Kinetic Spectrophotometric Determination of Nitrite by Catalytic Reaction of Bromopyrogallol Red and Bromate

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Summary: A sensitive kinetic spectrophotometric method for the determination of nitrite has been proposed, based on its catalytic effect on the oxidation of bromopyrogallol red (BPR) with bromate in sulphuric acid (0.15M). The decrease in absorbance at 467 nm is monitored spectrophotometrically after 5 min, with 20-1000 ng/ml nitrite. The presence of nitrate do not interfere the determination of nitrite. Coefficient of variation (C.V) for (n=10) was observed 0.86%. The nitrite has been determined in water samples and results are compared with standard spectrophotometric method.

Introduction

The occurrence of nitrite salts in environment and their use as food preservatives is wide spread [1]. However the concern about the role of nitrite in the formation of N-nitroamines has been increased, because many of which are shown as carcinogenic [1,2]. It is therefore desirable that sensitive methods are available for the determination of nitrite. A number of spectrophotometric methods have been proposed for the determination of nitrite, with varying degrees of success [3-7] including spectrophotometric method utilizing diazo coupling reaction with N-(1-naphthyl) ethylenediamine [6]. The spectrophotometric methods have been automated by using flow injection technique for nitrite [8-9].

The fluorometric [10,11], electrometric [12] and high performance liquid chromatographic (HPLC) methods [13] are also available for nitrite. Catalytic kinetic methods are relatively less reported [7,14-21]. A sensitive kinetic spectrophotometric methods for nitrite, based on nitrite induced catalysis of the reaction system, Fe(III)-SCN-I^- has been proposed [14]. Catalytic spectrophotometric method for nitrite using indicator reaction of bromate with Janus green [20] or

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pyridine-2-carboxaldehyde-2-pyridylhydrozone [16,17] have been reported.

Ensafi and Samimifer [21] have reported a kinetic spectrophotometric method for the determination of trace nitrite, based on its catalytic effect on reaction between potassium bromate and pyrogallol red in the acidic medium. A similar method is described here using bromopyrogallol red.

Bromopyrogallol red (5,5'-Dibromopyrogallolsulfonephthalein) has been used as metallochromic indicator and in the spectrophotometric determination of niobium(V) [22]. It has been used for kinetic spectrophotometric determination of cobalt chromium, vanadium and mercury [23-26] with hydrogen peroxide in alkaline media using borate buffer (pH 9.5).

Results and Discussion

In order to examine the effect of traces of nitrite on the oxidation of bromopyrogallol red (BPR) with bromate in acidic solution, the absorption spectra of BPR, BPR and bromate and BPR, bromate and nitrite systems in acidic media were recorded (Fig. 1). It was observed that uncatalysed reaction of BPR with bromate was slow and enhances considerably in the presence of nitrite. It was therefore considered possible to determine the nitrite by recording A_o-A at 467 nm. Fixed time method was used, because it is simple and convenient to measure absorbance after fixed time for both catalysed and uncatalysed reaction. In the present work 5 min was chosen as an optimum reaction time.

Effect of variables on the rate of reaction

In order to optimize the conditions for the catalytic determination of nitrite, effect of variables on change in absorbance between catalysed and uncatalysed reactions were examined.

It was observed that the catalysed reaction proceed effectively in acidic medium (below pH 3), thus, the reaction was examined in sulphuric acid at the final concentration 0.02M to 0.2M. The maximum change in absorbance (A_o-A) was

