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Development of a New Inhibition Kinetic Spectrophotometric Method for Determination of Resorcinol Based on its Inhibitory Effect on Formaldehyde Catalyzed Reaction Between Bromate and Janus Green

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A new, simple, sensitive and fast kinetic spectrophotometric method was developed for the determination of trace amounts of resorcinol over the range of 0.02-0.60 μg/mL. The method is based on the inhibitory effect of resorcinol on the formaldehyde catalyzed oxidation reaction of Janus Green by bromate in acidic media is reported. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Janus Green at 554 nm with a fixed-time 0.5-2.0 min from initiation of the reaction. The detection limit is 0.012 μg/mL and relative standard deviation of 0.04 and 0.08 μg/mL resorcinol for six replicate measurements was 2.5 and 2.9 %, respectively. The method was applied to the determination of resorcinol in water samples.

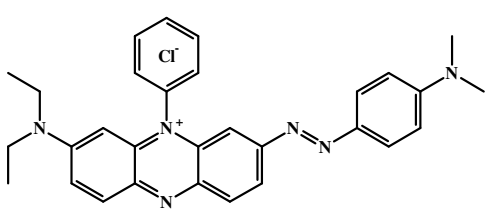
Key Words: Kinetic, Resorcinol, Janus green, Inhibitory, Bromate.

INTRODUCTION

Resorcinol is an important chemical intermediate in specialty chemicals manufacturing, such as light screening agents used to protect plastics from exposure to ultraviolet light. Resorcinol is used to manufacture dyestuffs, pharmaceuticals, flame retardants, agricultural chemicals, fungicidal creams and lotions, explosive primers, antioxidants, a chain extender for urethane elastomers and a treatment to improve mechanical and chemical resistance of paper machine fabrics. Resorcinol is one kind of phenolic compounds with high toxicity. It can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion, cyanopathy and even death[1]. Because of the important role of resorcinol in pharmacology and some industries, its determination at trace levels is of special interest. The major methods for the determination of resorcinol that have already been reported are high-performance liquid chromatography[2-6] and gas chromatography[7,8]. The separations of these methods are efficient, but require expensive instrument and therefore are expensive. Another resorcinol measurement method is ultraviolet-visible spectrophotometry[9]. This method is convenient but its sensitivity is low. Some of proposed kinetic spectrophotometric method for determination of resorcinol were expensive or their sensitivity are low[10,11]. Therefore, the need for a sensitive,

simple, rapid and sensitive kinetic spectrophotometric method for the determination of resorcinol is clearly recognized.

In this paper, a rapid, sensitive kinetic spectrophotometric method is developed and validated for the determination of phenylhydrazine. Here, we reported a kinetic method for trace determination of resorcinol, based on its inhibitory effect on the formaldehyde catalyzed oxidation reaction of Janus Green (**I**) by bromate in acidic media.



I: Structure of Janus green

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during the experimental studies. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 % v/v), rinsed with water and dried. Janus Green solution 1.95×10^{-4} M was prepared by dissolving 0.010 g of the compound (Merck) in water and solution was diluted to the mark in a 100 mL volumetric flask. Bromate stock solution 0.015 M, was prepared by dissolving 0.626 g of potassium bromate (M = 167) in water and diluting to 250 mL in a 250 mL volumetric flask.

An aqueous formaldehyde stock solution, 1000 μg mL^{-1}, was prepared by diluting 2.5 mL of 37 % w/v stock formaldehyde solution to 1 L with water. Standard stock resorcinol solution (1000 μg/mL) was prepared by dissolving 0.1 g of resorcinol in water and diluted to 100 mL in a 100 mL volumetric flask. Sulfuric acid solution was prepared by appropriate dilution of concentrated sulfuric acid (Merck). Stock solution (1000 μg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1 cm quartz cell. A model 2501 CECIL spectrophotometer with 1 cm glass cuvettes was used to measure the absorbance at a fixed wavelength at 518 nm. A thermostat water bath (Gallen Kamp Griffin, BGL 240 V) was used to keep the reaction temperature at 27 °C. A stopwatch was used for recording the reaction times

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 27 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.20-6.00 mg/mL resorcinol was transferred into a 10 mL volumetric flask and then 2 mL 1.95×10^{-4} M Janus Green,

1.4 mL 5 M H_2SO_4 and 1.4 mL 100 μg/mL formaldehyde were added to the flask. The solution was diluted to *ca*. 8 mL with water. Then, 1 mL of 0.015 M bromate was added and the solution was diluted to the mark with water. The solution was mixed and a portion of the solution was transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 554 nm for 0.5-2.0 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of resorcinol solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of bromate solution. Analytical signal was the difference between blank signal and sample signal(ΔA_b - ΔA_s).

