Rapid Spectrophotometric Determination of Phenoxazine

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Abstract:

A rapid high sensitive and inexpensive economic method has been developed for the Determination of phenoxazine by using molecular spectrophotometry. The method is based on the oxidation of phenoxazine by potassium (meta)periodate in acidic medium.

The oxidation conditions were selected to enhance the sensitivity and the stability of the pink colored species which shows an absorption maximum at 530 nm. The Beer's law was obeyed for phenoxazine concentration range from 1 to 6 µg mL^{-1} with 0.003 µg mL^{-1} detection limit and provided variation coefficients between 0.4 to 1.7 %. This method was successfully applied for the determination of phenoxazine in aqueous samples

Key words: phenoxazine, spectrophotometry, potassium metaperiodate.

Introduction:

Phenoxazine, firstly prepared in 1930 [1] and has found an extensive application, as the parent substance of a number of dyes and polymer derivates [2]. The physical properties make phenoxazine based compounds suitable for application in several industrial fields, including electro catalysis [3]. The hydrophobic phenoxazine ring promotes molecular aggregates in aqueous solution and such aggregates are important for several photo conversion applications such as photography [4].

Phenoxazine is a part of the chemical structure of antinomycine D, which is known to exert intensive anticancer activity on malignant tumors in children [5], and is a potent and low toxic chemosensitizer [6].

In recent years, phenoxazine derivatives have been widely used as chromogenic compounds in host-guest artificial photonic antenna system [7].

On the other hand phenoxazine has been used as analytical reagent for the determination of chlorine and nitrite in waters [8, 9]. Also, it was found to have potential applications for an ozone visual monitor, a reaction product with exceptional stability was formed[10].

On surveying the literature, it was not found any method for the spectrophotometric determination of phenoxazine and hence, the purpose of this study has been to develop a simple method based on the oxidation of phenoxazine by potassium (meta)periodate in acidic medium to produce a colored species showing an absorption maximum at 530 nm.

Materials and methods :

Apparatus

All the absorbance measurements were carried out by using a Hewlett-Packard (Waldbronn, Germany) model 8452, diode-array spectrophotometer, equipped with 89530A MS-DOS-UV-visible software with a response time of 0.1 second.

Reagents and solutions

All reagents used were of the highest purity and most solutions were

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prepared in ultra pure water with a resistivity of 18.2 MΩ cm, obtained from a Millipore Milli-Q system (Bedford, MA). Phenoxazine of 97.0% purity was obtained from Fluka (Buchs, Switzerland) and a stock standard solution was prepared daily by dissolving 25 mg phenoxazine in 100 mL absolute ethanol.

Hydrochloric acid of 37% was obtained from Scharlau (Barcelona, Spain). Potassium (meta)periodate of 99.8% purity was obtained from Fluka and a stock solution was prepared by dissolving 0.1(±0.0001) g in 250 mL ultra pure water in order to obtain 0.00174 mol L^{-1} KIO_4. The 10^{-4} mol L^{-1} KIO_4 working solution was prepared by dilution with ultrapure water. Both solutions were stable for long time at laboratory temperature.

General procedure

10 mL of sample were transferred to a 25 mL volumetric flask and 10 mL of concentrated HCl were added. The mixture was shaken and 1 mL 10^{-4} mol L^{-1} KIO4 was added and the volume was made up to 25 mL with ultra pure water. Absorbance measurements were carried out at 530 nm for the pink color by using a 1.0 cm quartz cell against reagent blank which was prepared in the same way but without phenoxazine.

Result and Discussion

UV-Spectrum of phenoxazine

Figure 1, shows the UV-spectrum of phenoxazine in water which presents three absorption maxima at 214, 236 and 312 nm. The absorbance maximum at 312 nm was selected in order to obtain the best selectivity.

This was done by carrying out a calibration graph through the preparation of a series of standard solutions of 0, 0.5, 2, 4, and 6 µg ml^{-1} of phenoxazine in volumetric flasks of 10 ml diluting to the mark with ultra pure water.

Table 1 demonstrates the optical characteristic of the determination of phenoxazine in the UV-region.

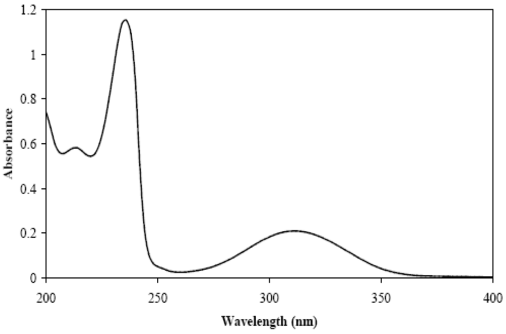


Figure 1: UV- absorption spectrum of 5 µg mL^{-1} of phenoxazine in 12% ethanol.

