Biomedicine and Chemical Sciences 2(1) (2023) 23-30

05-BCS-1322-323

Content lists available at:
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Biomedicine and Chemical Sciences

Journal homepage: https://journals.irapa.org/index.php/BCS

A Novel Yttrium(III) Complex for Estimating Dopamine in Pure and Pharmaceutical Dosage Forms

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ARTICLE INFO

Article history:
Received on: October 13, 2022
Revised on: November 20, 2022
Accepted on: November 20, 2022
Published on: January 01, 2023

Keywords:
Dopamine
Dosage forms
Redox reaction
Spectrophotometric method
Yttrium(III)

ABSTRACT

A simple, rapid, sensitive, accurate, precise, and cost-effective spectrophotometric method has been developed to estimate dopamine in pure and pharmaceutical dosage forms based on the redox reaction of dopamine in an acid medium with Yttrium(III) ion as an oxidizing agent. The latter suffers reduction to Yttrium(II) ion and reacted with 1,10-phenanthroline to form a colored product peaking at 510 nm. Beer's law is obeyed in the concentration range of 0.5-10 µg mL^{-1} with a molar absorptivity of $1.16x10^4$ L $mole^{-1}$ cm^{-1}, Sandall's sensitivity of 0.0131 µg.cm^{-2}, the recovery rate of dopamine in pharmaceutical dosage was in the range of 98.97 to 101.57%. The effects of variables such as oxidizing agent, reagent concentration, time of oxidation reaction, surfactant, formation constant of the complex, have been investigated to optimize the procedure. The results have been validated analytically and statistically. The proposed method has been successfully applied to estimate dopamine in pharmaceutical dosage forms.

1. Introduction

Dopamine chemically (3,4-dihydroxyphenethylamine) (Scheme 1). It is an essential agent for the central nervous, cardiovascular, hormonal, and renal systems. It is crucial for concentration, problem-solving, and memory (Zhuang et al., 2021; Ermiş et al., 2021). Abnormal dopamine levels are related to sleep and eating disorders, addictions, schizophrenia, concentration problems, hyperactivity, and social anxiety. Studies have also shown that dopamine deficiency is associated with Parkinson's disease (Latif et al., 2021). For this reason, the dopamine concentration must be within the desired range in the prescribed dose for an individual.

Although there are international protocols for the estimation of dopamine in pharmaceutical dosage forms (Prichard, 1884), the estimation of the dopamine was carried out using several methods; indirect determination of dopamine using azo coupling reaction with oxidized 2,4-dinitrophenylhydrazine in the concentration range of 0.1–1000 µmol L^{-1}, with limits of detection and limit of quantification of 0.47 and 0.25 µmol L^{-1}, respectively (Boumya et al., 2020). It also succeeded in the determination of dopamine using copper oxide nanodots (CuO nanodots–ITO) as an electrochemical sensor developed from a block copolymer template with a sensitivity of 326.91 µA mM^{-1} cm^{-2} and a detection limit of 0.03 µM with the presence of interfering substances such as acetaminophen, phenol, catechol, and hydroquinone (Bas et al., 2019).

The fluorometric determination of dopamine at pH 9 by reaction with molybdenum disulfide quantum dots, the assay works in the 0.1–100 µM concentration of dopamine and recoveries (97.6 - 102.2%) (Liu et al., 2018). A spectrophotometric method has been developed for the

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How to cite:

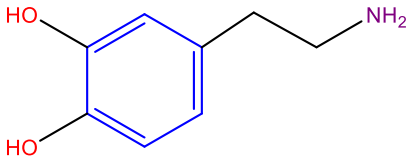
Nejres, A. M., & Najem, M. A. . (2023). A Novel Yttrium(III) Complex for Estimating Dopamine in Pure and Pharmaceutical Dosage Forms. *Biomedicine and Chemical Sciences*, *2*(1), 23–30.

