Notes

Spectrophotometric Determination of Hydrogen Peroxide by a Hydroquinone-Aniline System Catalyzed by Molybdate

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Hydrogen peroxide is used widely as an oxidant, a disinfectant and a bleaching agent in various industrial and household products.[1,2] Micro and trace determination of H_2O_2 is considerably important in clinical chemistry, analytical biochemistry and environmental science since H_2O_2 is produced in stoichiometric amounts during the oxidation of biological analytes (*e.g*. glucose) by dissolved oxygen in the presence of corresponding oxidase.[1-3] Owing to its importance, a large number of analytical methods have been developed for the determination of H_2O_2. These methods include titrimetry,[5] spectrophotometry,[6,7] fluorescence,[9,10] enzymatic methods,[11] chromatographic techniques[12,13] as well as electrochemical methods.[14,15]

Spectrophotometry has been chosen as the preferred method owing to its widespread use in analytical laboratories. At present the most widely used procedures in the determination of H_2O_2 are based on the reaction with chromogenic hydrogen donor in the presence of peroxidase or metalloporphyrins as enzyme mimetic of peroxidase.[16-18] However, peroxidase is expensive and its solutions are very instable whereas the use of metalloporphrins suffers from a very small difference between the absorption maximum of the reagent and the adduct.[17] An inexpensive procedure based on the reported catalysis of hydrogen peroxide reactions by Mo(VI)[19] has been utilized in this study.

Experimental Section

All chemicals were of analytical reagent grade and were used as received. Aqueous solutions of hydroquinone (0.25 mol/L) and anilinium sulphate (0.125 mol/L) and ammonium molybdate (0.5%) were made up by weight. Hydrogen peroxide solution (2.0×10^{-3} mol/L) was prepared by dilution of 30% H_2O_2 (Guaranted Grade). The solution was standardized iodometrically. Buffer solutions were prepared by mixing different amounts of 0.2 mol/L NaOH and 0.2 mol/L KH_2PO_4 to give solutions with pH 6.7, 7.0, 7.6. Buffer solutions in the pH 3-6 range were prepared using varying ratios of solutions of 0.2 mol/L NaOH and 0.2 mol/L acetic acid. Standard buffer solutions of pH 4.0 and 9.2 were supplied by BDH chemicals.

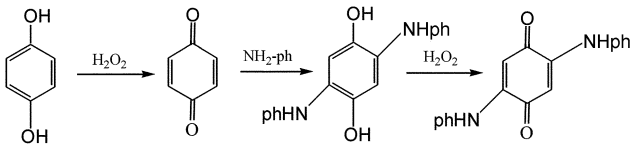
Apparatus. Absorption spectra were measured using UV-VIS spectrophotometer (PYE Unican, U K) on a 10 mm cell. A digital pH meter equipped with a combined glass-calomel electrode was used for pH measurements.

Procedure: Determination of H_2O_2.

In a 25 mL colorimetric tube 3.0 mL of 0.25 mol/L hydroquinone, 2.0 mL of 0.125 mol/L anilinium sulphate, 0.1 mL of 0.5% ammonium molybdate and varying amounts of standardized H_2O_2 solution were mixed and allowed to stand for 10 min. The solution was then diluted to the mark of 25 mL with distilled water and the absorbance was measured at 550 nm against a reagent blank in a 10 mm cell.

Results and Discussion

The formation of an addition product between the hydroquinone and aniline in the presence of H_2O_2 proceed as follows:



In this system hydroquinone is oxidized to pbenzoquinone by H_2O_2. 2 aniline are added, in successive stages, to pbenzoquinone, to yield the disubstituted quinone as the final product.[20] The UV-VIS spectrum of the product in aquous solution presented in Figure 1. It is obvious that a strong absorption peak with a maximum at 550 nm is formed.

Effect of pH. The dependence of the system on pH was studied over the pH 3.0-7.0 range. Figure 2. shows a flat peak of absorbance obtained in pH 3.0-5.0 range. The absorbance of the system is similar to that obtained in the absence of the buffer. The use of alkaline buffer was excluded because it gave different color.

