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Kinetic spectrophotometric determination of some sulfur containing compounds in pharmaceutical preparations and human serum

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Abstract

A kinetic spectrophotometric method was developed for the determination of carbocisteine, ethionamide, thioctic acid and penicillamine based on the catalytic effect on the reaction between sodium azide and iodine in aqueous solution. Ten to 100 μg ml^{-1} of carbocisteine and ethionamide, 0.1–1 μg ml^{-1} of thioctic acid and 0.01–0.1 μg ml^{-1} of penicillamine could be determined, respectively, by measuring the decrease in the absorbance of iodine at 348 nm by a fixed time method. The decrease in the absorbance in the first 5 min from the initiation of the reaction is related to the concentration of the drugs. The detection limits were 0.47, 0.71, 0.018 and 9.38×10^{-4} μg ml^{-1} for the four drugs, respectively. The proposed procedure was successfully applied in the determination of these drugs in pharmaceutical preparations and human serum.

Keywords: Carbocisteine; Ethionamide; Thioctic acid

1. Introduction

The importance of these sulfur compounds is due to the wide spread and different pharmacological effects. Carbocisteine is a mucolytic drug used for the treatment of disorders of the respiratory tract associated with excessive mucus, ethionamide is antibacterial (tuberculostatic agent), penicillamine is used for treatment of rheumatoid arthritis and in treatment of lead poisoning as chelating agent, it also used for elimination of copper in treatment of hepatolenticular degeneration (Wilson's disease) and thioctic acid is used for treatment of liver dysfunction and diabetic neuropathy and as an antidote to poisonous mushrooms (*Amanita* species) [1,2].

The published methods reported for the determination of these drugs include titrimetry [3–5], spectrophotometry [6–11], fluorometry [12], electro-analysis [13–16] and chromatography [17–22]. The catalytic kinetic spectrophotometric method is one of the most attractive approaches for the ultratrace determination of certain chemicals and has many advantages:

1) Selectivity due to the measurement of the evolution of the absorbance with the time of reaction instead of the measure of a concrete absorbance value.
2) Possibility of no interference of the colored and/or turbidity background of the samples.
3) Possibility of no interference of other active compounds present in the commercial product. If they are resisting the chemical reaction conditions established for the proposed kinetic method [23].

The aim of the present work was to establish a kinetic spectrophotometric method for determination of carbocisteine, ethionamide, penicillamine and thioctic acid in pharmaceutical dosage forms and human serum, based on the catalytic effect of these sulfur compounds on the iodine–azide reaction which has been widely applied to the determination of other compounds [24–33].

2. Experimental

2.1. Equipment

A Shimadzu (Model 1601 PC) UV–Visible spectrophotometer (Shimadzu, Kyoto, Japan) was used to

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measure the absorbance at 348 nm. The cell chamber was kept at a specified temperature using a Shimadzu thermostat Model T.C.C. Controller.

2.2. Reagents and materials

All reagents were of analytical reagent grade and the water was always double distilled water. Carbocisteine and Rhinathiol® syrup was offered Amriya Pharmaceutical Industries, Egypt.

Ethionamide and Trecator® tablets offered by Alexandria Theraplix Company, Egypt. Penicillamine and Artamine® capsules offered by Biochemie Company, Austria. Thioctic acid and Thiotacid® tablets offered by Eva Pharma for Pharmaceuticals, Egypt. Human serum was obtained from Blood Bank, Mansoura (University Hospital, Egypt). Stock solutions of the studied drugs were prepared by dissolving 100 mg of carbocisteine or thioctic acid in 3 ml of 0.4 M NaOH, ethionamide in 3 ml of 5 N HCl and penicillamine in distilled water. All solutions were completed to 100 ml with distilled water. Other concentrations were prepared by dilution with distilled water.

