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Kinetic spectrophotometric determination of trace amounts of nitrite ion using potassium bromate-murexide mixture in acidic media

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ABSTRACT

A new, simple, rapid, and cheap method for determination of trace amounts of nitrite ion is reported. Determination is based on reduction of bromate ion by nitrite ion, in the presence of murexide in acidic media. During reaction of bromate ion with nitrite ion, the reaction mixture is decolorized. The absorbance changes is then monitored spectrophotometricaly at 520 nm, at 25 °C. Dynamic range of calibration curve for nitrite ion is in the range of 1-22 $\mu g.mL^{-1}$. The effect of interfering ions was investigated. This method was successfully used for determinination of nitrite ion concentration in sausages.

Keywords: Kinetic-spectrophotometric determination, potasium bromate, murexide, nitrite ion.

INTRODUCTION

Modern analytical chemistry comprises a vast range of methods based on the physical, chemical or physicochemical changes exhibited by substances in chemical reaction, with or without prior separation of the analyte[1]. Thus, every process, regardless of its nature, takes place at a finite rate, tending to an equilibrium position, and therefore comprises two regions: the kinetic(dynamic) region, in which the system approaches equilibrium, and the equilibrium region, which occurs once all the processes involved in the system have attained equilibrium(Fig. 1)

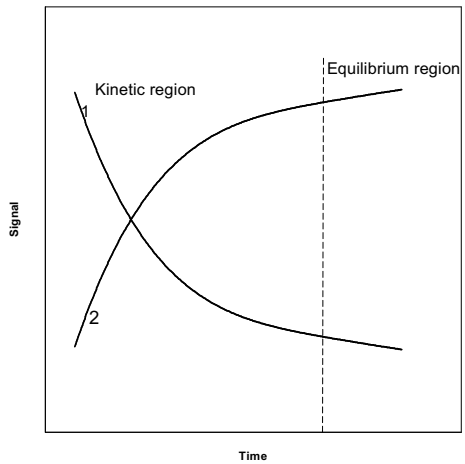

Fig. 1. Kinetic and equilibrium regions of a chemical reaction. Recording of the analytical signal as a function of time, for (1) disappearance of a reactant; (2) formation of a product.

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The determination of a given species by a kinetic method is based on the direct or indirect measurement of its reaction rate, which in turn involves measuring the change in the reactant or product concentration as a function of time. Thus, the reaction rate is defined as the number of moles of material consumed or formed per unit volume per unit time. Considering the following reaction;

$$A + B \rightarrow P \qquad P = \text{Products}$$

the reaction rate at time t will be given by the derivative of the concentration of each species involved, with respect to time.

$$\text{rate} = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} \quad (1)$$

and $$\text{rate} = k[A][B] \quad (2)$$

The kinetic determination of a given species can be performed by two different methods, differential and integral. In the differential methods, the initial rate of a chemical reaction (A + B $\rightarrow$ P), (where pseudo zero-order conditions are hold, the rate is not influenced by the concentration of A or B) is given by

$$v_0 = \frac{d[P]}{dt} \approx k[A][B] \approx \text{Const.} \quad (3)$$

If the reaction is of the first order in respect to A, then the initial rate will be given by

$$v_0 = \frac{d[P]}{dt} = k_A[A]_0 \quad (4)$$

Where k_A is the first-order rate constant and $[A]_0$ the initial concentration of A.

From Eq. (4) it follows that the plot of the initial rate as a function of $[A]_0$ will be a straight line which can be used as a calibration curve for determination of species A[1]. Thus, reaction rate can be applied for determination of nitrite ion concentration in the mixture of bromate, murexide in acidic medium.

Nitrite is known to react with secondary amines to produce carcinogenic N nitrosoamines [2]. Also, nitrites are undesirable in water due to its toxicity [3]. A great deal of interest has been generated concerning their potential health hazards. After ingestion, presence of nitrite in blood stream converts oxyhemoglobin to metahemogolobin, thereby intrefering with oxygen transport in the blood [4]. For these resons, different analytial methods are applied to determine the concentration of this ion in real samples specially foodstuffs.

