disperser solvent affects directly cloudy solution formation (water/extraction solvent/disperser solvent) [14]. Moreover, collection of the organic phase, polarity of the aqueous phase and change in droplets size can be affected by changing the disperser solvent volume [28]. Methanol volume in the range of 0–1700 μL containing 300 μL of methylene chloride was investigated. The absorbance was found to increase up to 1100 μL but dropped abruptly thereafter probably due to the extraction solvent increasing dissolution in water and thus lower extraction efficiency of the product (Fig. 3d) [14]. Therefore, 1100 μL was selected as the optimum volume for the subsequent experiments.

Effect of extraction time. In DLLME, extraction time is considered as the key factor and must be studied and evaluated. It is defined as the time interval between the injection of the mixture of disperser and extraction solvents and time of centrifugation process start [29]. For this purpose, different extraction times between 1 and 20 min were studied. The results indicated that the extraction time had no significant effect on the absorbance signal. This is because the endlessly large surface area between the extraction solvent and aqueous solution after cloudy solution formation; the color product disperses quickly into the extraction solvent. As can be seen, the most important advantage of DLLME is time independence.

Effect of centrifugation time and speed. Centrifugation is required to complete separation of the

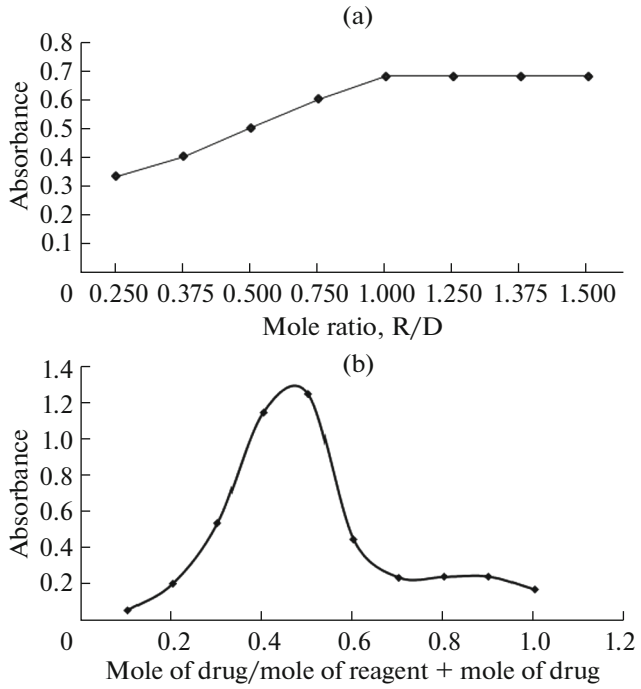


Fig. 4. Stoichiometric ratio of the reaction of Mo(V)–thiocyanate (R) with the carbamazepine (D) at 470 nm using molar ratio (a) and continuous variation methods (b).

extraction solvent from the aqueous phase. To obtain excellent extraction efficiency, centrifugation time and speed were evaluated in the ranges of 1–10 min and 1000–6000 rpm, respectively. Based on the results obtained, the best centrifuge time and speed were 5 min at 5000 rpm, respectively. Thus, all the subsequent experiments were performed at 5000 rpm for 5 min.

Effect of salt addition. The effect of salt was evaluated by adding different amounts of NaCl in the range of 0–12.5% (w/v). The results indicated that the signal intensity decreased as the salt concentration increased. This may be attributed to the increased viscosity of the bulk solution that resulted in a decrease in the diffusion rate that tended to restrict the movement of the analyte from the aqueous solution to the organic phase. Hence, further optimization was performed without salt addition.

Stoichiometry of the ion pair. The ion pair stoichiometry in the presence of ammonium thiocyanate excessive amount was determined by molar ratio (Fig. 4a) and continuous variation (Fig. 4b) methods in order to obtain the ratio between Mo(V) and CBZ. The results indicated that [Mo(V)–thiocyanate] : [drug] ion-pair was formed in the ratio of 1 : 1.

Method validation. The analytical features of the proposed method including linearity, correlation coefficient (r), linearity percentage (r^2, %), limit of detection (**LOD**), limit of quantification (**LOQ**) and enrichment factor (**EF**) are summarized in Table 1. LOD and LOQ were calculated based on $3s_b/m$ and $10s_b/m$, respectively, where s_b and m are standard deviation of the blank and slope of the calibration graph, respectively. EF was evaluated at the optimum conditions for five replicate extractions and was obtained from the slope ratio of the calibration graph after and before DLLME.