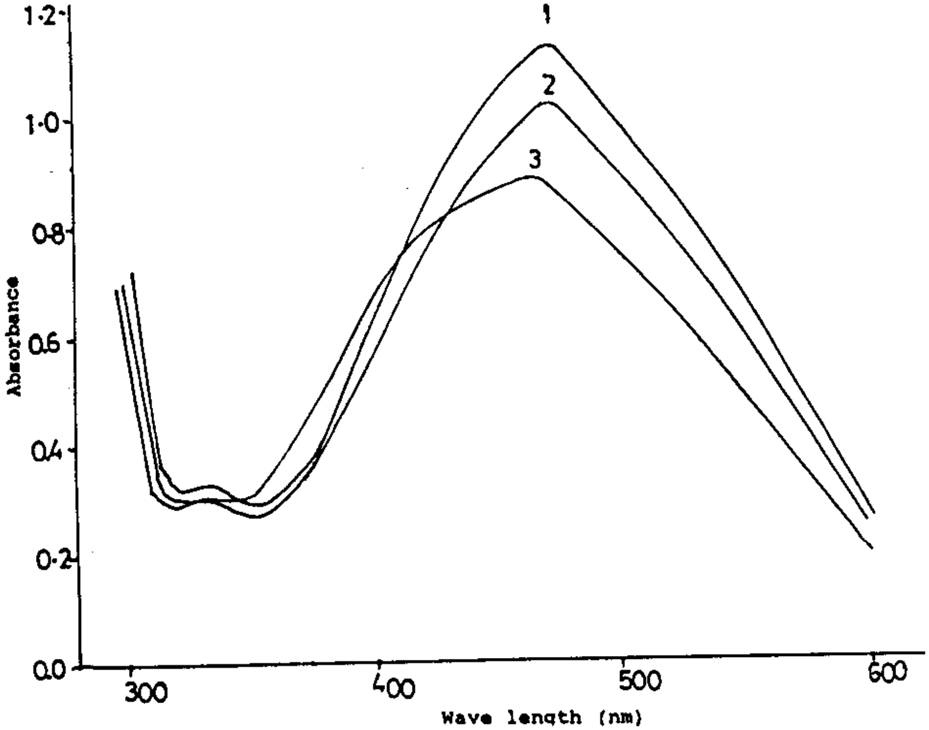

Fig. 1: Absorption spectra of (1) bromopyrogallol red (BPR) (2) BPR and bromate, (3) BPR, bromate and nitrite. Final concentration: BPR: 8x10^{-5}M, bromate: 6x10^{-3}M, nitrite: 0.2 µg/ml, sulphuric acid: 0.15M. Temperature: 30°C.

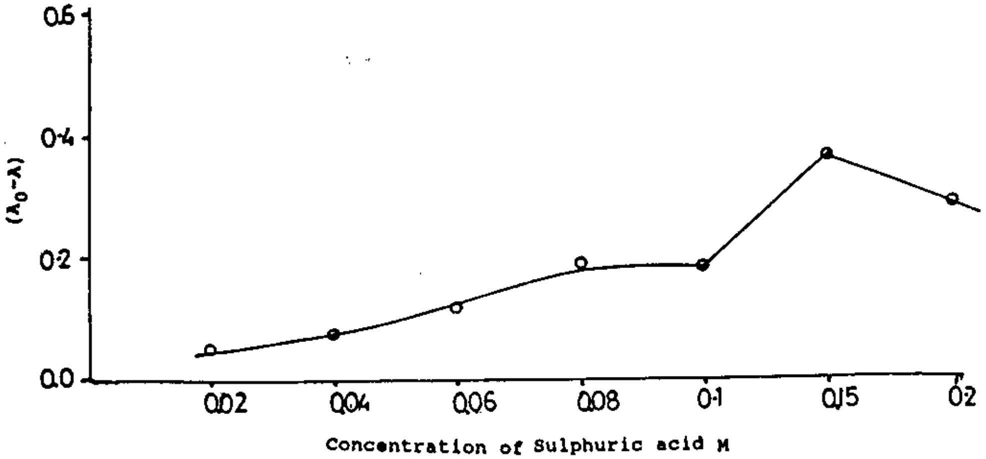

Fig. 2: Effect of concentration of sulphuric acid on A-A_0 at 467 nm. Final concentrations: BPR: $8x10^{-5}$M, bromate: $6x10^{-3}$M, nitrite: 0.4 µg/ml, Temperature: 30°C.