DOI: **https://doi.org/10.48112/bcs.v2i1.323**

determination of dopamine by reacting at pH 4.4 with an excess amount of $[Fe(phen)_3]^{3+}$ as an oxidizing agent and 1,10-phenanthroline as a reagent, the calibration curve rang 2.0–33.0 µM and recovery (97 - 99%) (Moghadam et al., 2011). It was also determined spectrophotometrically by the interaction with sodium 1,2-naphthoquinone-4-sulfonate at pH 9.4, this method obeyed Beer's law in the range of 0.16–40 $\mu g.mL^{-1}$ and recovery is over (99.5-100.6%) (Wang et al., 2002) by reacting the dopamine with 4-aminoantipyrine in alkaline medium, dopamine was determined spectrophotometrically, this method linearity range was limited 37.90 – 170.6 $\mu g.mL^{-1}$ and recovery of (98.62 – 102.9%) (Mohamed et al., 2009).

In a basic medium, several researchers have been able to estimate dopamine via reaction with diazotized sulfanilic acid. It obeyed Beer's law between 0.6–15 mg l^{-1},and recovery of 98.28% (Shaikh et al., 2008) and via oxidative coupling by Mesalazine in a basic medium, determined of Dopamine using the spectrophotometric method, it gave range of 2.731.25 $\mu g.mL^{-1}$, and recovery (99.41-102.13%) (Nejres & Najem, 2022). Many researchers are constantly trying to find modern, simple, sensitive, precise, and accurate methods and concordance for the purpose of estimating dopamine. In this research, the yttrium ion was chosen as an oxidizing agent and an assistant in the spectrometric estimation of dopamine.

Some studies indicate that Yttrium(III) behaves like 3d transition metal ions under hydrothermal conditions, with stable coordination (Stefanski et al., 2020). It has a coordination of eight and a square and prism structure (Guan et al., 2020). Yttrium(III) can enter into the coordinative interaction of forming colored complexes (Nghia et al., 2020). In this work, the Yttrium(III) responsible for providing yttrium chloride was used as an oxidizing agent in an acid medium, which is reduced to Yttrium(II), a coordination complex colored with 1,10-phenanthroline, giving a maximum wavelength at 510 nm.



Chemical Formula: $C_8H_{11}NO_2$
Molecular Weight: 153.18

Scheme.1. structure of dopamine

2. Materials and Methods

2.1. Chemical Materials and Instrumentation

All chemical reagents used in this work were of a high degree of purity. All spectrophotometric absorbance's were measured by JASCOV- 360 UV/Visible with 1-cm glass cells. used a HANNA pH211 pH meter. A BEL-sensitive balance was used to operate the excellent weighing procedures.

2.2. Solution

Stock solution of dopamine (500 $\mu g.mL^{-1}$) was prepared by dissolving of 0.050 g of dopamine in appropriate amount of distilled water and the volume was completed to 100 mL volumetric flask.

Standard solution was prepared by transferring 20 mL of stock solution and diluting it with distilled water to mark of volumetric flask 100 mL.

Hydrochloric acid (1M) was prepared by transferring of 8.500 mL from hydrochloric acid (11.6 M) to volumetric flask 100 mL and diluted by distilled water to mark.

Yttrium chloride hexahydrate (1×10^{-2}M) was prepared by dissolving of 0.303 g of Yttrium(III) in appropriate amount of distilled water and the volume was completed to 100 mL volumetric flask.

1,10-phenanthroline (5×10^{-2}M) was prepared by dissolving of 0.901 g in appropriate amount of ethanol and the volume was completed to 100 mL volumetric flask with same solvent.

2.3. Preparation of Pharmaceutical Dosage Forms

Dopamine stock solution (400 µg.mL-1) was prepared, by transferring 1 mL of (HAVER Dopasel 200 mg.5mL-1) and (Pharma sunny 40 mg. mL-1) ampules to a volumetric flask of 100 mL and diluted with distilled water to mark, when prepared work solution (100 µg.mL-1), diluting 25 mL from a stock solution in a 100 mL volumetric flask and diluted with distilled water.