Iodine solution (0.01 M) was prepared by dissolving 0.254 g of iodine in 100 ml of water containing 4.5 g of potassium iodide. Also, 10% (w/v) iodine solution was prepared. Sodium azide solution (1 M) was prepared by dissolving 6.501 g of sodium azide in 100 ml of distilled water. Phosphate buffer solutions of pH 1–10 were prepared using 0.1 M Na_2HPO_4 and 0.1 M NaOH [4].

2.3. Procedures

2.3.1. Construction of calibration graphs

An aliquot solution of the studied compounds containing 0.1–1 mg of carbocisteine and ethionamide, 1–10 μg of thioctic acid or 0.1–1 μg of penicillamine was transferred to a 10 ml volumetric flask followed by 1 ml of phosphate buffer. pH 6 for carbocisteine and thioctic acid, pH 4 for ethionamide, pH 1 for penicillamine. One milliliter of sodium azide solution (1 M) was added to the flask and the volume made up to about 8 ml using distilled water. The solution was kept in water bath at 25 °C for ethionamide and penicillamine. 20 °C for carbocisteine, 30 °C for thioctic acid for 3 min. Then 1 ml of 0.001 M iodine was added and the volume was adjusted to the mark with distilled water. The absorbance (A) was recorded at 348 nm versus time (in a kinetic mode) for 5 min. A Blank Experiment was carried out under the same conditions with the absorbance (A_0). The difference between the two absorbances ($A_0 - A$) was plotted against the drug concentrations to obtain the calibration graphs.

2.3.2. Procedure for the dosage form

An accurately weighed quantity of the mixed contents of 10 capsules or powdered (Pulverized) tablets or an accurately measured volume of the syrup equivalent to 100 mg of the drug transferred into a 100-ml volumetric flask and made up to the mark with distilled water.

Three milliliters of 0.4 M NaOH and 3 ml of 5 N HCl were firstly added in case of Rhinathiol® Syrup and Thiotacid® 300 mg tablets and Trecator® 250 mg tablets, respectively. The contents of the flask were sonicated for 5 min and filtered if necessary; and the above procedure was followed. The nominal content was calculated either from a previously plotted calibration graph or using the regression equation.

2.3.3. Procedure for spiked human serum

An aliquot of standard aqueous solution of 0.1–1 mg of carbocisteine and ethionamide, 1–10 μg of thioctic acid or 0.1–1 μg of penicillamine was added to 1 ml of plasma sample. One milliliter of 10% (w/v) trichloroacetic acid was added for each milliliter of the plasma for deproteination. The sample was blended on a vortex mixer and centrifuged at 3500 rpm for 10 min. Two milliliters of protein-free supernatant was transferred into 10 ml volumetric flask and the above procedure was then followed. A Blank value was determined by treating the sample free plasma in the same way.

3. Results and discussion

Iodine oxidizes azide in acid medium form iodide and nitrogen. This reaction is very slow at low concentrations of the reactants. This reaction is very much accelerated in the presence of sulfide or thiol containing compounds. This reaction can be followed spectrophotometrically by monitoring the change in the absorbance at 348 nm as shown in Fig. 1.

3.1. Optimization of the reaction conditions

3.1.1. Reaction time

There are many methods, such as fixed time, initial rate and rate constant, for measuring the catalytic effects among them, the fixed time measurement is the most conventional and simplest. The most suitable reaction time was found to be 5 min after the addition of iodine for all the studied sulfur compounds based on its correlation coefficient of the calibration curve as shown in Table 1.

3.1.2. pH effect

The effect of pH on the catalyzed (sample) and uncatalyzed (Blank) reactions was studied by using 1 ml of 0.001 M iodine solution and 1 ml of 1 M azide solution. The maximum difference of absorbance (ΔA) was