Determination of nitrite has been carried out by various methods. Among different analytical methods like ion chromatography [5, 6, 7], chemiluminescence [8,9,10], voltammetry [11, 12, 13], amperometry [14], potentiometry [15, 16, 17], flow injection [18, 19, 20, 21, 22, 23], capillary electrophoresis [24], and spectrophotometry [25, 26, 27, 28, 29], by far the later is the most widley used method. Several methods for determination of nitrite using reaction rate methods have been reported [30, 31, 32, 33, 34, 35, 36].

In this work, the optimal conditions for kinetic spectrophotometric determination of nitrite were stablished by varying the concentrations of potassium bromate, sulforic acid, and murexide in the reaction media. Also, the effects of ionic strength, and temperature were investigated on the reaction rate.

EXPERIMENTAL

All chemicals were of analytical-reagent grade and were used without further purification. Doubble distilled deionized water was used through out the experiments. A standard solution of nitrite (1000 $mg.L^{-1}$) was prepared by dissolving 1.5 g of sodium nitrite in water and diluting to 1000 mL with distilled water. Sulforic acid (1M) was prepared by introducing 54.39 mL of concentrated sulforic acid (98 % purity and d=1.84 $g.mL^{-1}$) into a 1000 mL volumtric flask and diluting to the mark with distilled water. Potassium bromate (0.1 M) was prepared by dissolving 16.701 g of potassium bromate in 1000 mL of water. Murexide stock solution was prepared by dissolving 0.0284 g of murexide in water and diluting to 100 mL in a volumetric flask. This solution was stored in dark place and was prepared daily.

Absorption spectra were recorded on a Chamspec model M350 UV-Vis. spectrophotometer using a 1-cm quartz cell. Absorbance readings at a fixed warelength (520 nm) were made on a shimadzu UV-120-2 spectrophotometer. The temperature was controlled with a circulating thermostat bath instrument with accuracy of ±0.1°C .

Recommended procedure

Into a 10-mL volumetric flask, 2 mL of 0.1 M potassium bromate, 1 mL of 8×10^{-4}M murexide, 2 mL of 2×10^{-3} M sulforic acid were added. The flask was thermostated for 10 min at 25°C, then an aliquot containing 1-22 $\mu g.mL^{-1}$ of nitrite ion was introduced and the stopwatch was turned on simultaneously and solution of flask diluted to the mark with distilled water. The reaction mixture was transferred immediately into the spectrophotometric cell and the absorbance at 520 nm was measured at 30 seconds and 3 minutes after beginning of the reaction. The difference between absorbances of the two readings was calculated as (ΔA).

Results and Discussion

In the absence of nitrite ion, there is slow reaction between murexide and potassium boromate. However, when nitrite ion is added, the reaction will occur with a faster rates, and there will be a color change from red to colorless. The changes in absorbance at 520 nm vs. time is shown in Fig. 2.

The effect of acidity on the reaction rate was studied by addition of H_2S0_4 solution to the test solution (Fig. 3). It is seen that in presence of H_2S0_4 up to 1.2×10^{-3} M the reaction rate remains constant. Therefore concentration of 0.001 M was selected as the best concentration for H_2S0_4. The influence of potassium bromate concentration was investigated and optimum concentration of potassium bromate was chosen to be 0.02 M (Fig. 4).

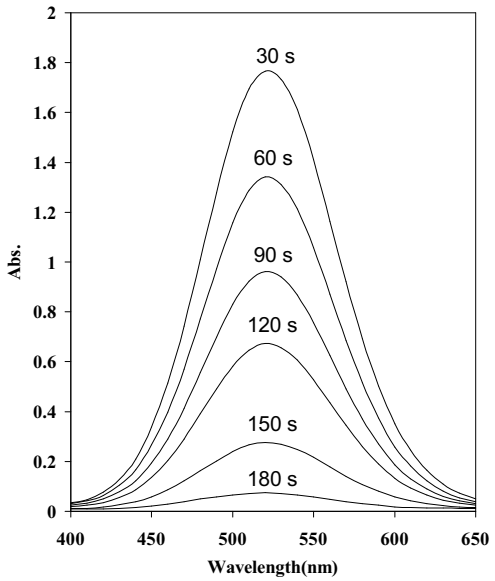

Fig. 2. Changes in absorbance vs. time.