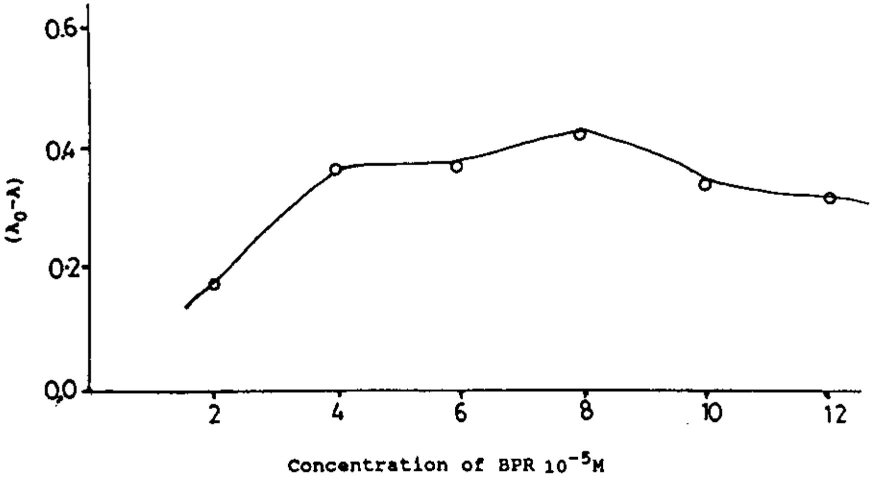

Fig. 3: Effect of concentration of BPR on A-A_0 at 467 nm. Final concentrations: bromate: $6x10^{-5}$M, nitrite: 0.4 µg/ml, and sulphuric acid 0.15M. Temperature 30°C.

observed at 0.15M sulphuric acid and was selected for the reaction (Fig. 2).

Next parameter examined was the effect of bromopyrogallol red at the final concentration, in the range of 2-$12x10^{-5}$M. It was observed that as the concentration of bromopyrogallol red increases, the absorbance of catalysed and uncatalysed reaction increases. (Fig. 3), but the final concentration of bromopyrogallol red was fixed at $8x10^{-5}$M to give appropriate absorbance within the limits of minimum photometric error.

Similarly the effect of potassium bromate concentration on the rate of reaction was studied in the range of $2x10^{-3}$M to $6x10^{-3}$M (Fig. 4). The final concentration $6x10^{-3}$M was selected, and was used throughout the study.

The reaction was examined at room temperature (30°C). Using the conditions it was possible to draw linear calibration curve by plotting A_0-A against concentration of nitrite in the range of 0-0.1 µg/ml and 0 to 1 µg/ml (Fig. 5a, 5b) with coefficient of correlation(r) of 0.999 for calibration