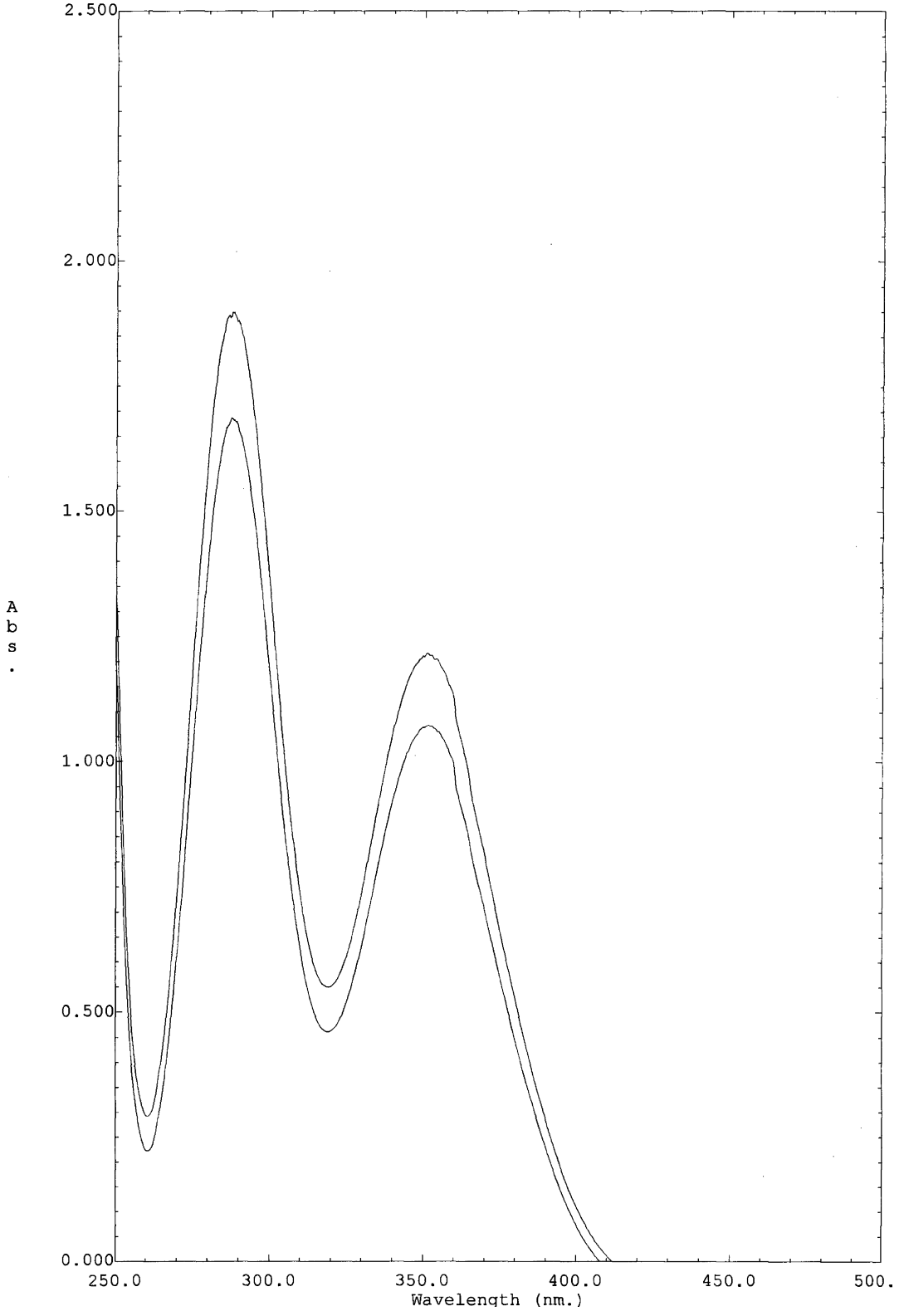


Fig. 1. Absorption spectra of the reaction product of sulfur drug with iodine/azide system:(A) Blank, (B) Reaction product of carbocistiene (100 μg ml^{-1}) using 1 ml (1 M) sodium azide solution.