Sample solutions containing different concentrations (0.02–0.2 μg/mL) of CBZ were analyzed according to the recommended DLLME procedure and the corresponding spectra of the sedimented phase were recorded in the range of 190–1100 nm. As shown in Fig. 5, the absorbance increased upon increasing CBZ concentration.

The repeatability and reproducibility of the proposed method were evaluated by processing five replicates with five different concentrations on the same day (intra-day) and over three days (inter-day),

Table 1. Analytical parameters of dispersive liquid–liquid microextraction method

Parameter	Analytical feature	
	before DLLME	after DLLME
Regression equation	$y = 0.0404x - 0.1436$	$y = 4.7789x + 0.0289$
Correlation coefficient	0.999	0.999
Linearity percentage, %	99.78	99.86
Linear range, μg/mL	5–40	0.02–0.2
ε[a], L/(mol cm)	9.6×10^3	1.13×10^6
LOD, μg/mL	4	0.01
LOQ, μg/mL	14	0.04
S[b], μg/cm	0.025	209×10^{-6}
EF	–	~118

[a] Molar absorptivity, [b] Sandell's sensitivity.

respectively. The results showed that the method was accurate and precise depending on the percentage recovery value and relative standard deviation (**RSD**, %) as illustrated in Table 2.

Recovery tests were adopted for serum and urine samples, these samples were spiked with five different concentrations of CBZ standard and subjected to the proposed DLLME method. Good recoveries for real samples in the range of 93–102% were obtained (Table 2).

Influence of foreign compounds. The effect of interfering compounds on the determination of CBZ was investigated. Sample solutions containing 0.06 μg/mL of CBZ and different concentrations of other possibly existing compounds and ions (such as starch, glucose, sucrose, lactose, creatinine, alanine, urea, uric acid, SO_4^{2-}, K^+, Ca^{2+}, PO_4^{3-}) were prepared according to the developed procedure. The results showed that most of the selected compounds and ions did not interfere even if were in 10, 100 or 1000-fold excess over the concentration of the analyte.

Application. Performance of the developed DLLME method was evaluated by quantification of CBZ in different samples (different pharmaceutical preparations, serum and urine). For CBZ quantification in pharmaceutical preparations, the procedure was adopted on the weight of 0.02 μg from each drug in order to obtain 0.1 μg/mL (this concentration was chosen as centroid in the calibration curve). The analytical results (recovery, %) for CBZ quantification in different tablet formulations obtained from three manufactories using the proposed method are illustrated in Table 3. The obtained results by the proposed DLLME method show applicability of the method for the determination of CBZ trace levels suggesting the capability of the developed DLLME method to overcome matrix effects. Results obtained were statistically compared to those obtained by British pharmacopeia's method using Student's *t*-test and variance ratio *F*-test at a 95% confidence level and the results between the procedures were found not to differ significantly. Moreover, the values of calculated *t*- and *F*-tests presented in Table 4 indicate that there is no significant difference between the proposed and standard methods in accuracy and precision values for the determination of CBZ in pharmaceutical preparations. Moreover, the results in Table 2 show the applicability of proposed DLLME method to quantify CBZ in urine and serum samples.

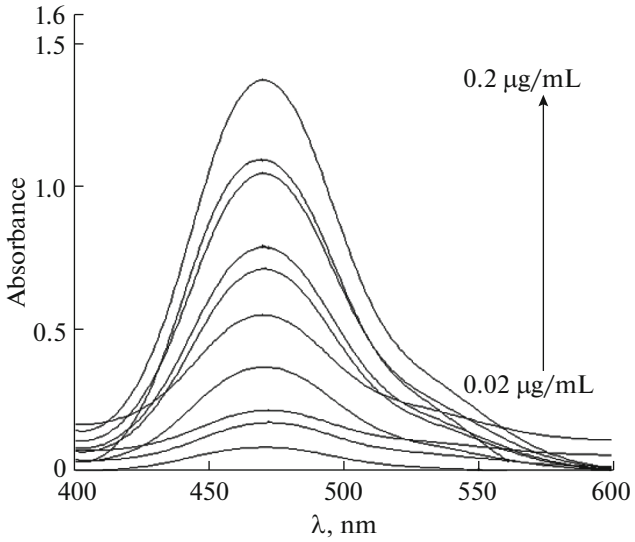


Fig. 5. UV-visible absorbance spectra of sediment phase in the presence of different carbamazepine concentrations.

