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ORIGINAL ARTICLE

Copper(II)–neocuproine reagent for spectrophotometric determination of captopril in pure form and pharmaceutical formulations

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KEYWORDS

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Abstract A simple, rapid, sensitive and accurate spectrophotometric method for the determination of captopril in pure form and pharmaceutical formulations is developed. The procedure is based on the reaction of copper(II) with captopril in the presence of neocuproine (NC) (2,9-dimethyl-1,10-phenanthroline) reagent in acetate buffer at pH 5.0. Copper(II) is reduced easily by captopril to Cu(I)–neocuproine complex, which shows an absorption maximum at 448 nm. Beer's law was obeyed in the concentration range 0.3–3.0 μg mL^{-1} with a minimum detection limit (LOD) of 0.039 μg mL^{-1} and a quantification limit (LOQ) of 0.129 μg mL^{-1}. For more accurate results, Ringbom optimum concentration ranges was 0.5–2.7 μg mL^{-1}. The apparent molar absorbtivity and Sandell sensitivity were calculated. The validity of the proposed method was tested by analyzing the pure and pharmaceutical formulations and compared well with those obtained by the official method and demonstrated good accuracy and precision.

1. Introduction

Captopril, (Fig. 1), 1-(3-mercapto-2-D-methyl-1-oxoproppyl)-l-proline (*S,S*), is used therapeutically as an antihypertensive agent. It acts as a potent and specific inhibitor of angiotensin-converting enzyme. In addition, it is used in the management of heart failure, following myocardial infraction and in diabetic nephropathy. About 60–75% of a dose of CPL is absorbed from the gastro-intestinal tract and peak plasma concentration is achieved in about an hour. About 30% of the drug is bound to plasma protein (Parfitt et al., 1999). The drug is listed in United States Pharmacopoeia (United States Pharmacopoeia et al., 2004), which recommends an HPLC method for its assay in bulk and tablet formulations.

Several methods have been reported for the quantitative determination of CPL in dosage forms and biological fluids, including: GC–MS (Liu et al., 1995, 1998; Rose, 1998), HPLC (Huang et al., 2006; Nishikawa et al., 2004; El-Gindy et al.,

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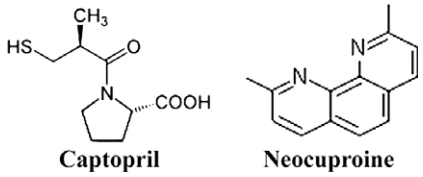

Figure 1 The chemical structure of captopril and neocuproine.

2004; Russell et al., 1997; Bahmaei et al., 1997; Bald and Sypniewski, 1997; Kok et al., 1997; Favaro and Fiorani, 1996; Salazar et al., 1999; Battermann et al., 1998; Khedr and El-Sherief, 1998), electrochemistry (Stefan et al., 2000a; Stefan et al., 2000b; Fraga et al., 1998; Riberio et al., 2003), chemiluminescence (Ouyang et al., 1999), capillary electrophoresis (Hillaert and Van-den-Bossche, 1999), flow injection chemiluminescence (Li et al., 2001), titrimetry (El-Brashy, 1995), atomic absorption spectrophotometry (El-Reis et al., 2000) and several spectrophotometric methods have been reported in the literature (Askal, 1991; Sastry et al., 1991a; Mahadik et al., 1991; Sastry et al., 1991b; Albero et al., 1993; Ibraham, 1994; Jovanovic et al., 1995; Sastry et al., 1996; Huan et al., 2005; Sachan et al., 1997; Sastry et al., 1998; Gumieniczek et al., 1998; Karlícek and Solich, 1998; El Walily et al., 1999; Shingare and Kale, 2000; Basavaiah et al., 2003a, b, c; Tzanavaras et al., 2003; Srivastava et al., 2003; Basavaiah and Nagegowda, 2004a; Basavaiah and Nagegowda, 2004b; Hosseinimehr et al., 2004; El-Shabrawy et al., 2004; Rahman et al., 2005; Huan et al., 2005; Shama et al., 2006; Chandru and Sharada, 2007; Suarez et al., 2007; Belal et al., 2008; Haggag et al., 2008; El-Enany et al., 2008). Comparison between the previous spectrophotometric methods for the determination of captopril are shown in Table 1. These methods suffer from a variety of disadvantages, such as use of sophisticated and time consuming techniques, require expensive instruments, low sensitivity, heating, extraction, require nonaqueous media and have higher Beer's law ranges.