2.4. Linearity and Calibration Curve Graph of Dopamine

The linear equation of Beer's law was used to describe the calibration graph prepared by applying the same procedure to solutions of the obtained drug reference standards when preparing a set of 10 mL volumetric flasks containing dopamine within the concentration range (0.5-10) $\mu g.mL^{-1}$ of dopamine. To each flask, 1.5 mL hydrochloric acid followed by 1 mL of Yttrium(III) was added. The solutions waited for 10 minutes at 30 C°, then 1.5 mL of 1,10-phenanthroline was added and waited for 20 minutes, and each flask was filled to volume with distilled water. The absorbance was measured at 510 nm against blank. The calibration graph was constructed by plotting the absorbance against concentration of dopamine Figure 1. The molar absorptivity coefficient and Sandall's sensitivity and reveals a very high sensitivity of the method. (Al-Hasnawi et al., 2020; Mostafa et al., 2021) were $1.16x10^4$ $L.mol^{-1}.cm^{-1}$ and 0.0131 $\mu g.cm^{-2}$ respectively.

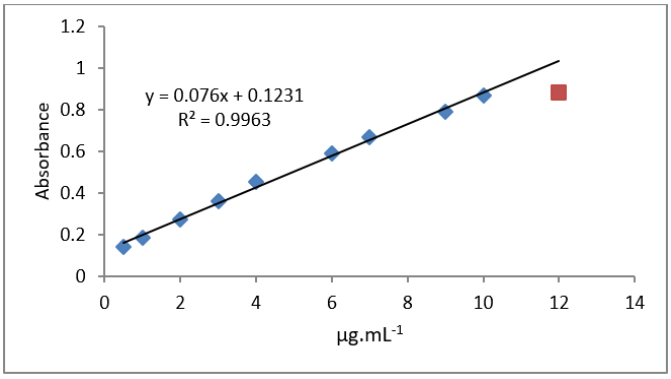
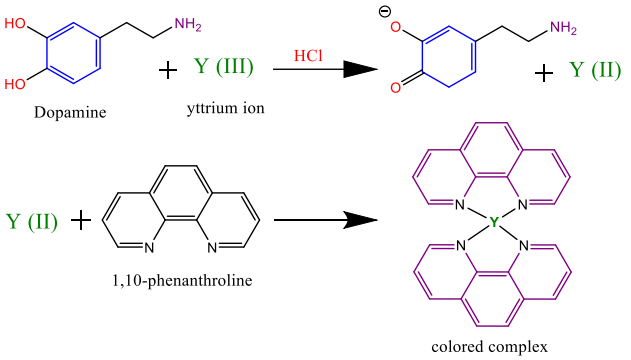


Fig. 1. Linearity curve of Dopamine concentration

3. Results and Discussion

Under the optimum conditions, dopamine suffers oxidation due to its reaction with the Yttrium(III), which acts as an oxidizing agent in an acidic medium. To produce Yttrium(II) quantitatively, the amount of Yttrium(II) was

determined by using 1,10-phenanthroline as a reagent; the orange-red product complex gave maximum absorbance at 510 nm. The suggested mechanism of the reaction is shown in Scheme 2.



Scheme. 2. The suggested reaction of dopamine: yttrium ion: 1, 10-phenanthroline

3.1. Development of Optimum Conditions

3.1.1. Selection of Type and Amount of Acid

The intensity of the color is affected when using different acids. The effects of several acids were studied and are shown in Table 1. A 1.0 mL of hydrochloric acid, nitric acid, acetic acid, and sulfuric acid, which have been concentrated at 1M, and add them to four volumetric flasks respectively, containing 5µg.mL^{-1} dopamine, followed by 1mL Yttrium(III), and 1.0 mL 1, 10-phenanthroline, and completed to 10 mL with distilled water. It was noticed that the hydrochloric acid gave the highest absorbance value.