Analytical quantitation with respect to extraction conditions of the proposed DLLME procedure with other reported methods was compared. Table 5 shows that the suggested DLLME method is faster and simpler than the previously reported methods providing a wide linear range and low detection limit.

CONCLUSIONS

Ion pair-DLLME coupled to microsample spectrophotometry for the extraction, preconcentration and determination of CBZ in pure and real samples was introduced for the first time. Ion pair preparation steps, extraction time and consumption of toxic solvents were minimized without affecting the sensitivity

Table 2. Accuracy and precision of the proposed method

Concentration, μg/mL	Intra-day repeatability (RSD, %, $n = 5$)				Inter-day reproducibility (RSD, %, $n = 15$)				Recovery, % ($n = 5$)			
	std.[a]	drug	urine	serum	std.	drug	urine	serum	std.	drug	urine	serum
0.02	1.7	1.3	1.7	1.4	1.6	1.7	1.8	1.8	92	93	93	100
0.06	0.7	0.4	0.6	0.7	0.8	1.2	0.9	1.2	96	100	95	95
0.1	0.3	0.4	0.5	0.4	0.3	0.5	0.8	0.5	97	98	95	101
0.15	0.2	0.4	0.3	0.3	0.2	0.4	0.4	0.4	95	101	101	101
0.2	0.1	0.2	0.2	0.3	0.1	0.4	0.3	0.3	100	100	101	101

[a] Standard.

Table 3. Determination of carbamazepine in pharmaceutical preparations using the proposed procedur

Sample	Pharmaceutical tablet content and manufacturer (200 mg)	Pharmaceutical weight equivalent to 0.02 μg of active ingredient, g	Theoretical content of active ingredient, mg	Practical content of active ingredient for proposed method, mg[a]	Practical content of active ingredient for standard method, mg[a]
1	Taver (Cyprus)	0.254 (0.14)[b]	200	184	198
2	Carbatol (Jordan)	0.459 (0.15)	200	189	186
3	Tegral (Egypt)	0.273 (0.22)	200	191	188

[a] Confidence limit of 95%, [b] RSD (%) is given in parenthesis.

Table 4. Comparison of linear range, limit of detection and extraction time for carbamazepine determination

Method	Linearity, μg/mL	LOD, μg/mL	Recovery, %	Sample	Extraction time, min	Reference
SPME/LC[a]	0.2–20	–	6	Human plasma	30	[30]
SBSE[b]/HPLC-UV	0.08–40	0.08	86.20–86.90	Human plasma	50	[5]
LLE/UV-Vis	10–350	3.36	100.3–100.6	Pharmaceutical preparation	1	[23]
LLE/HPLC	10–50	0.1	96.00–107	Blood and plasma	5	[31]
DLLME–IMS[c]	0.05–10	0.025		Pharmaceutical formulation	5	[26]
DLLME/HPLC	5–2.5 × 10^8	800	91	Urine	A few seconds	[32]
	5–5 × 10^8	1700	86	plasma		
DLLME/UV-Vis	0.02–0.2	0.01	92–100	Std.	None	Present study
	0.02–0.2	0.01	93–101	Drug		
	0.02–0.2	0.01	95–101	Serum		
	0.02–0.2	0.01	93–101	Urine		

[a] Solid phase microextraction/liquid chromatography, [b] stir bar-sorptive extraction, [c] ion mobility spectrometry.

of the method. The proposed method is rapid, efficient and economic indicated by the short analysis time, high sample throughput and low organic solvent consumption. The analysis time was reduced from ~30 min using LLE method to ~10 min using DLLME. Therefore, a total of six samples can be analyzed within an hour with the consumption of about 1.8 mL only of organic solvent comparable to the conventional LLE (2 samples per hour requiring ~60 mL of organic solvent). Besides employment of a usual laboratory equipment, wide linear range was obtained comparable to the conventional sample preparation methods (Table 5). Therefore, ion pair-DLLME introduces a good bridge between the sample solution containing trace levels of target analytes and microspectrophotometric injection and it can be used as an alternative method to the conventional extraction techniques.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper

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