The formation of the charge transfer complex between Cu(I) and neocuproine (NC) (2,9-dimethyl-1,10-phenanthroline) is the basis of the existing spectrophotometric method for the determination of trace amounts of reducing agents (Greenwood and Earnshaw, 1997). This was previously used to determine the biochemically important reductants such as cysteine (Ütem and Apak, 1991), Vitamin E (Ütem et al., 1997), ascorbic acid (Guclü et al., 2005), isoniazide (Safavi et al., 2004), certain proton pump inhibitors (Syed and Syeda, 2007) and ceftazidime (Moreno and Salgado, 2008) can be determined by reduction of Cu(II), followed by treating the Cu(I) with chromogenic reagent neocuproine.

The aim of the present study is to apply simple, accurate, selective, reproducible, and high sensitivity spectrophotometric method of the determination of captopril in pure form and pharmaceutical formulations based on its reducing ability.

2. Experimental

2.1. Apparatus

All absorption spectra were made using Kontron 930 (UV–Visible) spectrophotometer (German) with a scanning speed of 200 nm/min and a band width of 2.0 nm, equipped with

Table 1 Comparison between spectrophotometric methods for the determination of captopril.

Method	λ_{max} (nm)	Beer's law ($\mu g\ mL^{-1}$)	Detection limits ($\mu g\ mL^{-1}$)	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)	Reference
$FeCl_3$ + bipyridyl	523	0.25–25	–	–	26
Residual iodine	351				
Residual iodine–starch complex	620				
Palladium(II) chloride	380	up to 5×10^{-4} M	2.17	1.875×10^3	32
Ecess sodium nitrite/0.25 M HCl/cresyl fast violet acetate	555	0.1–0.5			33
Excess $KBrO_3$ + celestine blue	540	0.4–4.0			36
Carbon disulphide + divalent metals: cobalt(II)	390	16–48	0.878	3.00×10^3	39
Pallidium(II)	450	40–120	3.479	1.85×10^3	
Nikel(II)	364	30–80	1.838	1.30×10^3	
Sodium metavanadate in acetic acid medium + ferroin	510	2.5–20	0.18	7.31×10^3	44
Excess of iodate in sulphuric acid medium.	460	range 50–400	–	0.38×10^3	46
Excess of chloramine-T + metol and sulphanilic acid	520	0–30	0.95	5.23×10^3	47
Excess bromate–bromide reagent + methyl orange	510	0.25–2.0	–	7.08×10^4	48
DTNB reagent	412	$1–10\times10^{-5}$ M	3.2×10^{-7} M	13,553	49
Potassium iodate in HCl medium + CCl_4	510	120–520	–	–	51
Potassium permanganate in acidic medium	660	0.4–12.5	0.106	1.74×10^4	53
+ methylene blue (MB)	610	0.3–10	0.063	2.98×10^4	
Acid blue 74 (AB)	510	0.5–11	0.145	1.87×10^4	
Acid red 73 (AR)	520	0.4–8.3	0.093	2.63×10^4	
Amaranth dye (AM)	485	0.5–9.3	0.134	2.35×10^4	
Acid orange 7 (AO)					
Hexacyanoferrate(III)	510	0.25–12.00	0.08	9.14×10^3	55
2,4-Dinitrofluorobenzene (DNFB)		2.4–16.8	–	–	56
4-chloro-7-nitro-2,1,3-benzoxadiazole (NBD-Cl)	420	–	–	–	57
2,6-dichloroquinone-4-chlorimide (DCQ)	443	10–50	0.66	–	58
in dimethylsulphoxide.					
Cu(II) + neocopoin	448	0.3–3.0	0.056	4.223×10^4	Present work

10 mm matched quartz cells. Hanna pH-meter instrument (Portogal) (HI: 9321) was used for checking the pH measurements. All experiments were performed at 25 °C.

