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Spectrophotometric Determination of Niacin Using 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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A simple and sensitive spectrophotometric method is developed for the assay of niacin. The method is based on charge transfer complexation reaction of niacin as n-electron donor with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as π-acceptor to form highly coloured charge transfer complex with 1:1 stoichiometry. The coloured product was quantified at 464 nm under the optimized experimental conditions. Beer's law is obeyed over the concentration range of 5-130 µg/mL. The apparent molar absorptivity is calculated to be 1.02×10^3 L mol^{-1} cm^{-1}. Corresponding Sandell's sensitivity is 1.85, detection and quantification limits are also reported. The proposed method is applied successfully to the determination niacin in pure and commercial forms with good average recovery of 97.82 % and low relative standard deviation of < 1. Statistical comparison of the results was performed using the student's t-test and f-test at 95 % confidence level.

Keywords: Niacin, Spectrophotometry, Charge transfer complex, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone.

INTRODUCTION

Acceptors are aromatic systems containing electron withdrawing substituents such as nitro, cyano and halogen groups [1]. Electron donors are systems that are electron rich [2]. The interaction between electron donor and acceptor results in formation of charge transfer complex [3]. The term charge transfer denotes a certain type of complex, which results from interaction of an electron acceptor and an electron donor with the formation of weak bonds [4]. Charge transfer (CT) complexes have been widely studied [5-11]. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is an oxidizing reagent [12], dehydrating agent in synthetic organic chemistry as well as it is known for its interaction with drugs having donor sites in their structures and form ion-pair charge transfer complexes which offers a basis for quantification of drugs [13,14]. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone as π-electron acceptors often form highly coloured electron-donor, electron-acceptor or charge transfer complexes with various drugs. Vitamin B_3 (Niacin) chemically designated as [pyridine-3-carboxylic acid] [15] is one of the water soluble vitamins of the B-complex. It is an essential vitamin that is widely available in drug and health food stores. Niacin is sometimes prescribed in high dosages to lower cholesterol. People also take niacin supplements because they think niacin helps ease gastrointestinal disturbances. It is widely distributed among plants and animals [16]. Some analytical methods have been developed for the determination of niacin which includes HPLC [17], flow injection TLC [18], HPTLC [19-21]. Furthermore, spectrophotometric methods have been reported for the simultaneous estimation of atorvastation and niacin based on simultaneous equation and absorbance ratio method [22]. Some of the reported methods are time consuming, involves, liquid-liquid extraction step, costly and lack sensitivity. Spectrophotometric technique continues to be the most preferred methods for routine analytical work due to their simplicity and reasonable sensitivity with significant economical advantages [23]. Therefore the aim of this work is to determine a method of analysis of niacin that is fast, simple, sensitive and cost effective.

EXPERIMENTAL

All spectrophotometric measurements were carried out using a UV-1800 Shidmazu and 752W-UV-visible grating spectrophotometer with a silica glass cell of 1 cm thickness. All chemicals used were of analytical grade and were used as such. Pure niacin and tablet were supplied by Juhel Pharmaceuticals Ltd. Nigeria and Puritan's Pride, USA, respectively. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (98 % purity) was supplied by Sigma-Aldrich Chemie, Germany.

General procedure: Transfer serial volumes of 0.02, 0.06 to 0.56 mL in 0.04 step of the standard niacin (0.001 g/mL) solution equivalent to ranges of concentration (5.0-130 µg/mL) into different test tubes. Add 0.2 mL of buffer 8 into the set up and add 2 mL of methanol. Add equal volumes of DDQ

(0.001 g/mL) solution in methanol according to the stoichiometric ratio of the drug and reagent. Mix the content and allow standing for 70 min at 60 °C before analysis at 464 nm against a methanol blank.

Assay determination of Niacin-DDQ complex: One niacin tablet was finely powdered, an amount equivalent to 0.01 g was accurately weighed into a beaker and the content was shaken in other to extract the active ingredient and filtered to remove the excipient. The solution was made up to 10 mL with the same solvent to provide a theoretical 0.001 g/mL solution of niacin. Serial volumes similar to the one prepared for the general procedure were transferred to different test tubes and treated similarly before analysis at 464 nm against a methanol blank.

RESULTS AND DISCUSSION

Absorption spectra: A 2,3-dichloro-5-6-dicyano-1,4-benzoquinone solution in methanol displayed absorption peak at 350 nm (Fig. 1). Niacin showed absorption peaks at 219 and 259 nm (Fig. 2). A reddish colouration was obtained upon reaction of yellow DDQ solution and a colourless solution of niacin (Fig. 3), which was suggestive of charge transfer complex with an absorption peak at 464 nm.