Table 1
The absorbance of different acids (1M) concentration

Acids (1M)	HCl	HNO_3	CH_3COOH	H_2SO_4
Absorbance	0.2550	No reaction	0.0350	0.0356
λmax(nm)	510	-	367	447

Aliquots (0.25-2.0 mL) of hydrochloric acid were added to volumetric flasks. with the same sequence as the addition above, Figure 2. 1.5 mL of hydrochloric acid gave the highest absorbance value.

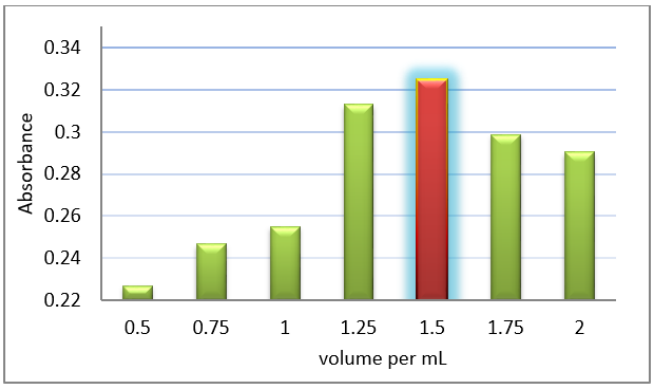


Fig. 2. Selected the appropriate amount of acid

3.2. Amount of Oxidizing Agent

As shown in Table 2, aliquots (0.5, 1.0, and 1.5 mL) of Yttrium(III) have been taken to study the effect of different amounts of oxidizing agent on the intensity of the color. It appears that 1.0 mL of Yttrium(III) ion was appropriate to provide high absorbance and the R^2 = 0.9769 determination coefficient.

Table 2
Optimization of the amount of oxidizing agent

µg.mL^{-1} Dopamine/10mL	Absorbance of Yttrium(III)		
	0.5mL	1.0mL	1.5mL
1	0.1133	0.1364	0.0886
3	0.1773	0.2515	0.1950
5	0.2380	0.3564	0.2932
7	0.2914	0.4232	0.4412
10	0.3733	0.5541	0.4879
12.5	0.3814	0.6151	0.5430
15	0.5105	0.6785	0.6080
R2	0.9746	0.9793	0.9446

3.3. Amount of Reagent

An aliquots (0.5, 1.0, 1.5, and 2mL) of 1,10-phenanthroline has been taken for the study of the effect of different amounts of reagent on intensity of the color, as shown in Table 3. It appears that 1.0 mL of 1, 10-phenanthroline was appropriate to provide high absorbance and the R^2 = 0.9890 determination coefficient.

Table 3
Optimization of the amount of reagent

µg.mL^{-1} Dopamine /10mL	Absorbance of 1, 10-phenanthroline			
	0.5mL	1.0mL	1.5mL	2.0mL
1	0.0631	0.1364	0.1382	0.1825
3	0.1073	0.2515	0.3011	0.3961
5	0.1372	0.3564	0.453	0.3961
7	0.1669	0.4232	0.5573	0.7222
10	0.2085	0.5541	0.6507	0.8458
12.5	0.2116	0.6151	0.7373	0.9166
15	0.2244	0.6785	0.7589	0.9518
R2	0.9285	0.9793	0.9295	0.9174

3.4. Order of Addition

series of 10 mL volumetric flasks containing 0.5 mL dopamine, 1.5 mL (1M) hydrochloric acid, and 1.0 mL of 1, 10-phenanthroline addition in a different sequence. Studied the effect through investigating absorbance at 510 nm. Best absorbance was achieved in the order of addition, Table 4.

Table 4
The order of addition of compounds of reacted

Order addition	Absorbance /nm
D+OX+R+A	0.3475
D+A+OX+R	0.3566
R+OX+A+D	0.3317
D; drug, OX; oxidizing agent, A; acid, R; reagent	

3.4.1. Effect of Temperature on Oxidation Process Reaction

To study of the effects of temperature on reaction depending on the intensity of resulting color (Nejres et al., 2020), transfer 5 and 10 µg.mL^{-1} of dopamine were transferred to two volumetric flasks, 10 mL for each temperature listed in the table5, followed by 1.5 mL of hydrochloric acid and 1.0 mL of Yttrium(III) ion, waited 10 min, after that 1 mL of 1, 10-phenanthroline was added. Showed the good absorbance given at 30°C; this temperature can easily be handled and guarantees that part of the reaction materials will not evaporate.

