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Dedicated to Professor Victor-Emanuel Sahini on the occasion of his 85th anniversary

A SPECTROPHOTOMETRIC METHOD FOR CAPTOPRIL DETERMINATION BY USING FLUORESCEIN NATRIUM-BROMINE SYSTEM

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A new simple and sensitive spectrophotometric method is described for the determination of captopril (CP) in pure form and in formulations. The procedure involves the addition of a known excess of bromate-bromide mixture to captopril in hydrochloric acid medium followed by the determination of surplus oxidant on the basis on its reaction with Fluorescein natrium (FL) by measuring the absorbance at 436 nm. The system obeys Beer's law for 0.2-4.50 μg mL^{-1} CP with a correlation coefficient of 0.9998. The limits of detection and quantification are calculated to be 0.06 and 0.19 μg mL^{-1}, respectively. The proposed method was applied successfully for the determination of CP in pharmaceutical formulations with mean recoveries of 99.76 to 100.36 per cent.

INTRODUCTION

Captopril, (CP, 1-[(2*S*)-3-mercapto-2-methyl-L-oxopropyl]-L-proline, Fig. 1) is a potent, competitive inhibitor of angiotensin-converting enzyme (ACE), the enzyme responsible for the conversion of angiotensin I (ATI) to angiotensin II (ATII). ATII regulates blood pressure and is a key component of the renin-angiotensin-aldosterone system (RAAS). Captopril may be used in the treatment of essential or renovascular hypertension and to treat congestive heart failure in combination with other drugs (e.g. cardiac glycosides, diuretics, β-adrenergic blockers). Captopril may improve survival in patients with left ventricular dysfunction following myocardial infarction and to treat nephropathy, including diabetic nephropathy.[1] Determination of captopril has previously been reported by capillary electrophoresis,[2] flow injection analysis,[3-6] high performance liquid chromatography,[7,8] gas chromatography-mass spectrometry,[9] potentiometry,[10] amperometry,[11] stripping voltammetry,[12] chronoamperometry, cyclic and differential pulse voltammetric techniques.[13] Some of these methods require many special sample preparations. The US Pharmacopoeia recommends volumetric and HPLC methods for the assay in bulk and tablet formulations.[14] The volumetric procedure is based on captopril titration in acid medium using an iodine solution in presence of excess of iodide, with starch as indicator. Taking into consideration that the methods based on modern instrumental techniques require expensive instrument and maintenance and involve several manipulation steps and derivatization reactions, many spectrophotometric methods were reported for captopril determination. Captopril cannot absorb at useful UV-Vis spectral region. For this reason, many indirect spectrophotometric methods are reported for the determination of captopril in its pharmaceutical dosage forms. These include: the use of reagents that react with captopril to form species that absorb in the visible region (by

complex formation;[3,15-18] coupling reactions;[19-24] redox reaction, based on captopril reducing action[4,25-37]). Kinetic spectrophotometric methods[35,37] were also reported. Captopril has also been assayed by chemiluminescence methods.[5,38]

In this article a simple and accurate spectrophotometric procedure to determine captopril, which would overcome the difficulties encountered in most visible spectrophotometric and HPLC methods, is proposed. The method involves treating a fixed amount of bromate-bromide solution in acid medium with captopril solution and determining the unreacted bromine by treating with a fixed amount of Fluorescein natrium dye solution and measuring the absorbance at 436 nm. The proposed method is compared with other reported spectrophotometric methods being more sensitive than previously reported ones. The statistical evaluation of the method was examined by determining its precision and accuracy. Accuracy and reliability of the proposed method were further ascertained by parallel determination by the reference method and by recovery studies. The method was applied to the determination of CP in tablets.

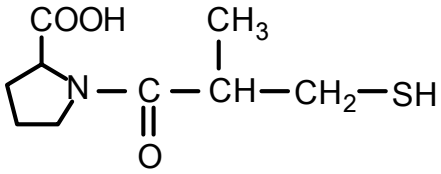

Fig. 1 – Structural formula of captopril.

RESULTS AND DISCUSSION

The thiol drug captopril has been reported to possess reducing properties, which could result in specific redox reaction with different oxidants, such as Ce(IV),[28] Fe(III),[29,35,36] chloramine-T,[30,31] Mn(VII),[32] bromine, generated in situ by the action of acid on a bromate-bromide mixture,[33] KIO_3,[34] Folin-Ciolteu reagent,[39] molybdophosphoric acid,[40] Cu(II),[41] V(V).[42] The reducing property of CP permits its indirect spectrophotometric determination by quantification of excess oxidant. The excess oxidant should be quantified taking into account that many dyes are irreversibly destroyed to colourless species by oxidizing agents in acid medium. The proposed method involves two stages: oxidation of CP with excess bromine (generated in situ) and estimation of excess oxidant using a known excess of FL dye. The excess FL dye remaining, is then measured colorimetrically at λ_{max}=436 nm. The effects of essential parameters are described.