2.2. Materials

An authentic sample of captopril was kindly supplied by Bristol Myers Squibb Egypt Co., Giza, Egypt. The commercial preparations were bought from the local market.

2.3. Standard solutions

A stock solution 1000 μg mL^{-1} of captopril was prepared by dissolving 0.1 g of captopril in 100 mL of bidistilled water. The standard solution was stable for one week when kept in the refrigerator. Working standards were prepared by appropriately diluting the above solution with the same solvent.

2.4. Reagents

All reagents were of analytical reagent grade. Double distilled water was used throughout the study.

A stock solution 1.0×10^{-2} M of Cu(II) was prepared by dissolving 0.241 g of $Cu(NO_3)_2{\cdot}3H_2O$ (Merck) in water and diluting to the mark in a 100 ml standard flask.

A 5.0×10^{-3} M stock solution of neocuproine hemihydrate (Merck) was prepared by dissolving 0.054 g of reagent in ethanol in a 50 mL standard flask and diluting to the mark with the same solvent.

Acetate buffer solutions of acetic acid–sodium acetate (pH 3.0–7.0) were prepared by following the standard methods. The pH of stock solution was adjusted to an appropriate value by addition of 0.2 M hydrochloric acid or sodium hydroxide with the help of pH meter (Perrin and Dempsey, 1974).

2.5. Recommended analytical procedure

Two mL of 5.0×10^{-3} M neocuproin solution, 1.0 mL of 1.0×10^{-2} M Cu(II) solution, 3.0 mL acetate buffer solution (pH 5.0) and a suitable volume (0.06–0.6 mL) of captopril standard solution 50 μg mL^{-1} were placed in a 10 mL volumetric flask and mixed. After 150 s, the absorption was measured at 448 nm against a neocuproin–copper(II) solution reagent blank.

2.5.1. Analysis of pharmaceutical formulations

Twenty tablets of the drug were weighed, grounded to a fine powder and mixed. A sample equivalent to approximately 10 mg of captopril was weighed accurately, transferred into a 100 mL calibrated flask and diluted to volume with water. Then, mixed well for 10 min using a magnetic stirrer to aid dissolution and filtered through a sintered glass crucible G4. An appropriate volume of the filtrate was diluted further with water so that the concentration of captopril in the final solution was within the working range. The recommended procedures under calibration curve were then performed.

3. Results and discussion

Captopril as all thiols was expected to undergo to some extent oxidative degradation such as the formation of disulphide and this suggests the investigation of an analytical procedure based on the specific reactivity of the thiol group.

The development of direct spectrophotometric methods for thiols is still a difficult task. The problem is to find a reaction that gives a minimum of side-products and interferences and a simple procedure.

Although reaction with Cu(II) ions is among the most commonly used procedures for determination of thiols, the only spectrophotometric method (Gawargious et al., 1976) utilizing this reaction is indirect and based on addition of excess Cu(II), collection of the Cu(I) mercaptide formed and spectophotometric measurement of the unreacted Cu(II) ions left in the solution:

$$4RSH + 2Cu^{2+} \rightarrow R\text{-}S\text{-}S\text{-}R + 2RSCu + 4H^{+}$$

The present work offers a quite different approach. When the copper(II)–neocuproine complex is used as the reagent, precipitation of Cu(I) mercaptide does not take place. Instead, the orange-yellow Cu(I)–neocupoine chelate is formed once, according to the equation:

$$2RSH + 2[Cu(NC)_2]^{2+} \rightarrow [Cu(NC)_2]^{+} + RS\text{-}SR + 2H^{+}$$

The reduction of Cu(II) to Cu(I) in the presence of neocuproine and subsequent complex formation between Cu(I) and neocuproine takes few minutes to complete. Fig. 2 shows the changes of the absorbance at 448 nm with time during the first few minutes from initiation of the reaction. As it is obvious, the absorbance reaches a maximum after about 2 min and remains constant afterwards. Therefore, all the absorbance measurements were performed after 150 s from initiation of the reaction.