Table 1. Spectral data for phenoxazine in UV- region

Parameter	UV-region
Color	Colorless
ג max (nm)	312
Beer’s law (µg mL^{-1})	0.5 – 8
Molar absorptivity (L mol^{-1} cm^{-1})	8244
Limit of detection (µg mL^{-1})	0.016
Regression equation:	
Slope (mL $µg^{-1}$ cm^{-1})	0.045
Intercept(a.u.)	0.0069
Correlation coefficient ®	0.9993
Variation coefficient(%)(n=5)	0.3 – 1.7

Oxidation of phenoxazine

Phenoxazine undergoes oxidation readily in a series of one electron steps to Yield radicals and ions and it has been described the oxidation of phenoxazine with Concentrated sulphuric acid [11] dimethylsulfoxide (DMSO)-acetic anhydride [12], Iodine in DMSO and aluminum trichloride in nitro methane [13], electrochemical Oxidation [14], flash photolysis [15] and cerium (IV), bromine and iron [16] xidation.

In the presence of hydrochloric acid, phenoxazine is oxidized by the dissolved O_2 . Different concentrations of HCl from 1 mol L^{-1} to 8 mol L^{-1}

were assayed and it was found that 5 mol L^{-1} HCl was the best one.

Figure 2 shows the UV-visible absorption spectra of the oxidation products Which indicate that phenoxazine is readily oxidized and yields four main absorption Bands at 210, 236, 310 and 530 nm. The latter band being the most selective but less Sensitive than the other ones.

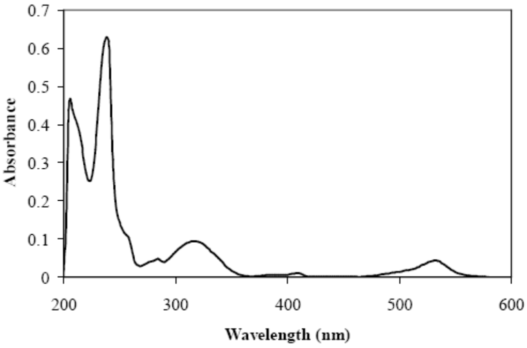


Figure 2: Study of the effect of dissolved O_2 on the UV-visible spectrum of 5 µg mL^{-1} Phenoxazine in acidic medium of 5 mol L^{-1} HCl.

Phenoxazine can be quantitatively oxidized by potassium (meta) periodate in 5 mol L^{-1} in hydrochloric acid medium. The effect of potassium (meta) periodate concentration was studied in the range from 10^{-6} to 10^{-3} mol L^{-1} . Figure -3- (A) shows that the best results were found at 10^{-5} mol L^{-1} KIO_4 and higher concentration of KIO_4 causes the destruction of the colored species. Figure-3- (B), shows the absorption spectrum of phenoxazine after oxidation by potassium (meta) periodate , and in this spectrum, it can be seen that the 530 nm absorption band has been dramatically increased as compared with spectra found in the absence of KIO_4.

The color development was very rapid and remained constant and stable for more than twelve hours even at temperatures till 100º C.

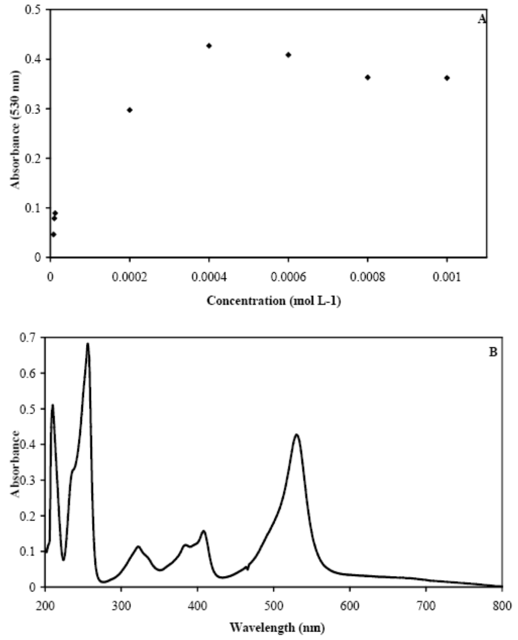
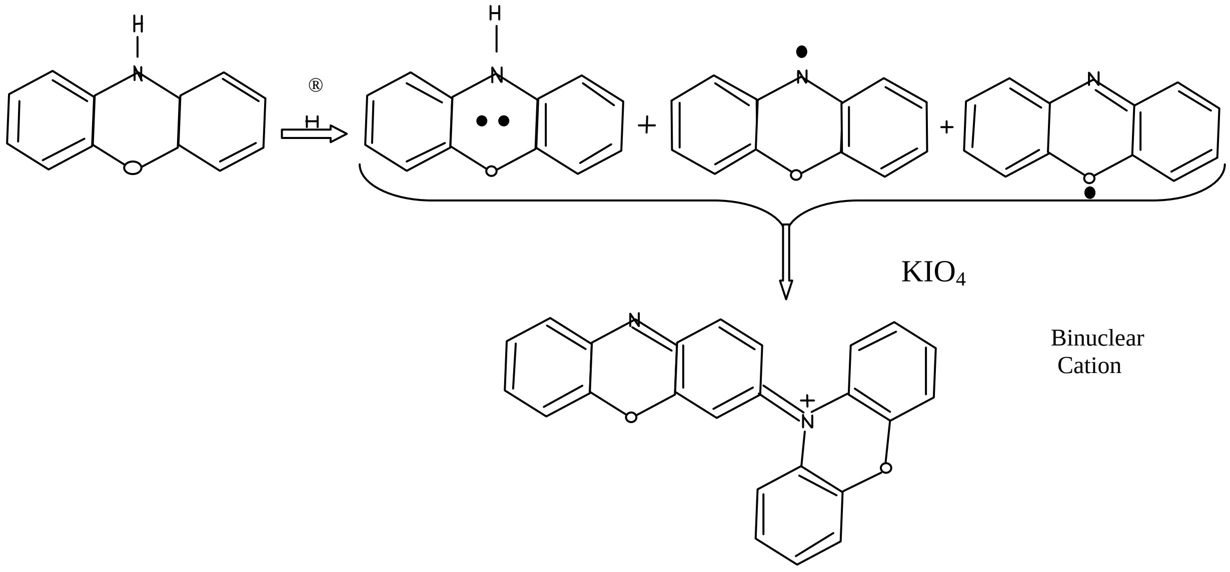


