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A New Inhibition Kinetic Spectrophotometric Method for the Determination of Resorcinol

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Abstract: A new, simple, inexpensive and fast kinetic spectrophotometric method was developed for the determination of trace amounts of resorcinol over the range of 0.02-0.80 µg/mL. The method is based on the inhibitory effect of resorcinol on the formaldehyde catalyzed oxidation reaction of of cresyl violet by bromate in acidic media is reported. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of cresyl violet at 596 nm with a fixed-time 0.5–2.5 min from initiation of the reaction.The detection limit is 0.017 µg/mL and relative standard deviation of 0.1 and 0.5 µg/mL resorcinol for six replicate measurements was 2.6 and 2.9 %, respectively. The method was applied to the determination of resorcinol in water samples.

Keywords: Inhibition kinetic, Resorcinol, Spectrophotometric method, Cresyl violet.

Introduction

Resorcinol is an important industrial chemical material used widely in the fields of rubber, plastics and organic synthesis industries, wood adhesives, fire retardants and UV stabilizer, *etc*. It is derived from various resins and tannins but most commonly by fusing sodium hydroxide with meta-benzene-disulfuric acid. Global output of resorcinol in 2004 was about 41.83 million tons. This compound is a moderate toxic substance and easily soluble in water[1]. There is a growing need for developing highly sensitive, simple methods to detect resorcinol in the wastewater at a low level. 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, we developed and validated a rapid, sensitive kinetic spectrophotometric method for the determination of resorcinol. Here, we report a kinetic method for trace determination of resorcinol, based on its inhibitory effect on the formaldehyde catalyzed oxidation reaction of of cresyl violet by bromate in acidic media.

Experimental

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Cresyl violet solution of 6.22×10^{-4} M was prepared by dissolving 0.020 g of the compound (MW= 321.3) in water and solution was diluted to the mark in a 100 mL volumetric flask.

Bromate stock solution of 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. 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.

Appartus

Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1.0 cm quartz cell. A model 2501 CECIL Spectrophotometer with 1.0 cm glass cuvettes was used to measure the absorbance at a fixed wavelength of 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 0.20-8.0 µg/mL resorcinol was transferred into a 10 mL volumetric flask and then 2 mL 6.22×10^{-4} M cresyl violet, 0.6 mL 5 M H_2SO_4 and 0.2 mL 1000 µg/mL formaldehyde were added to the flask. The solution was diluted to ca.8 mL with water. Then, 1.6 mL 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 596 nm for 0.5 2.5 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 deference between blank signal and sample signal(ΔA_b-ΔA_s).

Results and Discussion

Cresyl violet is a dye that can be oxidized with strong oxidizing agents at slow reaction. Formaldehyde can increasing rate of this reaction at ultra-trace level.We found that trace amount of resorcinol have a inhibitory effect on the this reaction. There are many methods, such as fixed time, initial rate, rate constant and variable time methods for measuring the kinetic species. Among these, the fixed time method is the most conventional and simplest, involving the measurement of ΔA at 596 nm (Figure 1). Therefore, by measuring the decrease in absorbance of cresyl violet for a fixed time of 0.5-2.5 min initiation of the reaction, the resorcinol contents in the sample can be measured. Cresyl violet has the following structure(Figure 2).