Table 1
Correlation coefficients for the calibration curves at different reaction times after addition of iodine solution

Reaction time	Correlation coefficient (r)			
	Carbocisteine	Ethionamide	Penicillamine	Thioctic acid
1	0.9320	0.9957	0.9969	0.9913
2	0.9336	0.9961	0.9977	0.9903
3	0.9371	0.9965	0.9983	0.9899
4	0.9657	0.9969	0.9987	0.9865
5	0.9999	0.9999	0.9999	0.9997
6	0.9772	0.9972	0.9988	0.9824

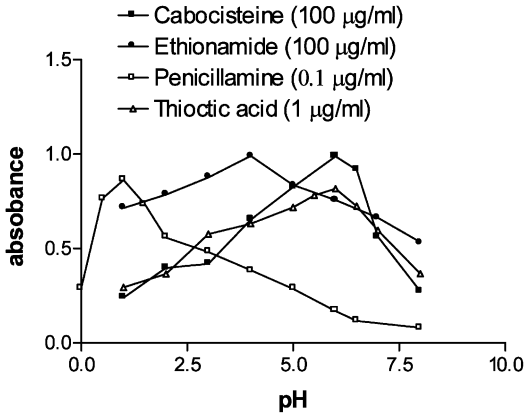


Fig. 2. Effect of pH on the reaction between thiol compounds and 1 ml (0.001 M) iodine solution, 1 ml (1 M) azide at $\Delta_t = 5$ min. (—■—) Cabocisteine (100 μg ml^{-1}), (— + —) ethionamide (100 μg ml^{-1}), (— □ —) penicillamine (0.1 μg ml^{-1}), (— △ —) thiodic acid (1 μg ml^{-1}).

observed at pH 6 for cabocisteine and thioctic acid, pH 4 for ethionamide and pH 1 for penicillamine as shown in Fig. 2.

3.1.3. Azide concentration effect

As shown from Fig. 3, 1 ml of sodium azide solution (1 M) was sufficient for all the studied compounds.

3.1.4. Iodine concentration effect

As the volume of 0.001 M iodine solution increased, the net reaction rate increased. So, volumes larger than 1 ml should not be used because iodine solution has a strong color. So, 1 ml of 0.001 M I_2 is used for all studied compounds.

3.1.5. Temperature effect

The effect of temperature was studied in the range of (5–60 °C). As the temperature increased, the rate of both catalyzed and un-catalyzed reactions increased up to 25 °C for ethionamide and penicillamine, 20 °C for carbocisteine and 30 °C for thioctic acid as shown in Fig. 4. Above these optimum temperatures, ΔA values decreased which suggested that the rate of un-catalyzed reaction was also accelerated, or iodine became lost due to volatilization upon heating.

3.1.6. Calibration graphs

By adjusting these conditions, rectilinear calibration graphs were obtained in the concentration ranges given in Table 2 besides the limits of detection and regression equations (Figs. 5 and 6).

(1) The percentage recoveries of the four studied drugs compared with that obtained

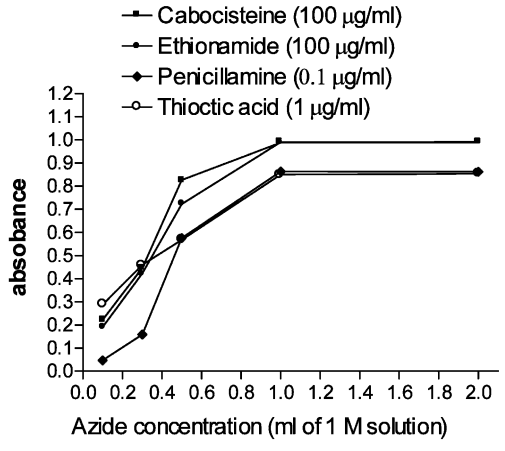


Fig. 3. Effect of azide concentration on the reaction between thiol compounds and 1 ml (0.001 M) iodine solution, 1 ml (1 M) azide at $\Delta_t = 5$ min. (—■—) Cabocisteine (100 μg ml^{-1}), (— ▲ —) ethionamide (100 μg ml^{-1}), (—?—) penicillamine (0.1 μg ml^{-1}), (—○—) thiodic acid (1 μg ml^{-1}).