RESULTS AND DISCUSSION

Janus Green is a dye that can be oxidized with strong oxidizing agents at slow reaction. Formaldehyde can increase the rate of this reaction at ultra-trace level[12]. It is found that trace amount of resorcinol have a inhibitory effect on this reaction. Therefore, by measuring the decrease in absorbance of Janus Green for a fixed time of 0.5-2.0 min initiation of the reaction, the resorcinol contents in the sample can be measured (Fig. 1).

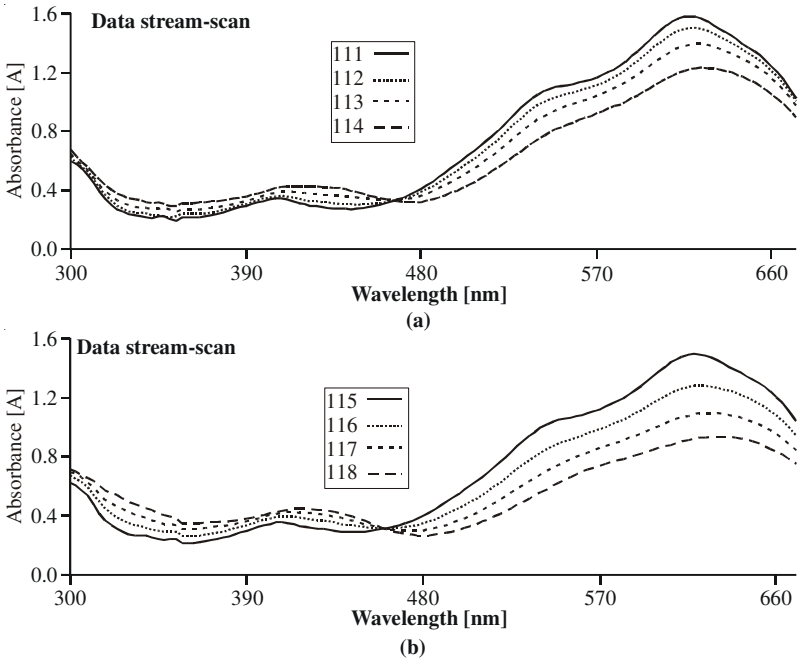


Fig. 1. Absorption spectrum for the resorcinol-Janus green -BrO_3^- system with time. Conditions: H_2SO_4, 0.7 M; Janus green, 3.9×10^{-5} M; BrO_3^- 9×10^{-4} M; formaldehyde 14 μg/mL, temperature, 27 °C; interval time for each scan, 0.5, 2.0, 3.5 and 5.0 from initiation of the reaction (a) in presence of 1 μg/mL of resorcinol (b) in absence of resorcinol

Influence of variables: In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, Janus green, formaldehyde and bromate concentration and temperature on analytical signal was studied.

The effect of sulfuric acid concentration on the analytical signal was studied in the range of 0.5 -1.2 M. (Fig. 2). The results show that the analytical signal increases with increasing sulfuric acid concentration up to 0.7 M and decreases at higher concentrations. Therefore, a sulfuric acid concentration of 0.7 M was selected for further study.

The influence of Janus green concentration on the analytical signal was studied in the concentration range of 2.7×10^{-5}- 4.7×10^{-5} M (Fig. 3). The results show that analytical signal increases with increasing Janus green concentration up to 3.9×10^{-5} M and decreases at higher concentrations. Therefore, a Janus green concentration of 3.9×10^{-5} M was selected for further study.

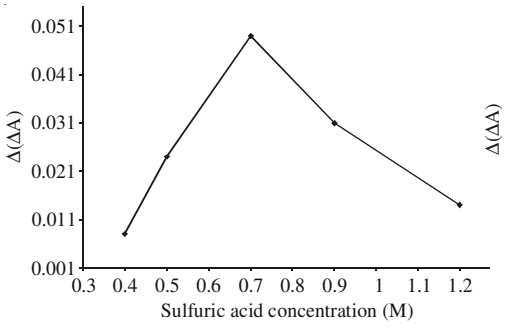


Fig. 2. Effect of H_2SO_4 concentration on the analytical signal. Conditions: Janus green, 3.9×10^{-5} M; BrO_3^- 2×10^{-2} M; formaldehyde 20 µg/mL, temperature, 27 °C and time of 1.5 min from initiation of the reaction

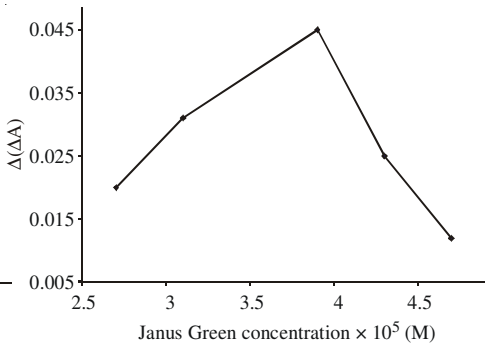


Fig. 3. Effect of Janus green concentration on the analytical signal. Conditions: H_2SO_4, 0.7 M; BrO_3^-, 2×10^{-2} M, formaldehyde 20 µg/mL, temperature 30 °C and time of 2 min from initiation of the reaction

Fig. 4 shows the effect of the bromate concentration on the analytical signal for the range of 9×10^{-3}-2.7×10^{-3} M. This analytical signal increases with increasing bromate concentration up to 1.5×10^{-3} M and decreases at higher concentrations. Therefore, a final concentration of 1.5×10^{-3} M of bromate was selected as the optimum concentration.