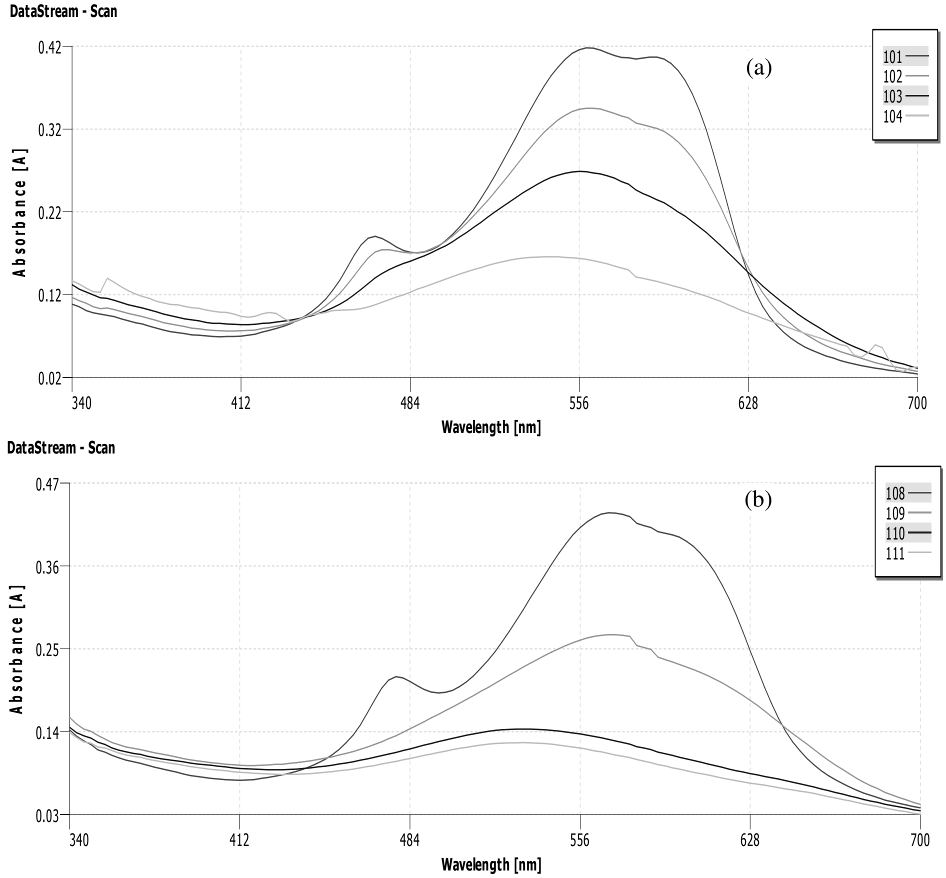

Figure 1. Absorption spectrum for the Resorcinol - Cresyl Violet -BrO_3^- system with time. (a) in presence of 0.4 µg/mL of Resorcinol (b) in absence of Resorcinol

Conditions: H_2SO_4, 0.3 M; Cresyl Violet, 1.24×10^{-4} M; BrO_3^- 2.4×10^{-3} M; formaldehyde 20 µg/mL, temperature, 27 °C; interval time for each scan, 0.5, 1.5, 2.5 ,3.5, and 4.5 from initiation of the reaction.

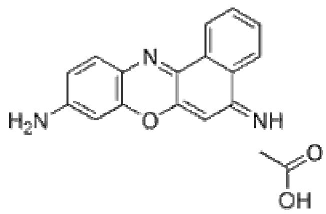

Figure 2. Structure of Cresyl Violet

Influence of variables

In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, cresyl violet, 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 0.2 -0.4 M. (Figure 3).The results show that the analytical signal increases with increasing sulfuric acid concentration up to 0.3 M and decreases at higher con-centrations. Therefore, a sulfuric acid concentration of 0.3 M was selected for further study.

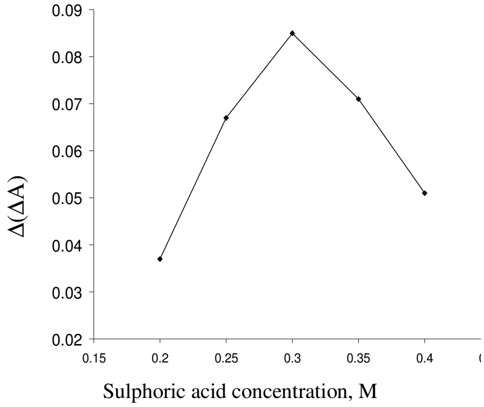

Figure 3. Effect of H_2SO_4 concentration on the analytical signal.

Conditions: Cresyl violet, 1.24×10^{-4} M; BrO_3^- 2.4×10^{-3} M; Formaldehyde 40 µg/mL, Temperature, 27 °C and Time of 2 min from initiation of the reaction.

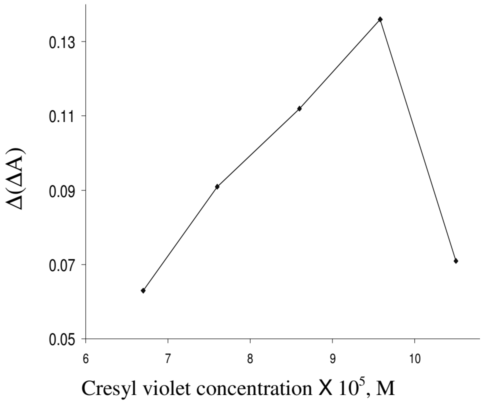

Figure 4. Effect of cresyl violet concentration on the analytical signal.