Table 5
Effect of temperature on oxidation process within the color reaction

Dopamine µg.mL^{-1}/10mL	Temperature C° 25	30	40	50	60
5	0.3584	0.3513	0.3690	0.4810	0.3735
10	0.4713	0.4786	0.5492	0.5678	0.5527

3.5. Stability of Product Reaction

The product's stability was investigated by measuring its absorbance over time, by preparing two different dopamine amounts (5 µg .mL^{-1}), The results are explained in table 6.

Table 6
The results for time stability of products

	Absorbance 5 µg.mL^{-1} of dopamine/10mL						
Time, min	0	10	20	30	40	50	60
30°C	0.3513	0.4257	0.5460	0.5397	0.5492	0.5188	0.4952

3.6. Effect of Surfactants

Under optimum conditions, the effects of surfactants (CTAB, CPC, and SDS) were studied Table 7. Three different concentrations were taken and added to volumetric flasks containing the reaction mixture and measured against the blank. No significant levels of surfactants were observed in absorbance.

Table 7
The effect of surfactants on the absorbance of product color

1000 µg.mL^{-1} surfactants	5 µg.mL^{-1}dopamine/10mL 1.0mL	2.0mL
CPC*	95.23	101.06
SDS**	95.12	99.28
CTAB***	93.90	96.88

CPC*; Cetylpyridinium chloride, SDS**; Sodium dodecyl sulfate, CTAB***; Cetrimonium bromide

3.7. Final Spectra of Reaction

In the same procedure of the obtained drugs, reference standards showed an orange-red colored product was produced in a solution containing Yttrium(III) with 1, 10-phenanthroline reagent in an acidic medium of hydrochloric acid (1M) in a final volume of 10 mL. After waiting for 20 min, the orange-red color developed a maximum absorbance wavelength at 510 nm against the blank solution Figure 3.

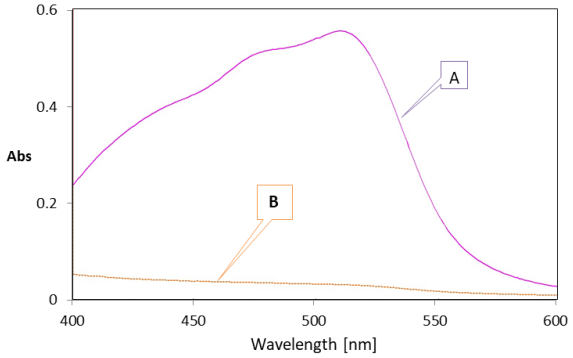


Fig. 3. Final spectra of reaction, A; spectrum drug (5 µg .ml-1)vs. blank, B; spectrum blank vs. distilled water

3.8. Stoichiometry of Product

The stoichiometry of the product, through the preparation of the same molar concentration for each drug and yttrium ion under the same conditions by applying the continuous variations (Job's) by a series of opposite volumes of the drug (0.1-0.9 mL) and the reagent (0.9-0.1 mL) were taken in volumetric flasks, and mole-ratio methods by taken various volumes (0.05-a series (Nejres & Moath, 2023), The results of both methods are in figure 4. It appeared the ratio was 2:1 between the drug and reagent, respectively.

