

## Kinetic Measurements of Nitrite by Bromopyrogallol Red

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(Received 11th August, 1996, revised 27th February, 1997)

**Summary:** A kinetic spectrophotometric method for the determination of trace amounts of nitrite (0.2-1.0) µg/ml has been proposed, based on its catalytic effect on the reaction between potassium bromate and bromopyrogallol red in acidic medium. The reaction is monitored spectrophotometrically by appearance of band at 348 nm with respect to blank by fixed time method (15 min). The method has been applied for quantitative determination of nitrite in water samples with coefficient of variation (C.V) within 4.2% (n=3).

### Introduction

The use of nitrite as food preservative is extensive, but increasingly concern has been reported in the formation of N-nitroamines, many of which are carcinogens [1].

For the determination of nitrite various analytical methods are reviewed [2,3]. The reported methods include spectrophotometric [4-6], fluorometric [7,8], electrometric [9,10] and high performance liquid chromatographic (HPLC) [11]. Some catalytic kinetic methods for nitrite have also been reported, involving the detection with spectrophotometer [12-14], fluorometer [15,16] or electroanalytical techniques [17]. Kinetic spectrophotometric methods are simple because they involve less expensive equipment and sensitive at sub µg/ml nitrite is generally obtained.

Ensafi and Saminifar have reported [12] a kinetic spectrophotometric method for the determination of nitrite based on its catalytic effect on the reaction between potassium bromate and pyrogallol red in acidic media. The reaction is monitored by measuring the decrease in colour of pyrogallol red at 467 nm by the fixed time method.

Recently bromopyrogallol red (BPR) has been used following a similar procedure as reported by Ensafi and Saminifar [12] with some improvement in the sensitivity for the determination of nitrite [18]. Furthermore, BPR has been used as metallochromic indicator and as a spectrophotometric reagent for niobium(V) [19]. It has also been used for kinetic spectrophotometric

determination of cobalt, chromium, vanadium and mercury with hydrogen peroxide in alkaline media using borate buffer (pH 9.5) [20-23]. In the present work again BPR has been used, but appearance of a band and increase in absorbance at 348 nm with nitrite concentration in acidic media is investigated. The reaction is monitored by spectrophotometry with respect to blank for determination of nitrite.

### Results and Discussion

The absorption spectra of BPR, BPR and bromate, and BPR, bromate and nitrite in acidic solution were recorded, to examine the effect of traces of nitrite on the oxidation of BPR with bromate. Fixed reaction time of 15 minutes was used. It was observed that BPR did not show a band at 348 nm, BPR in the presence of bromate indicated some absorbance at 348 nm, but the absorbance of BPR in presence of bromate and nitrite at 348 nm enhanced considerably. An attempt was therefore made to examine the change in absorbance at 348 nm with respect to blank with the concentration of nitrite, for its possible use for quantitative determination.

#### *Effect of variables on the rate of reaction*

In order to optimize the conditions for the catalytic determination of nitrite, effect of variables (pH, temperature, concentration of BPR and bromate) on the absorbance at 348 nm were examined.

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It was observed that catalysed reaction proceeded in acidic media (below pH 3), the reaction was therefore examined in sulphuric acid at final concentration between 0.08 and 0.4M. The maximum change in absorbance (A-B) was observed at 0.32M and was selected for the reaction (Fig. 2).

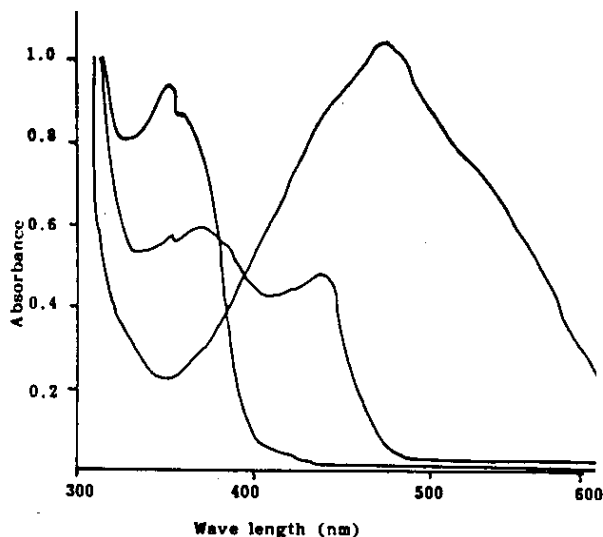


Fig. 1: Absorption spectra of (1) bromopyrogallol red (BPR), (2) BPR and bromate (3) BPR, bromate and nitrite. Final concentrations: BPR:  $8 \times 10^{-5}$ M, bromate:  $8 \times 10^{-3}$ M, nitrite: 1  $\mu$ g/ml, Sulphuric acid: 0.32M, Temperature: 30°C.