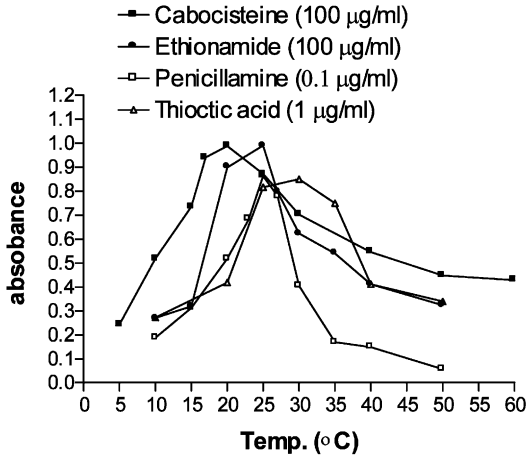
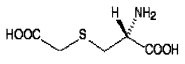
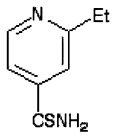
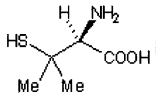
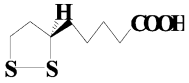


Fig. 4. Effect of the temperature on the reaction between thiol compounds and 1 ml (0.001 M) iodine solution, 1 ml (1 M) azide at $\Delta_t = 5$ min. (—■—) Cabocisteine (100 μg ml^{-1}), (— ▲ —) ethionamide (100 μg ml^{-1}), (— □ —) penicillamine (0.1 μg ml^{-1}), (— △ —) thiodic acid (1 μg ml^{-1}).

Table 2
Collective data for the studied compounds by sodium azide method

Compounds	carbocisteine	ethionamide	penicillamine	thioctic acid
Formula				
Chemical name	5-caboxymethyll-cysteine	2-Ethylpyridine-4-carbothioamide	d-3,3dimethyl cysteine	αLiporc acid≈1,2 Dithiolane (3-Pentanoic acid)
pH	6	4	1	6
Temperature	20°C	25°C	25°C	30°C
Conc. Range (μg/l)	10-100	10-100	0.01-0.1	0.1-1
Regression equation	Y=-3.14x 10^{-3} + 0.00986X	Y=3.48x 10^{-3} + 9.86 x 10^{-3} X	Y=-0.0136+8.795X	Y=-4.32x10^{-3} + 0.843X
Correlation coefficient	R=0.9999	0.99998	0.99997	0.9997
Detection Limit (μg/ml)	0.47	0.71	9.38x10^{-4}	0.018

Y →ΔA

Y → Conc. In μg/ml

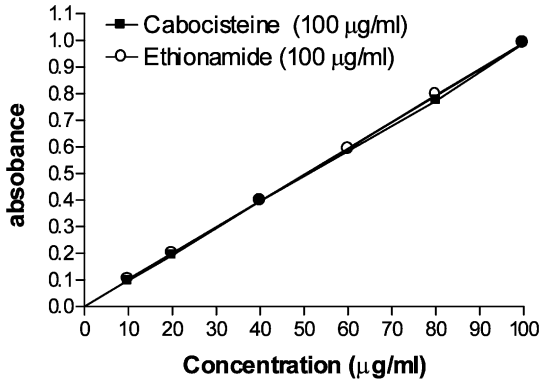


Fig. 5. Calibraion curve of ethionamide and carbocisteine at $\Delta_t = 5$ min, 1 ml azide (1 M). (—■—) Cabocisteine (100 μg ml^{-1}). (—○—) Ethionamide (100 μg ml^{-1}).

by the official methods [3] were given in Table 3.

(2) Statistical analysis were studied between the results of proposed and official methods [3] by calculating the student's t-test and variance ratio [34]. As shown in Table 3, there is no significant difference between the two procedures according to accuracy and precision.