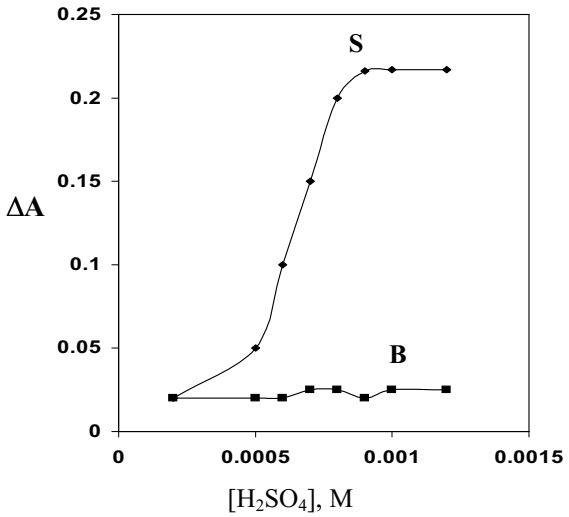

Fig. 3. Effect of sulforic acid concentration on reaction rate. S: Sample; B: Blank.

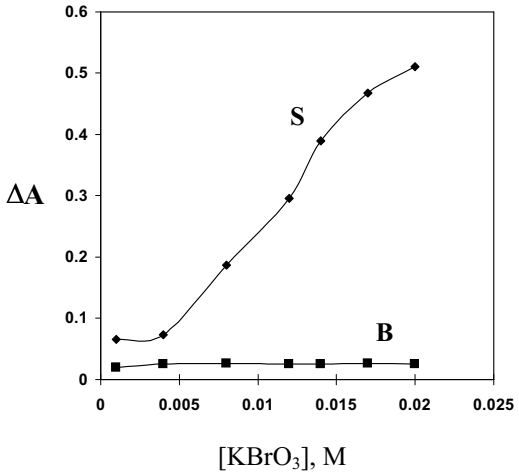

Fig. 4. Effect of potassium bromate concentration on reaction rate. S: Sample; B: Blank.

The effect of the concentration of murexide on the reaction rate was studied (Fig. 5).

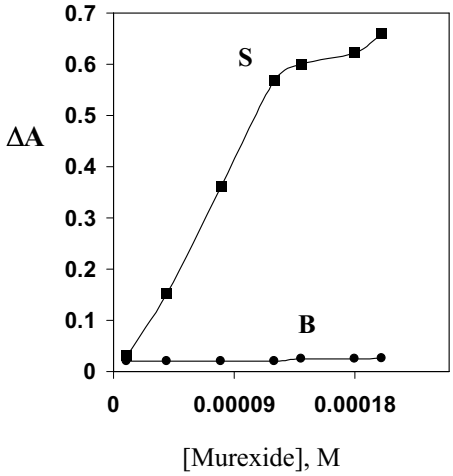

Fig. 5. Effect of murexide concentration on ΔA. S: Sample; B: Blank.

Optimum concentration of murexide was chosen to be 1.8×10^{-4} M. The effect of ionic strength on the reaction rate was investigated by using different concentration of sodium nitrate solutions, (Fig. 6). The results show that ionic strength doesn't have any effect on the reaction rate and fluctuations are due to random error of the experiment. Therefore, for further studies sodium nitrate was not added to solutions. The influence of temperature on the reaction rate was studied between 10 and 40°C. It is seen that the rate of reaction increases by increasing the temperature. Room temperature was chosen for convenience (Fig. 7).

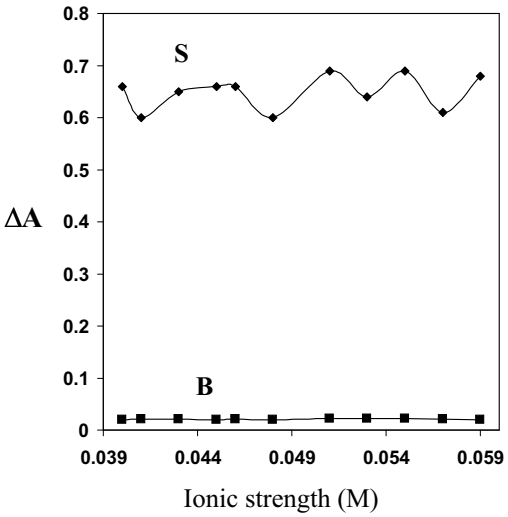

Fig. 6. Effect of ionic strength on the reaction rate. S: Sample; B: Blank.