3.1. Absorption spectrum

The reagent blank does not absorb in the visible range of spectrum, but when captopril reacts with $[Cu(NC)_2]^{2+}$, an orange-yellow colored $[Cu(NC)_2]^{+}$, is formed which has an absorbance maximum at 448 nm and was stable for at least 2 h. The absorption spectra of the products and reagent blank are shown in Fig. 3.

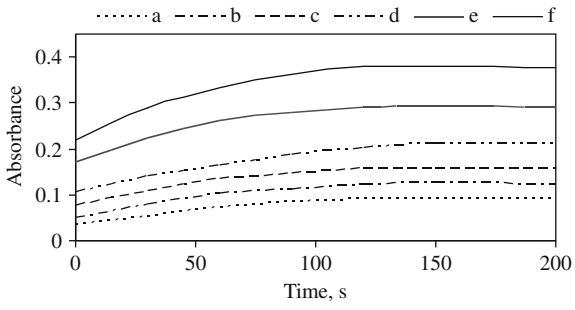

Figure 2 Kinetic curves for reduction of Cu(II)–neocuproine at different concentrations of captopril: (a) 0.5 μg mL^{-1}; (b) 1.0 μg mL^{-1}; (c) 1.5 μg mL^{-1}; (d) 2.0 μg mL^{-1}; (e) 2.5 μg mL^{-1}; (f) 3.0 μg mL^{-1}.

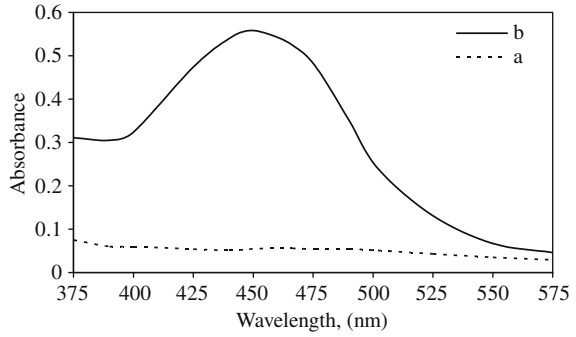

Figure 3 Absorption spectra of: (a) Cu(II)–neocuproine reagent blank; (b) Cu(II)–neocuproine in the presence of 3.0 μg mL^{-1} captopril.

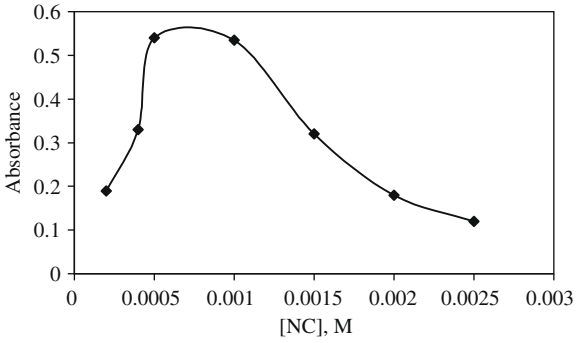

Figure 5 Effect of neocuproine concentration on the absorbance. Conditions: pH 5.0 (acetate buffer); Cu(II) concentration of 1.0×10^{-2} M; captopril concentration 3.0 μg mL^{-1}; temperature 25 °C.

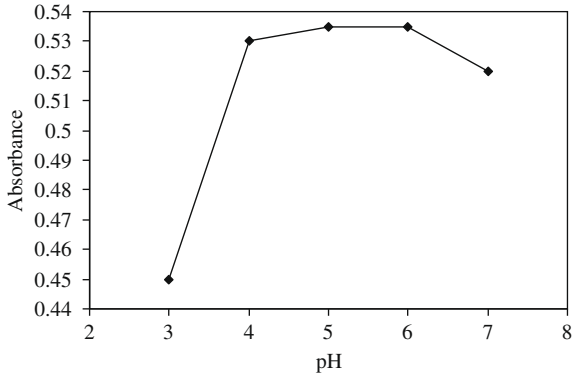

Figure 4 Effect of pH on the absorbance. Conditions: neocuproine concentration 5.0×10^{-3} M; Cu(II) concentration 1.0×10^{-2} M; captopril concentration 3.0 μg mL^{-1}; temperature 25 °C.