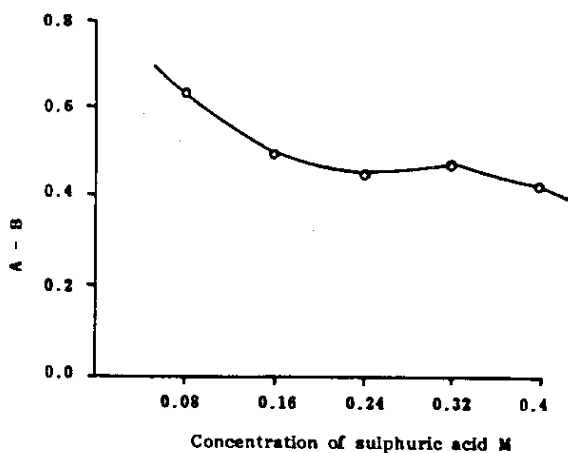


Fig. 2: Effect of concentration of sulphuric acid on A-B at 348 nm. Final concentrations: BPR:  $8 \times 10^{-5}$ M, bromate:  $8 \times 10^{-3}$ M, nitrite: 1  $\mu$ g/ml. Temperature: 30°C.

The effect of the concentration of BPR on the catalysed reaction showed that there was a sharp increase in the absorbance with increase in the concentration of BPR in the range of  $2 \times 10^{-5}$ M to  $6 \times 10^{-5}$ M but the absorbance remained fairly constant in the range of  $6 \times 10^{-5}$ M to  $1 \times 10^{-4}$ M. It was therefore final concentration of BPR was selected at  $8 \times 10^{-5}$ M for the catalytic reaction (Fig. 3) to get an stable absorbance for catalytic reaction.

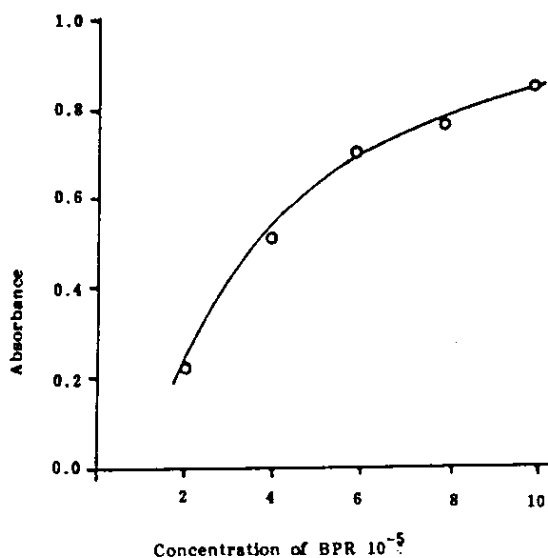


Fig. 3: Effect of concentration of BPR on absorbance at 348 nm. Final concentrations: Bromate:  $8 \times 10^{-3}$ M, nitrite: 1  $\mu$ g/ml, Sulphuric acid: 0.32M, Temperature: 30°C.

Similarly the effect of bromate concentration on the catalysed reaction was examined at final concentration within  $2 \times 10^{-3}$ M to  $10 \times 10^{-3}$ M and constant A-B was observed within the region (Fig. 4) and  $8 \times 10^{-3}$ M was considered as an optimum and was selected.

An increase in A-B with increase in temperature between 20 to 50 °C was observed, but the temperature of 30°C was selected because of the ease of the operation at the laboratory temperature.

Using the conditions it was possible to draw a linear calibration curve by plotting A-B versus concentration of nitrite (Fig. 5) and coefficient of correlation ( $r$ ) 0.991 was obtained using concentration between 0.2 to 1.0  $\mu$ g/ml.