Effect of time. The absorbance was measured continu-

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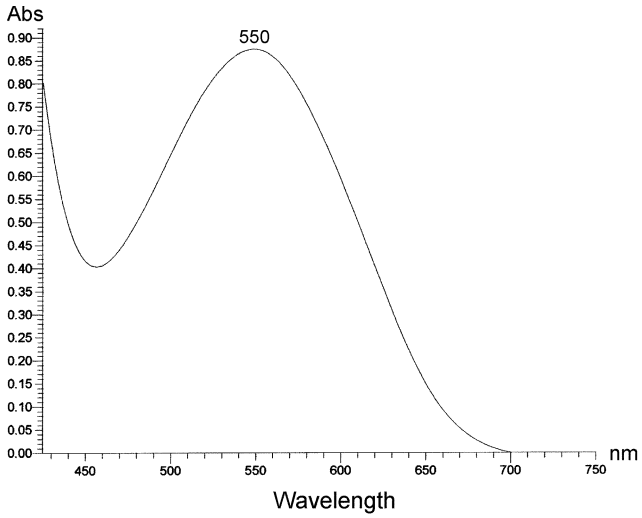

Figure 1. Electronic absorption spectrum of the addition product in aqueous solution at 295 K.

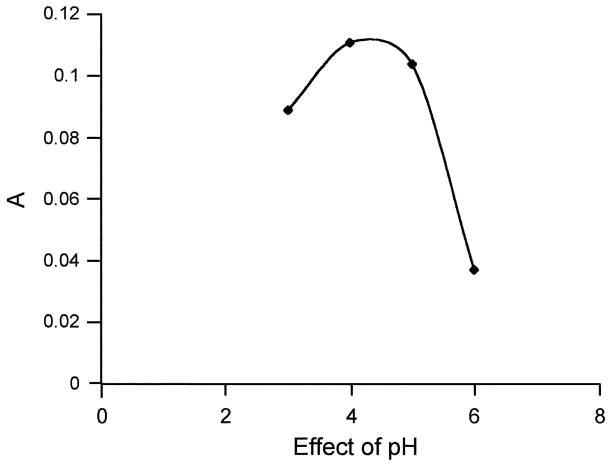

Figure 2. Effect of pH on the absorption of the addition product.

ously at room temperature (rt) for 50 min as shown in Figure 3. After about 12 min., the absorbance reaches a maximum and remains constant for at least 30 min. Therefore, an incubation period of 15 min. at (rt) was sufficient for the reaction to reach equilibrium.

Order of mixing the reactants. The influence of the addition order of the reagents was followed with four different groups.

Group I:

Hydroquinone + Anilinium sulphate + MoO_4^{2-} + H_2O_2

Group II:

Anilinium sulphate + H_2O_2 + Hydroquinone + MoO_4^{2-}

Group III:

Anilinium sulphate + MoO_4^{2-} + H_2O_2 + Hydroquinone

Group IV:

Hydroquinone + MoO_4^{2-} + H_2O_2 + Anilinium sulphate

The results of this study demonstrated that the sequences of mixing of groups I to III gave the same result but the sequence of group IV gave no colored product probably

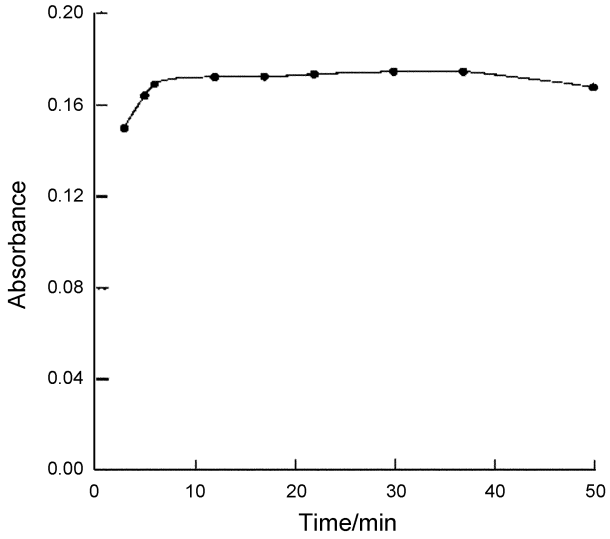

Figure 3. Effect of incubation time on the stability of the absorption of addition product.