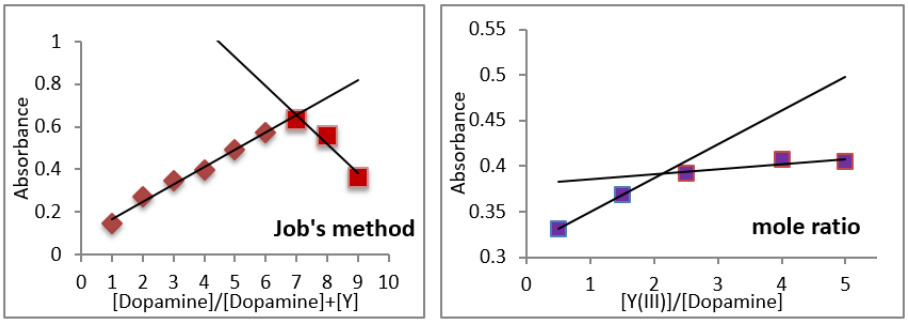


Fig. 4. The continuous variations (Job's) and mole-ratio methods plot

3.9. Formation Constant of Complex (k_f)

The formation constant of complex for reaction was calculated by using the equation (Abdel-Rahman et al., 2018)**:**

$$\mathbf{k_{f\,(2:1)}} = \frac{As/Am}{4(1-As/Am)^3 C^2}$$

After preparing equal molar concentrations of dopamine and Yttrium(III) (6.5×10^{-4} Mol.L^{-1}), the measurements are carried out in two phases .Whereas is arbitrarily selected from the absorbance values for a solution containing the same molar concentration of dopamine and Yttrium(III) with other additives in their optimal concentrations Where represents As, and Am is the absorbance for a different molar concentration of dopamine with excess Yttrium(III) , and C is the primary molar dopamine concentration. The results in table 8, the average (Ks) 46.2×10^{12} l.mol^{-1}.

Table 8
The formation constant of complex for reaction

Concern. Dopamine Mol.L-1	C2 Mol.L-1	As	Am	As/Am	$4(1-As/Am)^3C^2$	Ks
0.000026	6.76×10^{-10}	0.5542	0.5631	0.984	1.07×10^{-14}	9.21×10^{13}
0.000039	1.52×10^{-9}	0.6547	0.7295	0.897	6.56×10^{-12}	1.37×10^{11}

3.10. Accuracy and Precision

For investigation of the accuracy and precision of the proposed method, an aliquot (2, 4 and 5 µg.mL^{-1}) concentration of dopamine has been taken from a location within the linear part of the curve graph. Individually in three replicate measurements (Table 9).

Table 9
Accuracy and precision of proposed method

The concentration	Found*	SD	RSD%	E%	REC%
2	1.99	0.0017	0.6552	±0.470	99.53
4	4.01	0.0041	0.9099	±0.250	100.25
5	4.94	0.0045	0.8455	±1.200	98.8

* from the proposed method

3.11. Applications on Pharmaceutical Dosage Forms

The proposed method has been successfully applied for the estimation of dopamine in two pharmaceutical preparations: HAVER\Dopasel and pharma-sunny), The results for three concentrations are listed in Table 10; the results of the proposed method revealed an acceptable recovery, and the relative standard deviation was appropriate to evaluate the results of this method using a t-test (at three degrees of freedom and a 95% confidence level) has been investigated (Christian et al., 2013).

Table 10
The results of the proposed method on pharmaceutical preparations and t-test for it

pharmaceutical Dosage Forms	Concentrations µg .mL^{-1}	Dopamine present	Dopamine found	Relative error %	Recovery %	Measured values	RSD%	t-test*
HAVER Dopasel	200 mg.5mL^{-1}	2	2.01	0.57	100.57	201	1.19	±0.97
		4	3.99	-0.17	99.83	199.5	0.72	±0.43
		5	4.96	-0.72	99.28	198.4	2.08	±0.60
Pharma sunny	40 mg.1mL^{-1}	2	1.99	-0.48	99.52	39.8	0.87	±1.21
		4	3.95	-1.03	98.97	39.5	1.49	±1.21
		5	4.98	-0.28	99.72	39.8	1.27	±0.38

* British Pharmacopoeia standard method , 95% Confidence Interval of the Difference degrees of freedom; t-test 3.182

3.12. Standard Additions Methods

To confirm the estimation of dopamine in the pharmaceutical dosage forms without interference using standard addition methods. From figures 5(a,b) and Table 11, the proposed method successfully estimated without interference.