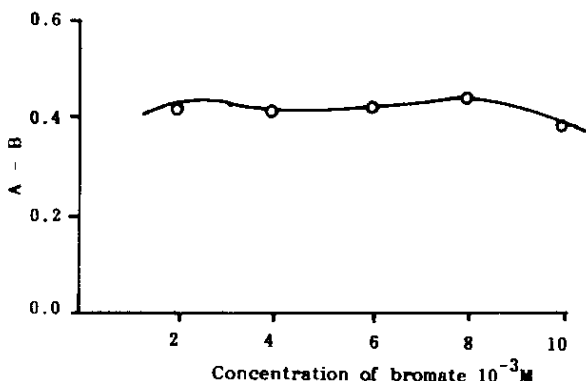


Fig. 4: Effect of bromate concentration on A-B at 348 nm. Final concentrations: BPR:  $8 \times 10^{-3} M$ , nitrite:  $1 \mu g/ml$ , Sulphuric acid: 0.32 M. Temperature:  $30^{\circ}C$ .

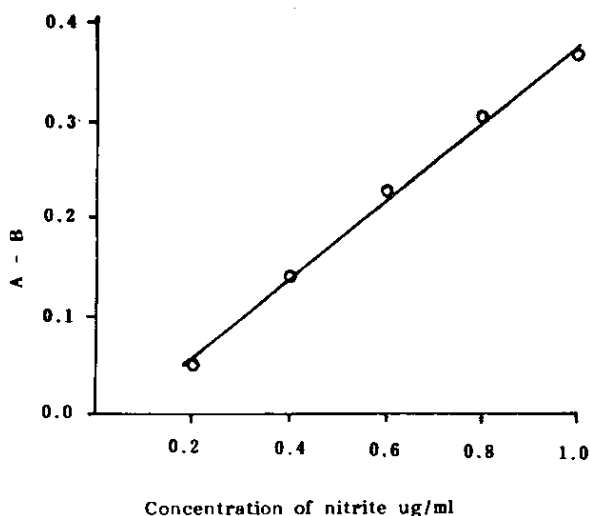


Fig. 5: Linear calibration curve of nitrite by plotting A-B against concentration  $\mu g/ml$ . Conditions as Fig. (1).

The coefficient of variation (C.V) for the replicate determination ( $n=10$ ) of nitrite  $0.2 \mu g/ml$  was observed 4.2%. The analyses of test solutions of nitrite were carried out and observed relative % error was within  $\pm 0.5-7.5\%$ .

The effect of diverse ions on the determination of nitrite, ( $1 \mu g/ml$ ) was also examined. It was observed that cobalt(II), zinc(II), copper(II), mercury(II), cadmium(II), nitrate, chloride and sulphate could be tolerated ten times the concentration of nitrite. Manganese (II),

molybdenum(VI) oxovanadium(IV), nickel(II), chromium(VI), lead(II), silver(I), chromate and borate slightly enhanced the absorbances at the concentrations similar to nitrite. However iron(II) interfere even at  $0.1 \mu g/ml$  levels by increasing the absorbance at 348 nm.

Finally water samples collected from ((1) Kotri barrage river Indus and from Fuleli canal near (2) Akhnud village and (3) CIA centre were analysed for the contents of nitrite. Nitrite concentrations found were 0.167, 0.143 and  $0.206 \mu g/ml$  with coefficient of variation (C.V) 1.62%, 2.44% and 1.323% respectively.

The samples were also analysed for nitrite by diazotized sulfanilic acid with N(1-naphthyl)ethylenediamine [24]. The results obtained were 0.162 and 0.132 and  $0.279 \mu g/ml$  for samples 1,2 and 3 with C.V of 1.52%, 2.33% and 2.8% respectively.

## Experimental

### Solutions

Potassium bromate ( $1 \times 10^{-1} M$ ) was prepared in water and volume adjusted to 100 ml. Solution of nitrite ( $1000 \mu g/ml$ ) was prepared in water and sodium hydroxide (50 mg) was added. The final volume was adjusted to 100 ml. Further solutions were prepared by appropriate dilutions with water daily. Sulphuric acid (1M) was prepared from sulphuric acid (96%) (Merck).

BPR ( $1 \times 10^{-3} M$ ) was prepared in water and added 3 ml of 0.25M sodium acetate. The pH of the solution was adjusted to 4 with 4M sulphuric acid and solution was filtered. The final volume was adjusted to 100 ml.