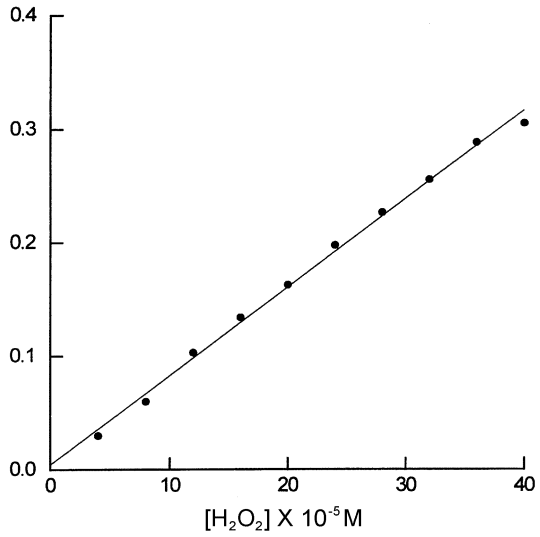

Figure 4. Calibration function for hydrogen peroxide.

caused by the oxidation of hydroquinone. Hence it can be infered that the formation of the coloured product only forms when the hydroquinone is oxidized in the presence of aniline. Hence it can be concluded that the correct order of mixing the reactants may follow any of the groups I-III.

Effect of amount of reagents. The absorbance is maximal and constant for 4.0×10^{-5} mol/L H_2O_2 when the concentrations of hydroquinone, anilinium sulphate and MoO_4^{2-} are in the range of 2-4 mL of 0.25 mol/L., 1-3 mL of 0.125 mol/L and 0.1-0.2 mL of 0.5% respectively. Accordingly 3.0 mL of hydroquinone, 2 mL anilinium sulphate and 0.2 mL MoO_4^{2-} are recommended for use.

Analytical characteristics. Linearity was shown by the calibration graph shown in Figure 4 for the determination of H_2O_2. Regression analysis of the curve is given by

$$A = 0.00015 + 0.8C$$

Table 1. Recoveries of hydrogen peroxide

H_2O_2 content of artificaial sample, ($\times 10^{-5}$ mol/L)	Added ($\times 10^{-5}$ mol/L)	Found ($\times 10^{-5}$ mol/L)	Recovery (%)
8	0	8.0, 8.3, 8.6, 7.9, 7.8, 8.0	
8	4	11.5, 11.8, 12.2, 11.5, 12.0, 12.3	99.03
8	8	16.0, 16.3, 16.6, 15.9, 15.8, 16.0	100.63

Table 2. Effect of interferences of inorganic salts $[H_2O_2] = 2.0 \times 10^{-4}$ mol/L

Substance	Amount (μg/mL)	Error (%)
Br^-	160	-0.5
SO_4^{2-}	1150	0
NO_3^-	370	0
HPO_4^{2-}	1.6	-7.6
Fe^{3+}	0.84	0
Mg^{2+}	72.9	0
Ag^+	0.26	0
K^+	234	0

when the concentration of H_2O_2 was 3.8×10^{-4} mol/L, and the apparent absorptivity was 8.0×10^2 L/mol.cm. The coefficient of variation for the determination of 6.0×10^{-5} mol/L H_2O_2 was 99.99% (n=6). Sandell sensitivity was 0.043 μg/mL.

A definite store of H_2O_2 and the reagents were added in the determination of H_2O_2 then the recovery values were determined by their absorbance from the calibration graph so the recoveries of artificial sample were investigated as listed in Table 1.

The interference of foreign substances in the determination of H_2O_2 (2.0×10^{-4} mol/L) was examined. The salt concentrations were five times higher than the limiting concentration specified in drinking water. The results of interference are summarized in Table 2.

In conclusion, the new method based on the addition product formation has been demonstrated to be reliable and with acceptable sensitivity for the determination of hydrogen peroxide in verities of product.

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