Effect of dye concentration. To establish the optimum concentration of the reagent, different volumes of 5×10^{-4} mol L^{-1} FL solution were used. The optimum volume used for the production of maximum and reproducible color intensity is 1 mL of 5×10^{-4} mol L^{-1} FL in 10 mL total volume.

Effect of acid concentration on the reaction between CP and Bromine. Preliminary studies showed that the optimum acid of the examined (sulfuric, hydrochloric and nitric acids) was hydrochloric acid. The effect of HCl concentration on the oxidation of CP by bromine was studied from 0.6 to 1 mol L^{-1} HCl solution and 10^{-5} mol L^{-1} CP solution. In the first step, mixtures of 1 mL 10^{-4} mol L^{-1} CP + water + 1 mL of bromate-bromide solution (30 μg mL^{-1} in $KBrO_3$) + 1 mL of 5 mol L^{-1} HCl were prepared by varying the acidity between 0.6-1 mol L^{-1}. Then, 1 mL of 5×10^{-4} mol L^{-1} FL solution was added and the contents were diluted to volume with water and mixed well. As we observe in Fig. 2, the analytical signal increased with increase of the concentration of HCl up to 0.70 mol L^{-1} and decreased for higher concentration. Thus, for further work, in the first step, mixtures of CP + water (up to 5 mL) + 1 mL of bromate-bromide solution (30 μg mL^{-1} in $KBrO_3$) + 1 mL of 5 mol L^{-1} HCl were prepared.

Effect of time on the oxidation of CP by bromate-bromide mixture. The oxidation time of CP by bromate-bromide mixture was determined by applying the recommended procedure for spectrometric measurements, in the following conditions: by varying the time of CP-bromine reaction (t_1=0.5-40.5 min, at 5 min intervals), at a fixed time of FL-bromine reaction (t_2=10 min). The absorbance measurement started at 30 s after adding the bromate-bromide solution. The absorbance time profile of CP-bromate-bromide-FL mixture showed full color increase after 10 min. Hence, the reaction time of CP with bromine of 10 minutes was chosen for further experiments. The effect of time after addition the dye indicated that shaken for 10 min is sufficient to give reliable results.

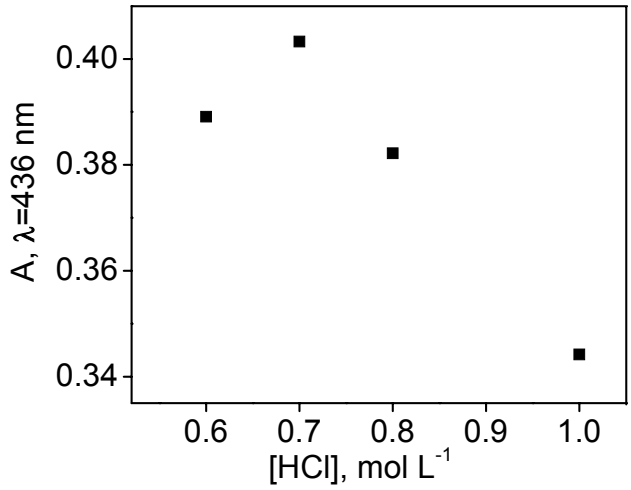

Fig. 2 – Effect of HCl concentration on the reaction between CP and bromate-bromide mixture. [FL] = 5×10^{-5} mol L^{-1}; [bromate] = 2×10^{-5} mol L^{-1}; [CP] = 10^{-5} mol L^{-1}.