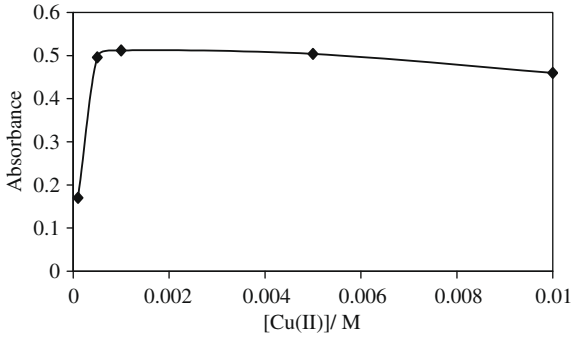

Figure 6 Effect of Cu(II) concentration on the absorbance. Conditions: pH 5.0 (acetate buffer); neocuproine concentration 5.0×10^{-3} M; captopril concentration 3.0 μg mL^{-1}; temperature 25 °C.

3.2. Effect of experimental parameters

The effects of variables such as pH, concentration of neocuproine and Cu(II) were studied to establish the best reaction conditions for the maximum sensitivity.

3.2.1. Effect of pH

The effect of pH on the reduction of Cu(II) by captopril and formation of Cu(I)–neocuproine complex was studied over the pH range of (3.0–7.0) of acetate buffer solutions. Fig. 4 illustrates the effect of changing pH on the absorbance of the solution mixture. The absorbance increased with increasing pH up to 4.0 and remains constant to pH 6.0. Therefore, pH 5.0 was selected for further studies. The influence of pH on Cu(II) reduction by captopril is expected since captopril has a thiol group and H^+ is involved in the oxidation–reduction process of this thiol group.

3.2.2. Effect of neocuproine concentration

The effect of neocuproine concentration was examined over the range 5×10^{-4} to 2.5×10^{-3} M. The results are shown in Fig. 5. As it can be seen, at high concentrations of neocuproine, the absorbance due to Cu(I)–neocuproine complex decreases. This might be due to the fact that high concentrations of neocuproine would result in a positive interference from Cu(II) which could have arisen from incomplete conversion of Cu(I) into the Cu(I)–neocuproine complex via mixed ligand complex formation, as suggested by Ütem and Apak (1991). A 5.0×10^{-3} M neocuproine concentration was thus chosen as the optimum conditions.

3.2.3. Effect of Cu(II) concentration

The influence of Cu(II) concentration on the absorbance in the concentration range of 1.0×10^{-1} to 1.0×10^{-4} M of Cu(II) was shown in Fig. 6. The oxidising power of Cu(II) in a solution containing neocuproine is dependent on the ease of formation of $[Cu(NC)_2]^+$. An excess of Cu(II) can exhibit an affinity for neocuproine, thereby preventing the preferential quantitative formation of $[Cu(NC)_2]^+$. Thus, large excess of Cu(II) competes with Cu(I) for complex formation with neocuproine. A 1.0×10^{-2} M was selected as the optimum Cu(II) concentration.

3.3. Analytical performance

3.3.1. Method validation

The validity of the method was tested regarding linearity, specificity, accuracy, repeatability and precision according to ICH

Q2B recommendations (Guidance for Industry Bioanalytical method Validation et al., 2001).

3.3.1.1. Linearity. The absorbance–concentration plot was rectilinear over the range of 0.3–3.0 μg mL^{-1} with a minimum detection limit of 0.039 μg mL^{-1}. Linear regression analysis of the data gave the following equation:

$$A = 4 \times 10^{-3} + 0.1877C \ (r = 0.9998).$$

Where, A is the absorbance in 1 cm cell and C is the concentration of the drug in μg mL^{-1} and r is the correlation coefficient.