Conditions: H_2SO_4, 0.3 M; BrO_3^-, 2.4×10^{-3} M, Formaldehyde 40 µg/mL, Temperature, 27 °C and Time of 2.0 min from initiation of the reaction.

The influence of cresyl violet concentration on the analytical signal was studied in the concentration range of 8.7×10^{-5}- 1.36×10^{-4} M (Figure 4). The results show that analytical signal increases with increasing cresyl violet concentration up to 1.24×10^{-4} M and decreases at higher concentrations.Therefore, a cresyl violet concentration of 1.24×10^{-4} M was selected for further study.

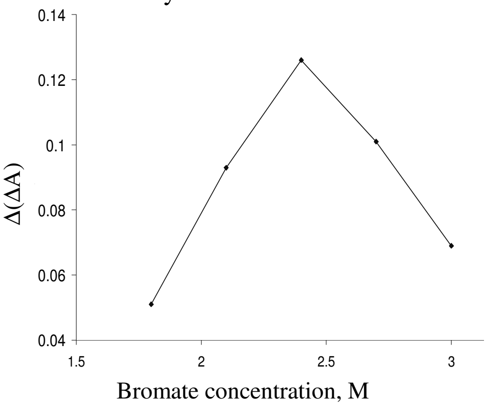

Figure 5. Influence of BrO_3^- concentration on the analytical signal.

Conditions: H_2SO_4 ,0.3 M; Cresyl Violet 1.24×10^{-4} M formaldehyde 40 µg/mL; Temperature, 27 °C and time of 2 min from initiation of the reaction

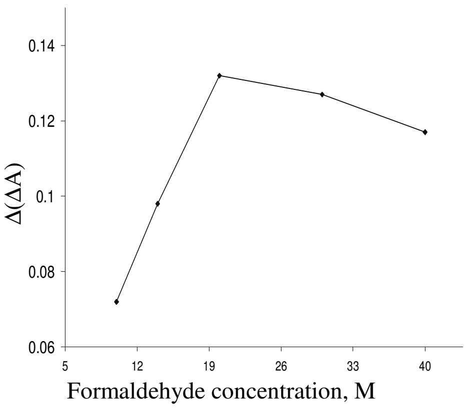

Figure 6. Influence of formaldehyde on the analytical signal.

Conditions: H_2SO_4, 0.3 M; Cresyl violet 1.24×10^{-4} M; BrO_3^- 2.4×10^{-4} M; Temperature, 27 °C and time of 2 min from initiation of the reaction.

Figure 5 shows the effect of the bromate concentration on the analytical signal for the range of 1.8×10^{-3}- 3×10^{-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 2.4×10^{-3} M M of bromate was selected as the optimum concentration.

Figure 6 shows the effect of the formaldehyde concentration on the analytical signal for the range of 10-40 μg mL^{-1}. Analytical signal increases with increasing formaldehyde concentration up to 20 μg mL^{-1} and decreases at higher concentrations. Therefore, a final concentration of 20 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 20–40 °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.

Calibreation 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 0.5-2.5 min from intiation of the reaction because it provided the best regresion and sensitivity. Under the optimum conditions described above, a linear calibration range 0.020-0.80 μg/mL of resorcinol. The equation of the calibration graph is $\Delta A=9 \times 10^{-5} C + 0.0474$ (n=7, r =0.9994). 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 3δ limit of detection was 0.017 μg/mL. The relative standard deviation for six replicate determination of 0.1 and 0.5 μ g/mL resorcinol was 2.6 and 2.9 % 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% the results are summarized in Table 1. The results show that method is relatively selective for resorcinol determination.

Table 1. Effect of foreign ions on the determination of 0.1 μg/mL resorcinol.

Species	Tolerance Limit ($w_{ion}/w_{Resorcinol}$)
Mn^{+2} , Hg^{+2}, Te(IV), Se(IV), $C_2O_4^{-2}$, HSO_4^-,CO_3^{2-},HCO_3^- , Tatarate, Borate,	1000
Co(II), Pb(II)	800
Ethanol, methanol, ethanolamine, SO_3^{2-}	500
SCN^-	50
Br^-	30
I^- ,Cl^-	5

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	100	94	94	2.6
Well water	500	528	105.6	2.8

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.

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, low limit of detection and good precision and accuracy compared to other kinetic procedures.

Aeknowledgments

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