### Analytical procedure

An aliquot of solution (1-5 ml) containing (5-25  $\mu g$ ) nitrite was transferred in 25 ml flask and 2 ml (4M) sulphuric acid and 2 ml of BPR ( $1 \times 10^{-3} M$ ) were added. To this solution 2 ml of bromate ( $1 \times 10^{-1}$ ) was added and stop watch was started. The final volume was adjusted to 25 ml immediately. The absorbance was measured at 348 nm after 15 min using water as a reference solution. A reagent blank was also prepared

following the same procedure, except addition of nitrite was omitted. The absorbance of the blank at 348 nm (B) was subtracted from the analyte absorbance (A). All the measurements were recorded at the room temperature (30°C). The amount of nitrite in test solution was determined from calibration curve prepared by recording A-B against the concentration of nitrite.

#### Sample analyses

Three water samples were collected (1) from right bank of kotri barrage river Indus, (2) Fuleli canal near Akhund village (3) from Fuleli canal, near C.I.A. Centre Hyderabad. The water samples were collected from the surface of water in clean 1L plastic bottles. The samples were filtered and 15 ml was taken and analytical procedure was followed.

#### Equipment

A Hitachi 220 spectrophotometer was used for the absorbances measurements with 1 cm silica cuvettes. pH measurements were made on Orion model 420 pH meter with glass electrode and combined reference electrode.

#### References

1. K.K. Choi and K.W. Fung, *Analyst*, **105**, 241 (1980).
2. W. Fiddler, R.C. Doerr, R.A. Gales and J.B. Fox, *J. Assoc. of Anal. Chem.*, **67**, 525 (1984).
3. J.B. Fox, *CRC Crit. Rev. Anal. Chem.*, **15**, 283 (1985).
4. P. MacCarthy, R.W. Klusman and J.A. Rice, *Anal. Chem.*, **59**, 308R (1987).
5. C.J. Martinez, J. Catalyted. C.H. Medina, *Microchem. J.*, **43**, 143 (1991).
6. A. Chaurasia and K.K. Verma, *Talanta*, **41**, 1275 (1994).
7. P. Damiani and G. Burini, *Talanta*, **33**, 649 (1986).
8. N. Jie, J. Yang and F. Meno, *Talanta*, **40**, 1009 (1993).
9. S. Sabharwal, *Analyst*, **115**, 1305 (1990).
10. M.M. Malone, A.P. Doherty, M.R. Smyth and J.G. Vost, *Analyst*, **117**, 1259 (1992).
11. J.P. de Kleijn and K. Hoven, *Analyst*, **109**, 527 (1984).
12. A.A. Ensafi and M. Saminifer, *Talanta*, **40**, 1375 (1993).
13. C. Sanchez-Pedeno, M.T. Sierra, M.I. Sierra and A. Sanz, *Analyst*, **112**, 837 (1987).
14. R. Montes, J.J. Laserna, *Talanta*, **34**, 1021 (1987).
15. R. Montes and J.J. Laserna, *Anal. Sci.*, **7**, 467 (1991).
16. Z.Zhang, H.Wu. M. Beng, D. Lin. *Fenxi Huaxue*, **20**, 91 (1992).
17. J.Zhi-Liang, Q. Hai-Cuo and W. Da-Qiang, *Talanta*, **39**, 1239 (1992).
18. A.A. Khaskheli, G.M. Mastoi, I.A. Ansari and M.Y. Khuhawar, *J. Chem. Soc. Pak.*, **18**, 3 (1996).
19. M.E. Diaz Garcia and Sanz-Medel, *Talanta*, **32**, 189 (1985).
20. R. Belcher, T.V. Ramakreshna and T.S. West, *Talanta*, **12**, 581 (1965).
21. D. Costache and S. Sasu, *Rev. Roum. chim.*, **18**, 931 (1973).
22. I.A. Ansari, *Sindh Univ. Res. J. (Sci.Ser.)* **18**, 137 (1986).
23. A.A. Khaskheli and I.A. Ansari, *J. Env. and Anal. Chem.*, **2**, 13 (1993).
24. APHA Standard Methods for the Examination of Water and Waste Water, 14th ed. Washington DC (1976).