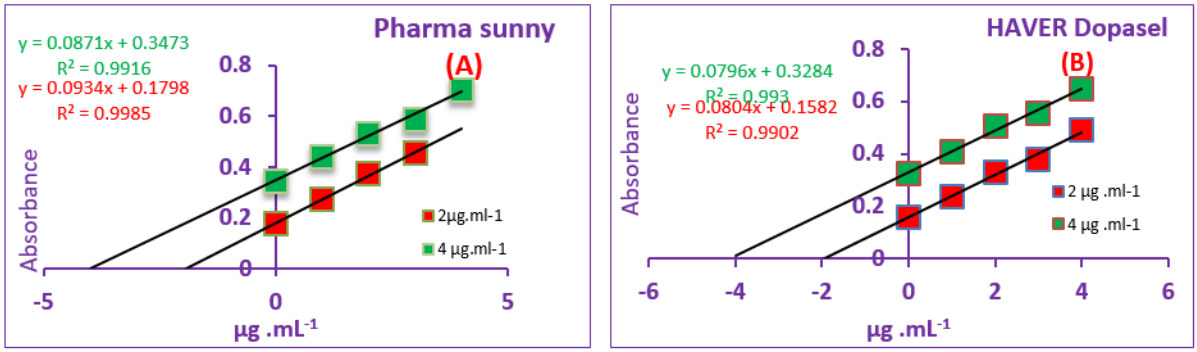


Fig. 5. Standard addition of two pharmaceutical Dosage Forms of dopamine

a) pharma sunny , b) HAVER Dopasel

Table 11
The results of dopamine estimation by using standard additions methods

pharmaceutical Dosage Forms	Amount present µg .mL^{-1}	Amount found µg .mL^{-1}	Recovery %
Pharma sunny	2	1.93	96.5
	4	3.98	99.5
HAVER Dopasel	2	1.96	98
	4	4.12	103

3.13. Comparison of Proposed Method

Many of the available spectrophotometric methods were previously used for the determination of dopamine in pharmaceutical preparations. Some of those methods were compared to the proposed method in Table 12.

Table 12
Compared to the proposed method with methods used previously

Type of reaction	oxidizing agent /Reagent	Wave-length (nm)	Medium of reaction	Beer's law µg.mL^{-1}	*ε, l.mol^{-1} .cm^{-1}	Sandell's sensitivity index µg.cm^{-2}	Reference
redox	Yttrium(III) / 1, 10-phenanthroline	510	acid	0.5-10	1.16x10^4	0.0131	This work
redox	Chromate ion/ indigo-carmine	610	acid	2.0-52	0.19×10^4	0.0806	(Saleem, 2019)
redox	$KMnO_4$	610	alkaline	0.2– 4.36	-	-	(Al-Salahi et al., 2022)
redox	Fe ion/ Potissum Ferricynide	735	acid	0.05-6	3.2 × 10^4	-	(Guo et al., 2009)

4. Conclusion

In the present work, the study carried out the model of dopamine by spectrophotometry using yttrium chloride (III). Because it is a novel complex method, when compared with the other methods, the significant advantages of the proposed method are as follows:

- Simple, rapid, sensitive, accurate, precise, and economical.
- The apparent molar absorption coefficient of indirect estimation and Sandal's sensitivity were 1.16x10^4 L.mol^{-1}.cm^{-1} and 0.0131 µg.cm^{-2}, respectively.
- The recovery rate of dopamine in pharmaceutical dosage forms the range was from 98.97 to 101.57%, which indicates the common excipients in these samples did not affect the estimation of dopamine using this method.

Accordingly, using 1, 10-phenanthroline-Y(III) to estimate dopamine in pharmaceutical dosage forms has an essential value and is practical.

Acknowledgement

The authors are thankful to their colleague Radwan Nidal, and the university of Mosul, Mosul, Iraq, and for providing essential research facilities to carry out this research.

Competing Interests

The authors have declared that no competing interests exist.

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