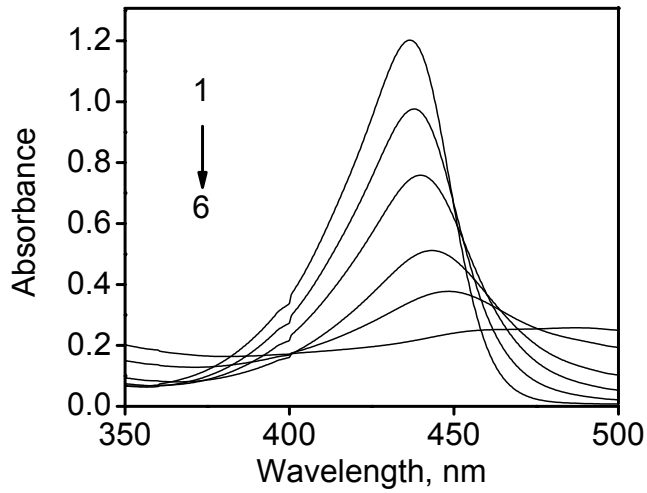

Fig. 3 – Effect of bromate concentration on the oxidation of CP. [bromate]$\times10^5$, mol L^{-1} = 0 (1); 0.5 (2); 1 (3); 1.5 (4); 2 (5); 2.5 (6). [CP] = 10^{-5} mol L^{-1}; [FL] = 5×10^{-5} mol L^{-1}.

Effect of bromate concentration on the oxidation of FL. Preliminary experiments revealed that the optimum acidity for the oxidation of FL by bromate-bromide mixture was obtained in presence of HCl 0.5 mol L^{-1}. In these conditions, by adding increasing concentrations of bromate, to a fixed concentration of FL, the oxidation and thus the concomitant decrease in the absorbance of FL was observed (Fig. 3). The composition of the reaction product between FL and bromine, generated in situ, was established by adopting the molar ratio method.[43] The plot of FL absorbance versus molar ratio (bromate/FL) has indicated that one mole of bromate is equivalent to 3 moles of FL.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (1)$$

Therefore, bromine, generated in situ by the action of bromate-bromide mixture in acid medium (1), reacts with FL with consumption of one mole of Br_2 per each mole of FL.

Stoichiometry of the reaction between CP and bromine. The molar ratio method was employed to evaluate the combining ratio between CP and bromate. The plot of absorbance versus molar ratio (bromate/CP) has revealed that about one mole of bromate is needed for one mole of CP (Fig. 4). This behavior reveals that three moles of bromine, generated in situ by the action of bromate-bromide mixture (see equation (1)), reacts with one mole of CP. Therefore, bromine can be reduced to bromide by thiol group (-SH) of captopril (R-SH) as follows:

$$R\text{-}SH + 3Br_2 + 3HOH \rightarrow R\text{-}SO_3H + 6HBr \quad (2)$$

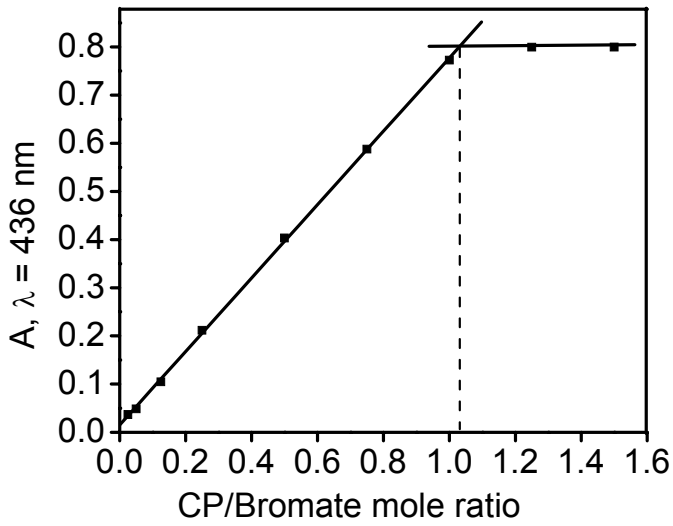

Fig. 4 – Molar ratio plot for the reaction between CP and bromate-bromide. [bromate] = 2×10^{-5} mol L^{-1}. [CP] = $(0.1\text{-}2.5)\times10^{-5}$ mol L^{-1}; [FL] = 5×10^{-5} mol L^{-1}.

Analytical Parameters. The Lambert-Beer law limit, regression equation and correlation coefficient, obtained by linear square treatment of the results are given in Table 1. The detection limit (LOD) and the quantification limit (LOQ) were calculated using the following equations, according to IUPAC definition:[44] LOD = 3S/k; LOQ = 10S/k, where S is the standard deviation of seven replicate determination values under the same conditions as for the sample analysis in the absence of the analyte, and k is the sensitivity, namely the slope of the calibration graph. Table 2 presents a comparison between the proposed method and other reported methods. As it could be seen in this table, some of the reported procedures have higher detection limits.[19,20,32,36,42] Moreover, some of the reported methods are alike or more sensitive but have drawbacks such as having a narrow linear dynamic range,[18,28,33,36,37] involving organic solvents[15,20,27,34] or heating.[20]

Accuracy and precision. To test the accuracy and precision of the proposed method, six successive measurements on the sample solution were carried out on three different drug concentrations within the linearity range. The small RSD% (< 2.7) and percent recovery E% (< 100.9), indicate high precision and good accuracy (Table 3).