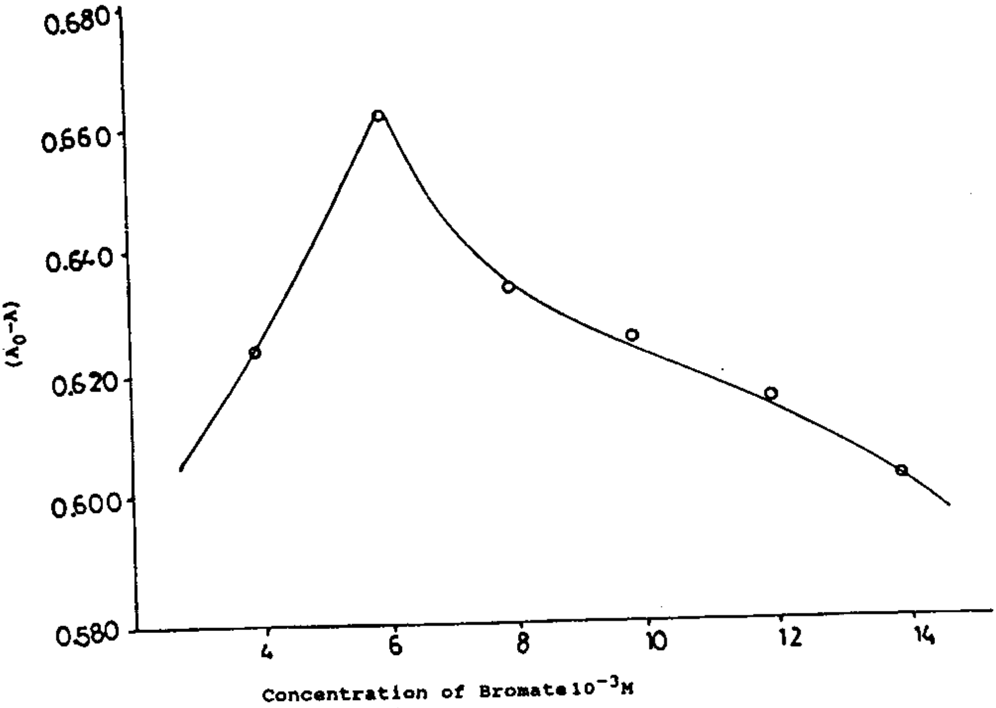

Fig 4: Effect of bromate concentration on A-A_0 at 467 nm. Final concentrations: BPR: $8x10^{-5}$M, nitrite: 1.0 µg/ml, sulphuric acid: 0.15M. Temperature: 30°C.

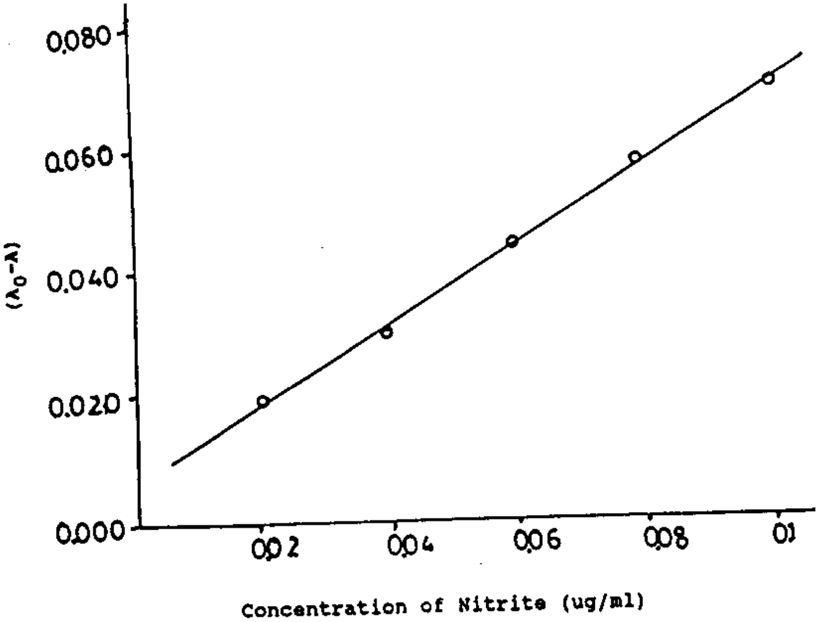

Fig. 5a: Linear calibration curve of nitrite. Concentration and conditions as Fig. (1).