A linear calibration curve was obtained under optimum conditions in the concentration range of 1 to 22 $\mu g.mL^{-1}$ with a square of correlation coefficient of 0.9992 and a regression equation of $\Delta A= -5.9\times10^{-4} + 0.01335C$, where C is the concentration of nitrite ion in $\mu g.mL^{-1}$.

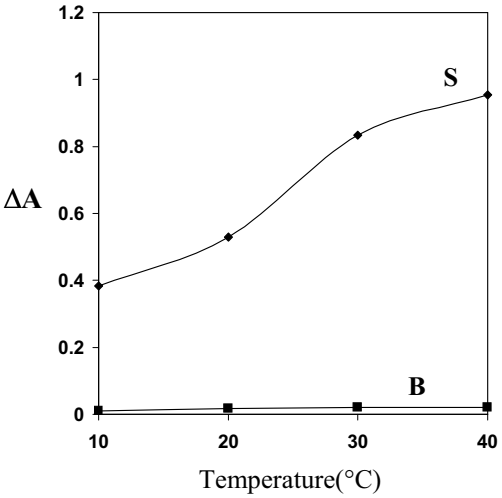

Fig. 7. Influence of temperature on the reaction rate. S: Sample; B: Blank.

The relative standard deviation of 10 replicate determinations of 15 μg.mL^{-1} nitrite was 2.17%. LOD of the method was 0.89 μg.mL^{-1}.

In order to study the effect of various anions and cations on the determinations of nitrite, a fixed concentration of nitrite ion (15 μg.mL^{-1}) was taken with different amounts of foreign ions and a relative error of 4% was considered tolerable. The results are summarized in Table 1. As can be seen there is no interference effect on the determination of nitrite ions. In order to evaluate the applicability of the method to the real sample, it was applied to the determination of nitrite ion in sausage samples. Sausage product (5 g), previously homogenized, was weighted into a 250 mL Erlenmyere flask; 0.25 mL of sodium tetraborat (0.099M) and 150 mL of water were added and the mixture was heated to 70 °C on a steam bath. The mixture was transferred to a 250 mL volumetric flask; 40 μL of potassium hexacyano ferrate (II)(0.288M) solution and 40 μL of zinc acetate (1.171M) solution were added and was diluted to the mark with distilled water. Afterwards, the solution was filtered. Finally, reagents of kinetic spectrophotometric method were transferred to a 10 mL volumetric flask and 1 mL of the solution containing nitrite was added and made up to volume with distilled water. Then the above mentioned procedure for determination of nitrite was applied. The results are shown in Table 2.

Table 1. Effect of foreign ions on the determination of nitrite

Foreign Ion Added	Concentration (μg.mL^{-1})
K^+, Cl^-, Na^+	10000
Mg^{2+}, Ni^{2+}	1000
Hg^{2+}, Ca^{2+}	500
CH_3COO^-, CrO_4^{2-}	300
F^-	200
CO_3^{2-}	100
$Fe(CN)_6^{4-}, Zn^{2+}, B_4O_7^{4-}$	25

Initial sample contained 15 ppm of nitrite ion.

CONCLUSION

The kinetic spectrophotometric determination of nitrite was applied for determination of contents of foodstuff such as sausage. The proposed method offers sufficient selectivity, sensitivity , high accuracy and reproducibility. LOD of the method was 0.89 μg.mL^{-1} and reproducibility for 10 replicate analysis was 2.17%.

Table 2. Comparison of the results obtained by standard Griess with the present method

Sample	Griess method (%)	Present method(%)
Sausage(1)	0.10(2.4)[a]	0.10(2.0)
Sausage(2)	0.10(1.9)	0.11(2.1)
Sausage(3)	0.11(2.1)	0.10(3.0)
Sausage(4)	0.12(2.0)	0.10(2.3)
Sausage(5)	0.10(2.1)	0.10(2.1)
Sausage(6)	0.09(2.2)	0.11(2.0)

a: Values in the parenthesis were data based on three replicate analysis.

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