The limit of quantification (LOQ) was determined by establishing the lowest concentration that can be measured according to ICH Q2B (Guidance for Industry Bioanalytical method Validation et al., 2001). The results are shown in Table 2. The limits of detection (LOD) were determined by establishing the minimum level at which the analyte can be reliably detected, and the results are also abridged in Table 2. LOQ and LOD were calculated according to the following equation (Guidance for Industry Bioanalytical method Validation et al., 2001):

$$\mathrm{LOQ} = 10\sigma/S$$

$$\mathrm{LOD} = 3.3\sigma/S.$$

Where, σ: the standard deviation of the intercept of regression line. S: Slope of the calibration curve.

The proposed methods were evaluated for the accuracy as percent relative error (% RE) and the precision as percent relative standard deviation (% RSD) (Table 2). Statistical analysis (Miller and Miller, 2005) of the results, obtained by the official (United States Pharmacopoeia et al., 2004) and the proposed methods using student's t-test and variance ratio F-test, show no significant difference between the performance of the two methods regarding the accuracy and precision, respectively (Table 2).

Table 2 Analytical parameters and application of the proposed method and official method for the determination of captopril in pure form.

Parameters	Proposed method	Official method (2)
Wavelengths, λ_{max} (nm)	448	
Beer's law limits (μg mL^{-1})	0.3–3.0	
Ringbom limits (μg mL^{-1})	0.5–2.7	
Molar absorptivity ε, (L/mol^{-1} m^{-1})	4.223×10^4	
Sandell's sensitivity (ng cm^{-2})	5.15	
Regression equation (y)[a]		
Intercept (a)	0.004	
Slope (b)	0.1877	
Correlation coefficient (r)	0.9998	
LOD (μg mL^{-1})	0.039	
LOQ (μg mL^{-1})	0.129	
No. of experiments	6	3
Mean found (% ± SD)	100.04 ± 0.75	99.89 ± 0.78
RSD	0.75	0.78
RE	0.307	0.45
Variance	0.56	0.61
Calculated t-value (2.36)[b]	0.23	
Calculated F-value (5.79)[b]	1.08	

RE, relative error; RSD, relative standard deviation; LOD, limit of detection; LOQ, limit of quantification; ε, molar absorptivity coefficient.

[a] $A = a + b{\cdot}C$, where, A is the absorbance, a is the intercept, b is the slope and C is the concentration of drug in μg mL^{-1}.

[b] The theoretical values of t and F at $P = 0.05$.

3.3.1.2. Precision, accuracy and specificity. In order to determine the accuracy and precision of the proposed methods, solutions containing four different concentrations of captopril were prepared and analyzed in six replicates. The relative standard deviation as precision and percentage relative error (Er%) as accuracy of the suggested method were calculated at 95% confidence level can be considered satisfactory. Precision was carried out by six determinations at four different concentrations. The percentage relative error calculated using the following equation:

$$\mathrm{Er}\% = [(\text{founded} - \text{added})/\text{added}] \times 100$$

The inter-day and intra-day precision and accuracy results are shown in (Table 3). The analytical results of accuracy and precision show that the proposed method has good repeatability and reproducibility.

3.3.1.3. Robustness of the method. The robustness of the method adopted is demonstrated by the constancy of the absorbance with the deliberated minor changes in the experimental parameters such as pH, volume of NC, 2.0 ± 0.2 mL, and change in the volume of Cu(II) (1.0×10^{-2} M), ±0.1 mL. These minor changes that may take place during the experimental operation did not affect the absorbance of the reaction product.

Table 3 Evaluation of the inter-day and intraday precision and accuracy for captopril obtained by the proposed method.

Taken (μg mL^{-1})	Inter-day			Intraday		
	Recovery[a] (%)	Precision (RSD%)[a]	Accuracy (Er%)	Recovery[a] (%)	Precision[a] (RSD%)	Accuracy (Er%)
0.5	98.94	1.12	−1.06	99.90	0.66	−0.10
1.0	99.57	0.92	−0.43	99.92	0.90	−0.08
2.0	99.92	0.81	−0.08	99.30	0.45	−0.70
3.0	100.20	0.108	0.20	100.15	1.17	0.15
0.5	98.94	1.12	−1.06	99.90	0.66	−0.10

RSD%, percentage relative standard deviation.