Stoichiometric ratio: Mole ratio method [24] was employed to establish the composition of the complex. Result shows a molar ratio of 1:1 (niacin: DDQ) was obtained (Fig. 4). This may be attributed to the availability of one center as electron donating group, which is the primary amine. A similar result has been reported DDQ [25]. **Scheme-I** shows the proposed interaction of niacin and DDQ. Molecular interactions between donors and acceptors are generally associated with the formation of intensely coloured charge transfer complex [5].

Maximum time for charge transfer complexation: Although the colour developed instantaneously (Fig. 5), maximum complexation was attained at 70 min at room temperature.

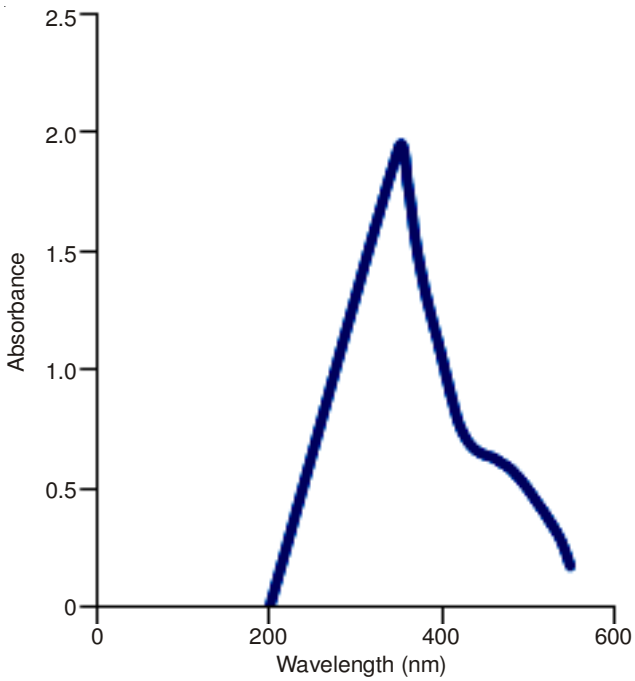


Fig. 1. Absorption spectra of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone

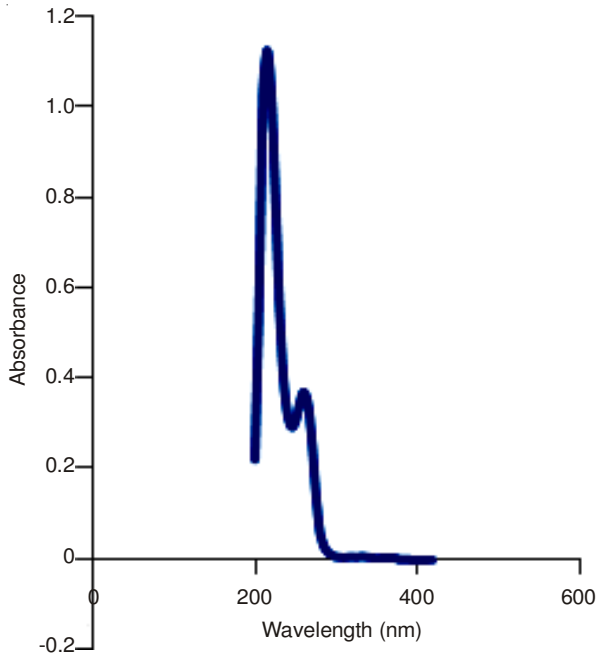


Fig. 2. Absorption spectra of niacin

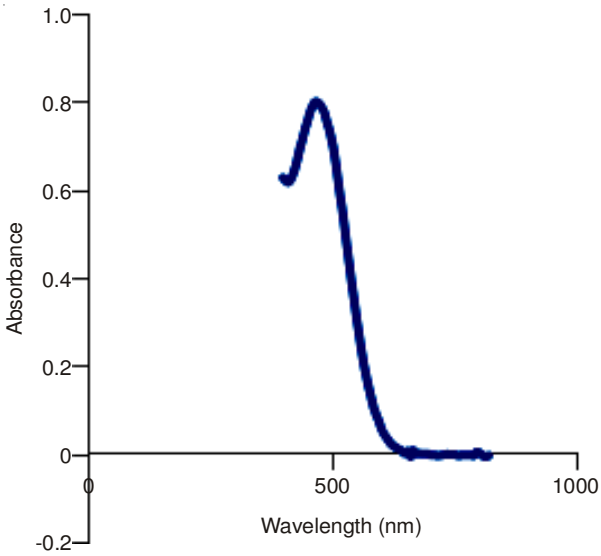


Fig. 3. Absorption spectra of niacin-DDQ complex

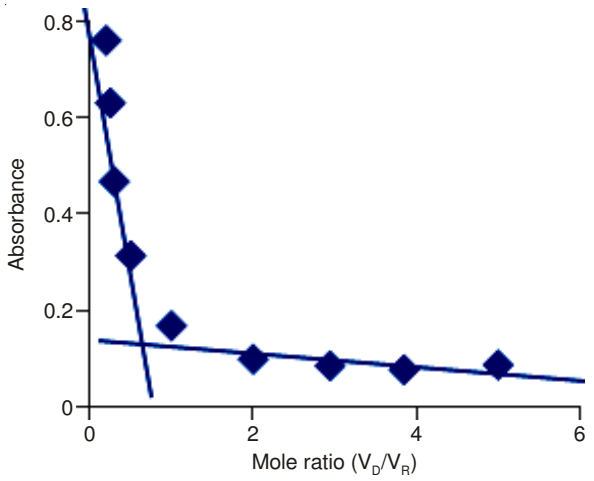
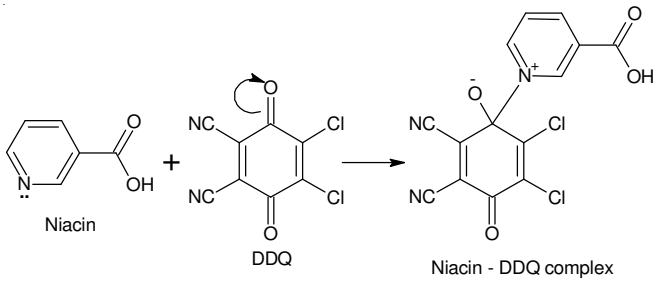


Fig. 4. Mole ratio of the drug V_d and V_r are the volume added drug and reagent, respectively



Scheme-I: Proposed charge transfer reaction between niacin and DDQ

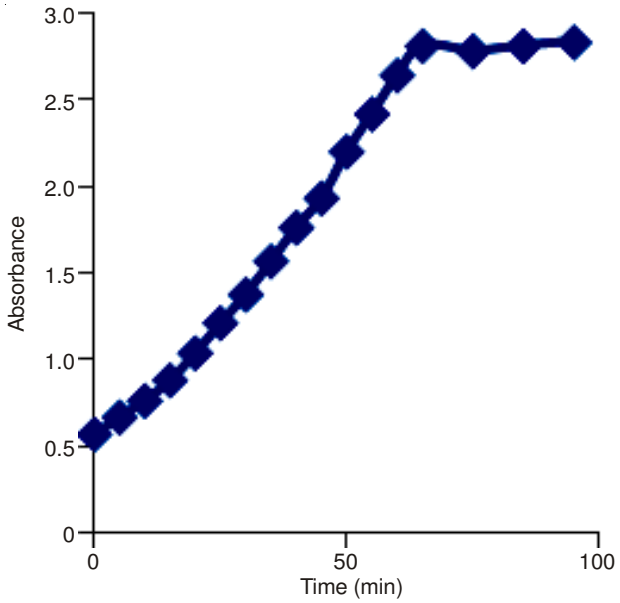


Fig. 5. Effect of time on complex formation

Effect of temperature on the stability of complex: The plot (Fig. 6) of absorbance *versus* temperature for the niacin-DDQ complex shows the maximum peak at 60 °C, although there was an increase in complex formation from 0 to 20 °C, a drop was noted at 30 °C and subsequent increase from 50 °C. This shows the unstable nature of the complex resulting from production of other compounds.

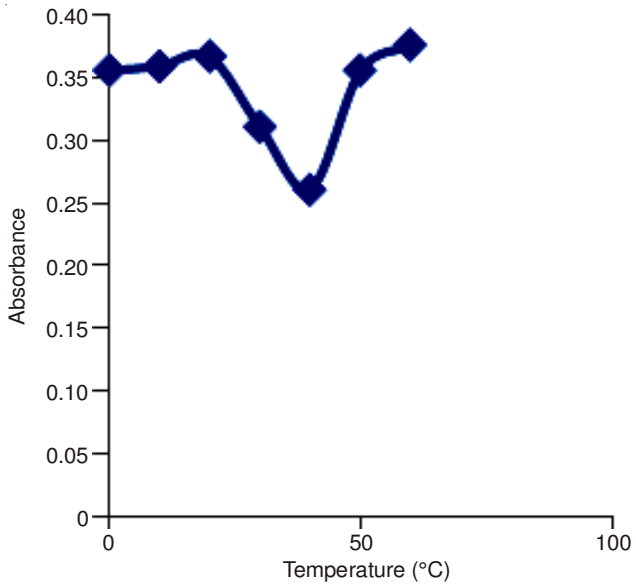


Fig. 6. Effect of temperature on the complex

Effect of pH: Buffer 1-13 were used for the pH studies. Result from a plot of pH against absorbance reveals that the maximum is shown to be at pH 8 (Fig. 7). This indicates that the complex formation is favourable in alkaline medium.