Recovery Studies. To ensure the accuracy and reproducibility of the results obtained, to a fixed and known amount of the drug in the pre-analyzed tablet solutions, pure CP was added in three different levels and the total amount was determined by the proposed method. The percent recoveries of the pure drug added (Table 4) indicated that the absorbance in the proposed spectrophotometric method was not affected by the commonly encountered excipients such as talc, starch, lactose, gum acacia, sodium alginate and magnesium stearate.

Application. The proposed method was applied for the quantification of CP in commercial tablets. The results were compared with those obtained using the official method.[14] Statistical analysis of the results did not detect any significant difference between the performance of the proposed methods and reference method with respect to accuracy and precision as revealed by the Student's t-value and variance ratio F-value. The results of assay are given in Table 5.

Table 1

Statistical data for the regression equation of the proposed method

Parameter	Value
λ_{max}, nm	436
Linear range, μg mL^{-1}	0.2-4.5
Correlation coefficient, r	0.9998
Linear regression equation	$A= 0.1756\times[CP]^a + 0.0145$
Standard deviation of the regression line, s_o	0.003
LOD, μg mL^{-1}	0.06
LOQ, μg mL^{-1}	0.19

[a]concentration of CP, μg mL^{-1}

Table 2

Comparison of the proposed method with existing spectrophotometric methods for the determination of captopril

Reagents	Linear range, μg mL^{-1}	LOD, μg mL^{-1}	Ref.
Cu(II) + neocuproin	0.3 - 3.0	0.056	18
2,6-dichloroquinone-4-chlorimide (DCQ) in dimethylsulphoxide	10 - 50	0.66	19
2,4-dinitrofluorobenzene, pH 8	2.4-16.8	0.38	20
Ce(IV)	0.1 - 1.3	0.016	28
Excess of chloramine-T + indigocarmine	0 - 5	0.068	30
$KMnO_4$ - methylene blue	0.4 - 12.5	0.106	32
Excess bromate - bromide + methyl orange	0.25 - 2.0	-	33
Excess $KBrO_3$ + celestine blue	0.4 - 4	0.13	36
Sodium azide and I_2	0.1 - 1.5	0.02	37
Excess V(V) + ferroin	2.5-20	0.18	42
Excess bromate - bromide + fluorescein natrium	0.2 - 4.5	0.06	This work

Table 3

Evaluation of the accuracy and precision of the proposed method

CP, μg mL^{-1}		S, μg mL^{-1}	RSD, %	R, %
Taken	[a]Found ± $tS/N^{-0.5}$			
1.09	1.1 ± 0.03	0.03	2.67	100
2.17	2.19 ± 0.04	0.04	1.96	100.9
3.26	3.27± 0.05	0.05	1.42	100.3

[a] Mean±95 % confidence limit, for N=6; t=2.57=t-distribution for confidence level of 95 % with N-1 degrees of freedom
S=Standard deviation; RSD=Relative standard deviation; R, %= percent recovery

Table 4

Results of recovery study using standard-addition method

Drug formulations	Amount of captopril taken, μg	CP, μg		Amount of CP added[c] ± S, μg	Recovery of CP added, %
		added	found		
Captopril LPH[a]	10	-	10.65	-	-
25 mg/tablet	10	4.35	14.98	4.33±0.25	99.5
	10	8.69	19.40	8.75±0.62	100.6
	10	13.04	23.58	12.93±0.55	99.2
Europril[b]	10	-	10.77	-	-
25 mg/tablet	10	4.34	15.11	4.34±0.35	99.8
	10	8.69	19.59	8.82±0.11	101.4
	10	13.04	23.69	12.92±0.50	99.1

[a] Labormed Pharma, Bucharest, Roumania

[b] Europharm Holding S.A., Brasov, Roumania

[c] Mean of three measurements ± standard deviation (S).

Table 5

Determination of CP content in tablets of Captopril using the proposed and the official methods

Drug formulation	Found[a], % ± SD		t-Value[b]	F-Value[b]
	Proposed method	Official method		
Captopril LPH 25 mg CP/tablet	99.76±0.37	99.72±0.33	0.18	1.26
Europril 25 mg CP/tablet	100.36±0.50	99.86±0.44	1.68	1.29

[a] Values are mean of six determinations.
[b] Theoretical value for t- and F-values for five degrees of freedom and 95% confidence limits are 2.57 and 5.05, respectively.