(3) The proposed method was successfully applied for determination of the studied sulfur drugs in their different dosage forms, as shown in Table 4, compared with the results obtained by the reference methods [4,6,35,36].

(4) The proposed procedure was applied for the determination of the studied drugs in spiked human serum, the regression equations were $Y = -0.02 + 6.9 \times 10^{-3}X$, $Y = -0.01\,541 + 6.8 \times 10^{-3}X$, $Y = 2.84 \times 10^{-3} + 5.81X$ and $Y = -3.2 \times 10^{-4} + 0.5744X$ with correlation is efficient $(r) = 0.9995$, 0.9989, 0.9992 and 0.9993 for cabocisteine, ethionamide, penicillamine and thioctic acid, respectively. The presence of indigenous compounds in serum samples did not interfere with the analysis. The percentage recoveries of these compounds in spiked human serum was given in Table 5.

Table 3
Application of the proposed method to the determination of the studied thiol compounds

Comp.	Proposed method			Official method [3]	
	Taken (μg ml^{-1})	Found (μg ml^{-1})	Rec. [a] (%)	Taken (mg)	Rec. (%)
1-Carbocisteine	100	100.56	100.56	100	100.36
	50	50.16	100.32		
	40	40.41	101.025	150	99.16
	30	30.19	100.63		
	20	19.85	99.25	200	99.46
	10	10.19	101.9		
Mean ± SD			100.61 ± 0.86	99.66 ± 0.624	99.66 ± 0.624
Student's *t*-test			1.688	(2.365) [b]	(2.365) [b]
F-test			1.9	(19.3) [b]	(19.3) [b]
2-Ethionamide	100	100.73	100.73	100	99.67
	80	80.73	100.91		
	60	60.06	100.1	150	98.56
	40	40.08	100.2		
	20	20.16	100.8	200	100.58
	10	10.19	101.9		
Mean ± SD			100.67 ± 0.58	99.6 ± 1.012	99.6 ± 1.012
Student's *t*-test			2.247	(2.36) [b]	(2.36) [b]
F-test			3.04	(5.79) [b]	(5.79) [b]
3-Penicillamine	0.1	0.0997	99.7		
				100	101.49
	0.08	0.0804	100.5		
				150	99.5
	0.06	0.0600	100		
				200	100.75
	0.04	0.0398	99.5		
	0.02	0.0201	100.05		
	0.01	0.0099	99		
Mean ± SD			99.87 ± 0.588	100.58 ± 1.0058	
Student's *t*-test			1.37	(2.36) [b]	
F-test			2.92	(5.79) [b]	
4-Thioctic acid	1	1.00	100	50	99.91
	0.8	0.79	98.75		
	0.6	0.6000	100	100	101.63
	0.4	0.402	100.5		
	0.2	0.199	99.5	150	99.68
	0.1	0.098	98		
Mean ± SD			99.45 ± 1.16	100.41 ± 1.066	100.41 ± 1.066
Student's *t*-test			1.197	(2.36) [b]	(2.36) [b]
F-test			1.184	(19.3) [b]	(19.3) [b]

[a] Each result is the average of three separate experiments.
[b] The values between brackets are tabulated student's *t*-test and variance ratio test (at $P = 0.05$) [34].

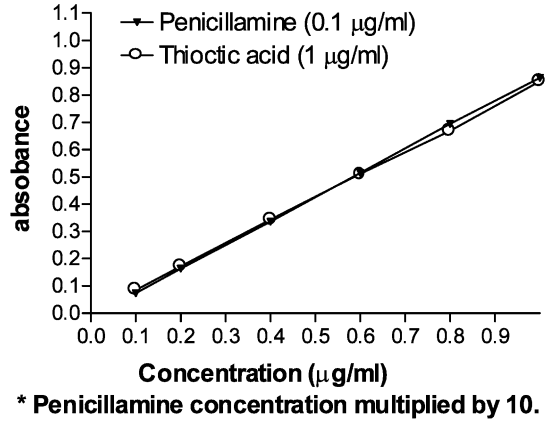


Fig. 6. Calibraion curve of penicillamine and thioctic acid at $\Delta_t = 5$ min, 1 ml azide (1 M). (— ▼ —) Penicillamine (0.1 μg ml^{-1}), (— ○ —) thiodic acid (1 μg ml^{-1}).