Figure3: (A) Effect of the potassium metaperiodate concentration on the absorption at 530 nm of a phenoxazine solution of 5 µg mL^{-1}. (B) UV-visible spectrum of the Oxidation product of 5µg mL^{-1} phenoxazine by using 10^{-5} mol L^{-1} KIO_4.

The proposed reaction mechanism may be similar to that proposed by Hanson and Norman [17] which is showed in the following scheme:



Analytical figures of merit

The optical characteristics for the determination of phenoxazine after oxidation by potassium (meta) periodate were established from a series of standard solutions on the concentration range from (1 - 6 µg mL^{-1}). Table-1 the analytical figures and merit of the proposed method.

Table2. Spectral data for phenoxazine in UV-visible region

Parameter	Uv-region	Visible region
Color	Colourless	Pink
λ max (nm)	312	530
Beer's law (µg mL^{-1})	0.5 – 8	1- 6
Molar absorptivity (L mol^{-1} cm^{-1})	8244	16778
Limit of detection (µg mL^{-1})	0.016	0.003
Regression equation:		
Slope (mL µg^{-1} cm^{-1})	0.045	0.091
Intercept(a.u.)	0.0069	0.0097
Correlation coefficient ®	0.9993	0.9996
Variation coefficient(%)(n=5)	0.3 – 1.7	0.4 – 1.7

Analysis of phenoxazine in water

The proposed method was applied to the determination of phenoxazine in spiked tap water.

Table 2, shows the obtained results of added quantities of phenoxazine and the standard deviation which provides quantitative recoveries in the range between 95.3 to 98.7 % in spite of the presence of interfering ions which are normally present in tap water.

Table3. Determination of phenoxazine in spiked tap water

Phenoxazine added (µg mL^{-1})	Phenoxazine found (µg mL^{-1})	Recovery (%)
1.5	1.430 ± 0.006	95.3 ± 0.4
2.5	2.43 ± 0.08	97 ± 3
3.5	3.33 ± 0.08	95 ± 2
4.5	4.44 ± 0.01	98.7± 0.2

(n=3)

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التقرير الطيفي السريع لمركب الفينوكسازين

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الخلاصه :
يتضمن البحث تطوير طريقه جديده للتقدير الكمي لمركب الفينوكسازين في محاليله المائيه باستخدام مطيافيه الامتصاص ما فوق البنفسجيه-المرئيه للمركب في محيط حامض الهيدروكلويك باستخدام بيرايودات البوتاسيوم في درجه حراره المختبر حيث تتكون صبغهورديه مستقره حتى عند درجات الحراره العاليه وذائبه في الماء وتعطي اعلى امتصاص عند طول موجي 530 نانوميتر ,يشير الرسم البياني الخطي للامتصاص مقابل التركيز بان قانون بير ينطبق ضمن مدى التركيز من 1 الى 6 مايكروغرام/لتر وكانت قيمه الامتصاص المولاريه مساويا الى 16778 وانحراف قياسي نسبي اقل من 0.4 الى 1.7 % . تمت دراسه الظروف المثلى للتفاعل وطبقت الطريقه على تحديد تركيز المركب في محاليله المائيه.