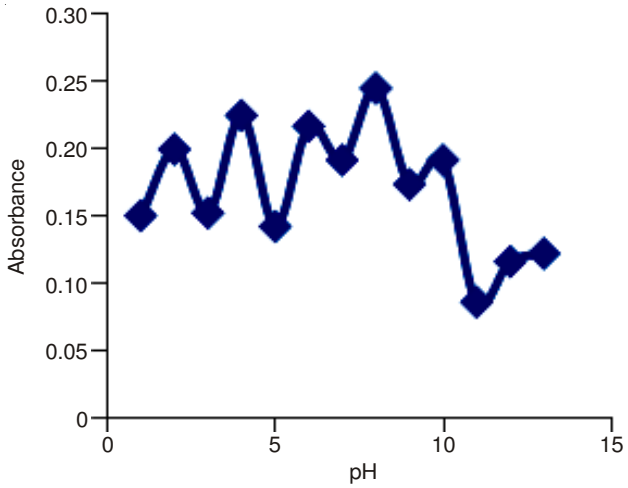


Fig. 7. Effect of pH on niacin-DDQ complex

Validation procedure using Beer's law: Fig. 8 is the least square fit of absorbance *versus* concentration for the niacin-DDQ complex at 464 nm, from the linear equation:

$$A_{464\ nm} = 0.005\ [D] - 0.020 \quad (1)$$

where [D] is the concentration of niacin in µg/mL. R^2 has the value of 0.954. This reveals that between concentration range of 5-130 µg/mL, Beer-Lamberts law is obeyed. This ensures the possibility of determining the drug within this range of concentration. This is different when compared to a reported work [22].

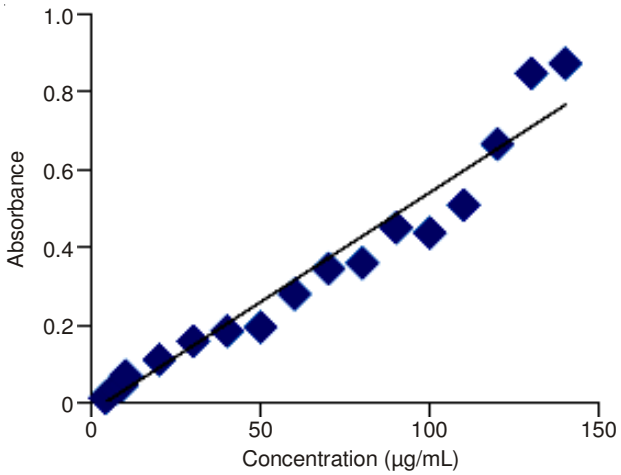


Fig. 8. Beer's plot of niacin-DDQ complex

The limit of detection (LOD) and limit of quantification (LOQ) were determined using the following equation:

$$LOD = \frac{3.3 \times \sigma}{s},\ LOQ = \frac{10 \times \sigma}{s} \quad (2)$$

The values of limit of detection, limit of quantification, apparent molar absorptivity and Sandell's sensitivity are all presented in (Table-1) using ICH guidelines [26].

TABLE-1
OPTIMUM CONDITIONS, STATISTICAL DATA AND REGRESSION EQUATION OF NIACIN COMPLEX

Parameters	Values
Molar absorptivity (L mol^{-1} cm^{-1})	1.02×10^3
Sandell's sensitivity (μg cm^{-2}/0.001A)	1.85
Regression equation Y[a]	
Slope (b)	0.005
Intercept (c)	0.02
LOD	1.78
LOQ	5.4
Correlation coefficient	0.954
Percentage recovery[b] (%)	97.82

[a]Seven independent analyses; [b]Average mean of three determinations

The average percentage recovery and standard deviation of niacin were found to be 97.82 % with relative standard deviation of < 1 (Table-2). The relative standard deviation indicate the precision and reliability of the proposed method with a t-test value of 0.34 and f-test value of 0.81 at 95 % confidence level which does not differ variably from an earlier report [23].

TABLE-2
APPLICATION OF THE PROPOSED METHOD FOR THE ASSAY OF NIACIN

Taken (μg/mL)	Found (μg/mL)	Recovery (%)	RSD (%)	Er (%)	t-test	f-test
6	5.75	95.83	0.090	-0.04	0.34	0.81
8	7.53	94.12	0.130	-0.06		
10	10.46	104.68	0.130	0.05		
30	28.88	96.27	0.020	-0.04		
70	68.38	97.69	0.003	-0.02		
90	89.54	99.49	0.002	-0.01		
110	106.34	96.67	0.002	-0.03		

Conclusion

The proposed spectrophotometric method for the determination of niacin is simple, rapid, accurate and economical as compared to all the methods used previously. The proposed method has been validated and successfully applied for the qualitative determination of niacin with good accuracy of 94-104.68 % Hence the proposed method is good for the quantitative analysis of niacin.

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