Fig. 5 shows the effect of the formaldehyde concentration on the analytical signal for the range of 4-24 µg mL^{-1}. Analytical signal increases with increasing formaldehyde concentration up to 14 µg mL^{-1} and decreases at higher concentrations. Therefore, a final concentration of 14 µg mL^{-1} of formaldehyde was selected as the optimum concentration.

The effect of the temperature on the analytical signal was studied in the range 20-45 °C with the optimum of the reagents concentrations. The results showed that, as the temerature increases up to 27 °C, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_b - \Delta A_s$). Therefore, 27 °C was selected for further study.

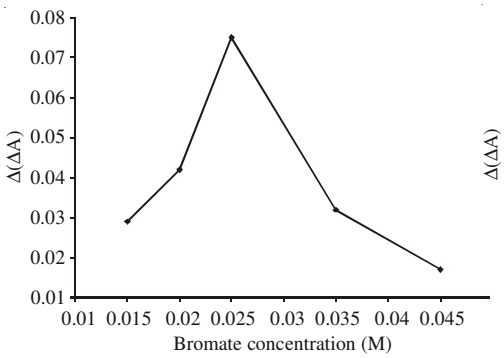


Fig. 5. Influence of BrO_3^- concentration on the analytical signal. Conditions: H_2SO_4, 0.7 M; Janus green 3.9×10^{-5} M formaldehyde 20 µg/mL; temperature 27 °C and time of 1.5 min from initiation of the reaction

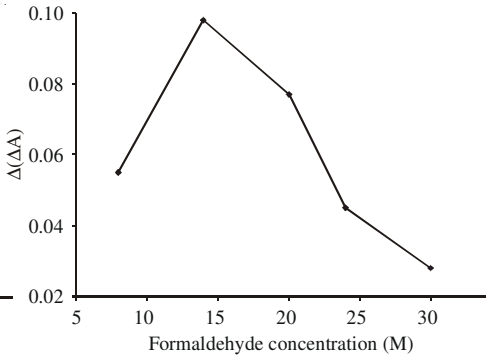


Fig. 6. Influence of formaldehyde on the analytical signal. Conditions: H_2SO_4, 0.7 M; Janus green, 3.9×10^{-5} M; BrO_3^- 9×10^{-4} M; temperature 27 °C and time of 1.5 min from initiation of the reaction

Calibration graph, precision and limit of detection: Calibration graph were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-2.0 min from intiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.020-0.60 µg/mL of resorcinol. The equation of the calibration graph is $\Delta A = 0.1994C + 0.011$ ($n = 7$, $r = 0.9998$). The calibration graph was constructed by plotted of $\Delta A = \Delta A_b - \Delta A_s$ at a fixed-time method *versus* resorcinol concentration. The experimental limit of detection was 0.012 µg/mL. The relative standard deviation for six replicate determination of 0.04 and 0.08 µg/mL resorcinol was 2.5 and 2.8 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 0.1 µg/mL resorcinol was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % (Table-1). The results show that method is relatively selective for resorcinol determination.

Sample analysis: In order to evaluate the applicability of the proposed method, water samples were analyzed to determine resorcinol contents. The results are presented in Table-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 0.1 μg/mL RESORCINOL

Species	Tolerance limit ($w_{Ion}/w_{Resorcinol}$)
Na^+, K^+, Rb^+, Mn^{2+}, Pb^{2+}, Hg^{2+}, Te^{4+}, Se^{4+}, $C_2O_4^{2-}$, HSO_4^-, CO_3^{2-}, HCO_3^-, BO_3^{3-}, Tatarate	1000
Ethanol, methanol, ethanolamine	600
SCN^-, $S_2O_3^{2-}$, SO_3^{2-}	50
I^-, Br^-	1

TABLE-2
DETERMINATION OF RESORCINOL IN SYNTHETIC SAMPLES

Sample	Resorcinol added (ng/mL)	Resorcinol found (ng/mL)	Recovery (%)	RSD (n = 5)
Well water	–	–	–	–
Well water	70	75.0	107	2.8
Well water	100	94.5	94.5	1.9

Conclusion

The kinetic-spectrophotometric method developed for the determination of resorcinol is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures.

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