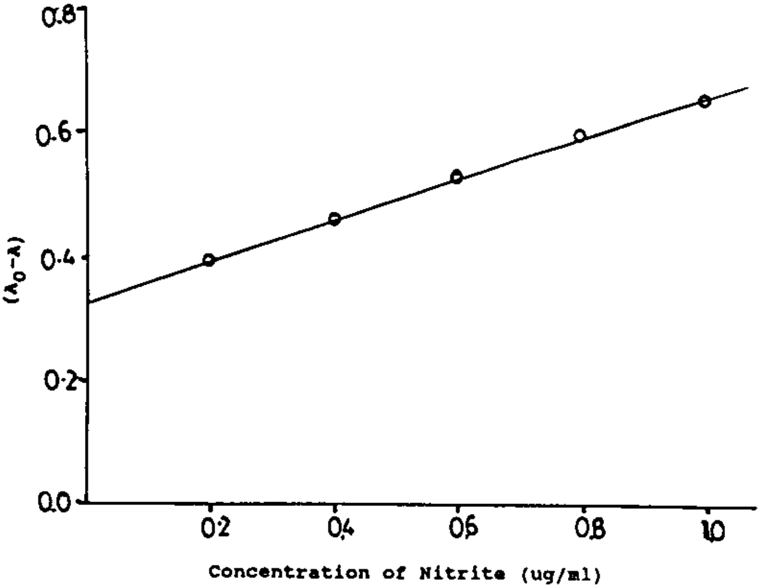

Fig. 5b: Linear calibration curve of nitrite. Concentration and conditions as Fig. (1).

curve with 0-0.1µg/ml. The following regression equation was obtained.

$Y = 0.065\ b + 0.0072$, where b is concentration µg/ml.

The standard deviation and coefficient of variation for replicate determination (n=10) of nitrite at the final concentration of (0.1 µg/ml) were observed 0.008 and 0.85% respectively.

In order to check the validity of the calibration curve, test solution of nitrite were analysed and relative % error found was within ± 3.33-10%.

The effect of diverse ions on the determination of nitrite (0.1 µg/ml) was also examined. It was observed that nickel(II), Zinc(II), mercury(II), borate, nitrate, acetate could be tolerated up to ten times the concentration of nitrite. However cobalt(II), copper(II), iron(II) and chromate enhanced the catalytic reaction at the concentration similar to the nitrite and interfered the determination.

Finally the water samples collected from River Indus and Fulleli canal were analysed for the contents of nitrite. Nitrites concentrations found were in the range of 0.052 and 0.058 µg/ml respectively with coefficient of variation 0.197 and 0.2437% (n=3). The samples were also analysed for nitrite by diazotiazed sulfanilic acid with N-(1-naphthyl) ethylenediamine [27] and results obtained were 0.056 µg/ml and 0.059 µg/ml for river Indus and Fulleli canal respectively, and a reasonable correlation is obtained.

Experimental

Solutions

Potassium bromate ($1x10^{-1}$M) was prepared by dissolving 0.167g in water and volume adjusted to 100 ml. Solution of nitrite (1000 µg/ml) was prepared by dissolving 0.15g of $NaNO_2$ in water and was added sodium hydroxide (50 µg). The final volume was adjusted to 100 ml. Sulphuric acid (1M) was prepared from sulphuric acid (96%) (Merck).

Bromopyrogallol Red ($1x10^{-3}$M) was prepared by dissolving a mass 55.8 mg in water and was added 3 ml of 0.25M sodium acetate. The pH of the solution was adjusted to 4 with 4M sulphuric acid and the solution was filtered. The final volume was adjusted to 100 ml.

Analytical procedure

To a 25 ml volumetric flask was transferred an aliquot of solution (1-5 ml) containing 0-25 μg nitrite, 3.75 ml (1M) sulphuric acid and 2 ml of bromopyrogallol red ($1x10^{-3}M$ w/v). The solution was then added 1.5 ml ($1x10^{-3}M$) bromate and stop watch was started. The final volume was adjusted to 25 ml. The absorbance of the solution against water was measured at 467 nm after 5 min. A reagent blank was also prepared following the same procedure, except addition of nitrite was omitted. The absorbances A and Ao were labeled for test solution and blank respectively. Temperature of room and solution at the time of measurements was noted (30°C). The amount of nitrite in test solution was determined from calibration curve prepared from known amounts of nitrite.

Equipment

A Hitachi 220 spectrophotometer was used for absorptions measurements with 10mm silica cuvettes. pH measurements were made on Orion model 420 A pH meter with glass electrode and combined reference electrode. A stop-watch was used for recording of the time.

Sample analysis

Two water samples were collected (1) from left bank of River Indus near national highway bridge and (2) Fulleli canal near C.I.A. center. The water samples were collected from the surface of the water in clean 1L plastic bottles. The samples were filtered and 15 ml was taken and analytical procedure was followed.

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