EXPERIMENTAL

Apparatus and chemicals. The absorbance measurements were performed on a UV-VIS spectrophotometer Jasco V-530 apparatus (Jasco, Japan), using quartz cells of 1-cm path length.

All chemicals were of analytical reagent grade. Doubly-distilled water was used throughout. Fluorescein sodium salt (FL), disodium 2-(6-oxido-3-oxo-3H-xanthen-9-yl) benzoate, was provided by Matrix Marketing GmbH-Switzerland. Stock solution of FL 5×10^{-4} mol L^{-1} was prepared by dissolving 18.81 mg of dye in water and diluting to 100 mL in a calibrated flask. A bromate-bromide solution equivalent to 1000 μg mL^{-1} $NaBrO_3$ and 10-fold excess of NaBr was prepared by dissolving accurately weighed 100 mg of $NaBrO_3$ (Merck) and 1 g of NaBr (Merck) in water and diluting to the mark in a 100 mL calibrated flask. This solution was diluted to obtain working concentration of 30 μg mL^{-1} $NaBrO_3$. Aqueous solution of hydrochloric acid (5 mol L^{-1}) was prepared by diluting 111 mL of HCl (Merck, 37%, Sp. gr. 1.18) to 250 mL with water and used in spectrophotometric studies. Captopril (CP) standard (Fig. 1) (purity > 99.9%) was supplied by Fluka, Buchs-Switzerland. A stock standard CP solution (10^{-3} mol L^{-1}) was prepared by dissolving 54.3 mg Captopril in water to a final volume of 250 mL and used for preparation of a working standard solution of 10^{-4} mol L^{-1}. The reference solutions were prepared in the range $0.005\text{-}0.25\times10^{-4}$ mol L^{-1} (equivalent to 0.11-5.43 μg mL^{-1} CP), by using the working solution of CP 10^{-4} mol L^{-1}. Two brands of tablets labeled to contain 25 mg Captopril were purchased from the local market. Eppendorf vary-pipettes (10-100; 100-1000 and 500-2500 μL) were used to deliver accurate volumes.

General procedure. Accurately measured volume of CP solution equivalent to 0.11–5.43 μg mL^{-1} ($0.5\text{-}2.5\times10^{-5}$ mol L^{-1}) was transferred into a series of 10 mL standard flasks. The volume was adjusted to 5 mL by adding bidistilled water. Then, 1 mL of bromate-bromide solution (30 μg mL^{-1} in $KBrO_3$) was added to each flask followed by acidification by 1.0 mL of 5 mol L^{-1} HCl and the mixture was left to stand for 10 min, with occasional shaking. Later, 1 mL of 5×10^{-4} mol L^{-1} FL solution was added and the contents were diluted to volume with water and mixed well. The cell was stoppered and mixed well and absorbance measured at 436 nm, after 10 min, against water as reference. Blank experiments were also performed by adding bidistilled water instead of CP solutions. The difference between the absorbance of samples in the presence and in the absence of CP was taken into consideration.

Procedure for recovery tests. Known amounts of pure drug in three different levels were added to a fixed amount of the drug in the formulation (pre-analyzed), and the total amount of the drug was determined by using the proposed procedure. Percent recovery of the added pure drug was calculated from: $\%\text{Recovery} = [(A_1 - A_2)/A_3)]\times100$ where A_1 is the total amount of the analyte found, A_2 is the amount of the analyte present in the formulation and A_3 is the amount of the pure analyte added to formulation.

Procedure for determination of captopril in pharmaceutical formulation. Six tablets of the drug were accurately weighed and ground into fine powder. The average weight of tablet was calculated. An accurately weighed portion of the resulting powder, equivalent to 5 mg of CP was dissolved in water. Then it was filtered through a Whatman no. 42 filter paper directly into a 100 mL standard volumetric flask. The residue was washed three times with water for complete recovery of the drug. The washings were added to the volumetric flask, which was then filled to the mark with the same solvent. Appropriate volumes of the filtrate were analyzed by applying the recommended procedure under calibration curve.

CONCLUSIONS

The described method allows the determination of captopril in pure form and in formulated products. The experimental data are considered to indicate good linearity, accuracy, repeatability and sensitivity. The proposed method permits the determination of a concentration down to 0.2 μg mL^{-1} CP. Fluorescein natrium is a suitable reagent for the spectrophotometric determination of captopril in pure and pharmaceutical preparations. The proposed method requires a simple apparatus for routine quality control of the drug.

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