Er%, percentage relative error.

[a] Mean of five determination.

Table 4 Application of the standard addition technique for the determination of captopril in pharmaceutical preparations using the proposed method.

Preparations	Taken (μg mL^{-1})	Added (μg mL^{-1})	Recovery[a] (%)	
			Proposed method	Reference method Sastry et al. (1996)
Capoten tablets[b] (25 mg captopril/tablet)	0.5	–	100.90	
		0.5	101.20	
		1.0	101.05	
		1.5	101.30	
		2.0	99.80	
		2.5	100.50	
	Mean ± SD		101.09 ± 0.37	101.99 ± 0.54
	t[e]		3.07	
	F[e]		2.13	
Farcopril plus tablets[c] (50 mg captopril and 25 mg of hydrochlorothiazide/tablet)	0.5	–	99.55	
		0.5	99.95	
		1.0	100.05	
		1.5	99.25	
		2.0	98.85	
		2.5	100.20	
	Mean ± SD		99.64 ± 0.52	100.48 ± 0.85
	t[e]		1.62	
	F[e]		2.67	
Capozide tablets[d] (25 mg captopril and 12.5 mg of hydrochlorothiazide/tablet)	0.5	–	99.60	
		0.5	100.45	
		1.0	100.15	
		1.5	100.30	
		2.0	99.85	
		2.5	98.70	
	Mean ± SD		101.01 ± 0.65	101.99 ± 0.54
	t[e]		2.59	
	F[e]		1.45	

[a] Mean of three different experiments.
[b] Capoten™ tablets containing 25 mg of captopril each (batch # F91772) product of Bristol Myers Squibb Co., Giza, Egypt.
[c] Farcopril tablets containing 50 mg of captopril and 25 mg of hydrochlorothiazide each (batch # 843); product of Pharco pharmaceuticals Alexandria, Egypt.
[d] Capozide tablets containing 50 mg of captopril each (batch # D91058) product of Smith Kline Beechane, LLC, (GSK), Giza, Egypt.
[e] Calculated t and F-values; tabulated t- and F-values for five degrees of freedom; and 95% confidence limits ($p = 0.05$) are 2.36 and 5.79 (69).

3.4. Effects of interference

The criterion of interference was an error of not more than ±3.0% in the absorbance. To test the efficiency and selectivity of the proposed method to pharmaceutical formulations. A systematic quantitative study was undertaken by measuring the absorbance of solutions containing 3.0 μg mL^{-1} of captopril by varying the additives and excipient such as glucose, lactose, fructose, calcium, hydrogen phosphate, magnesium stearate and starch. The excipients present in all tablets are not interfering for drug. Hydrochlorothiazide which is frequently co formulated with captopril in capozide and farcopril plus tablets did not interfere with the proposed method.

3.5. Analytical applications

The proposed method was applied to the determination of captopril in commercial tablets. Common tablet excipients did not interfere with the assay. Moreover, to check the validity of the proposed method, dosage forms were tested for possible interference with standard addition method. The performance of the proposed methods was assessed by calculation of the t-test (for accuracy) and a variance ratio F-value (for precision) compared with the official method (United States Pharmacopoeia et al., 2004). (for 95% confidence level with five degrees of freedom (Miller and Miller, 2005)).

The results showed that the t- and F-values were less than the critical value, indicating that there was no significant difference between the proposed and reference method (Sastry et al., 1996) for captopril as shown in Table 4. Because the proposed method was more reproducible with high recoveries than the reference method, they can be recommended for the routine analysis in the majority of drug quality control laboratories.

4. Conclusions

A Cu(II)–neocuproine proved to be a suitable reagent for the determination of captopril in pure form and its pharmaceutical preparations. The high molar absorptivity (ε) of the proposed method is a decisive advantage since the interference from associated excipients was not observed. The proposed method is simple, time saving and reproducible. Thus, the proposed method can be used as an alternative for rapid and routine

determination of captopril in bulk samples and various pharmaceutical formulations in quality control and industry.

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