Table 4
Application of the proposed method to determination of the studied thiol compounds in dosage forms

Comp.	Proposed method			Reference method	
	Taken (μg ml^{-1})	Found (μg ml^{-1})	Rec. [a] (%)	Taken	Rec. (%)
Rhinathiol® syrup [b] (2 g carbocisteine/100 ml)	40	40.368	100.92	10 μg ml^{-1}	101.2 [6]
	80	80.10	100.125	20 μg ml^{-1}	100
	100	100.637	100.637	30 μg ml^{-1}	98.57
				40 μg ml^{-1}	98.93
				50 μg ml^{-1}	101.023
Mean ± SD			100.56 ± 0.402	99.945 ± 1.1896	
Trecator® tablets [c] (250 g/tablet)	60	58.74	97.9	50 mg	98.92 [4]
	80	78.87	98.59	100 mg	99.81
	100	99.35	99.35	150 mg	98.14
Mean ± SD			98.61 ± 0.72	98.96 ± 0.836	
Artamine® capsules [d] (250 mg/capsules)	0.1	0.0998	99.88	3 μg ml^{-1}	99 [35]
	0.04	0.0394	98.55	8 μg ml^{-1}	100.25
	0.02	0.0199	99.42	12 μg ml^{-1}	100.33
Mean ± SD			99.28 ± 0.675	100.35 ± 0.66	
Thiotacid® tablets [e] (300 mg/tablet)	0.2	0.1975	98.74	400 μg ml^{-1}	99 [36]
	0.4	0.3941	98.54	300μg ml^{-1}	99.5
	0.6	0.5893	98.23	200 μg ml^{-1}	100.25
Mean ± SD			98.5 ± 0.257	99.583 ± 0.629	

[a] N.B.: The results are the average of six separate determinations.
[b] Amyria Pharmaceutical Company, Egypt.
[c] Alexandria Theraplix Company, Egypt.
[d] Biochemie Company, Austria.
[e] Eva Pharma for Pharmaceuticals & Medical appliances, Egypt.

Table 5
Application of the proposed method to the determination of the studied thiol compounds in human serum

Carbocisteine		Ethionamide		Penicillamine		Thioctic acid	
Conc. (μg ml^{-1})	Rec. (%)	Conc. (μg ml^{-1})	Rec. (%)	Conc. (μg ml^{-1})	Rec. (%)	Conc. (μg ml^{-1})	Rec. (%)
10	102.3	20	98.35	0.01	100.48	0.2	101.33
40	97.74	40	97.91	0.02	100.31	0.4	102.3
70	99.53	60	97.8	0.04	99.67	0.6	98.68
80	100.97	80	99.74	0.08	100.92	0.8	100.92
100	101.2	100	101.3	0.1	101.86	1	101.39
Mean ± SD							
100.548 ± 1.87		99.02 ± 1.49		100.786 ± 1.0616		100.924 ± 1.35	

4. Conclusion

(1) The results suggested that the observed decrease in the absorbance at 348 nm was mainly due to the catalytic effect of the studied sulfur containing compounds on the reaction between iodine and azide, rather than a direct reaction between iodine compounds.

(2) In conclusion, the proposed method was accurate, precise, sensitive, rapid, low cost, relatively selective and was successfully utilized in determination of the studied compounds in dosage forms as well as in human serum samples.

(3) Our method allows the determination of lesser amounts of the studied compounds than those detectable by the official methods that require non-aqueous titration for carbocisteine, ethionamide, and penicillamine whereas thioctic acid is not reported in the USP or BP and determined by iodometry as cystine [3].

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