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Kinetic Spectrophotometric Determination of Phenylhydrazine Based on Its Inhibitory Effect on the Oxidation of Crystal Violet by Bromate in Micellar Medium

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A new, simple and selective kinetic spectrophotometric method is described for the determination of trace amounts of phenylhydrazine, which is based on its inhibitory effect on the reaction between crystal violet and bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the change in absorbance of crystal violet at 630 nm. The calibration graph was linear in the range of 0.20-1.2 μg/mL. The detection limit (3δ) was 0.12 μg/mL. The relative standard deviations for 6 replicate measurements of 0.5 and 0.8 μg/mL of phenylhydrazine were 1.9 and 2.5 %, respectively. The potential interfering substances were studied in the presence of phenylhydrazine. The proposed method was applied to the analysis of water samples.

Key Words: Phenylhydrazine, Inhibitory, Crystal violet, Micellar, Bromate.

INTRODUCTION

Phenylhydrazine, hydrazine and its derivatives are important industrial chemicals with many applications. They are used in the pharmaceutical, polymer and dye industries and in agriculture[1]. In addition to being reactive and explosive, phenylhydrazine is volatile and highly toxic, being readily absorbed by oral, dermal or inhalation routes of exposure. Adverse health effects on people living near hazardous waste sites caused by hydrazine and its derivatives have been described[2]. Contact with phenylhydrazine irritates the skin, eyes and respiratory tract. It may also cause skin sensitization as well as systemic poisoning[3]. Therefore, the need for a sensitive, simple and reliable method for the determination of phenylhydrazine is clearly recognized. Different classical and instrumental methods have been reported for determination of phenylhydrazine in various samples. These include spectrophotometry[4-8], titrimetry[9] and gas chromatography[10]. These methods either lack sufficient sensitivity or are time consuming. Due to their high sensitivity, kinetic spectrophotometric methods are of interest for trace determination of some species. A few kinetic procedures have been reported for determination of phenylhydrazine. Some of these procedures include determination of trace quantities of phenylhydrazine

on the basis of its inhibition effect on the decolorization of methyl orange and Victoria Blue 4-R by bromate[11,12], the simultaneous determination of hydrazine and phenylhydrazine based on their reactions with *p*-(dimethylamino) benzaldehyde (DAB)[13] and the simultaneous determination of hydrazine and phenylhydrazine using the H-point standard addition method HPSAM[14].

Here, we report a kinetic method for trace determination of phenylhydrazine, based on its inhibitory effect on the oxidation of crystal violet by $KBrO_3$ in acidic and micellar media.

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Crystal violet ($C_{25}H_{30}N_3Cl$) solution 4.9×10^{-4} M was prepared by dissolving 0.01 g of the compound (Merck) in water and solution was diluted to the mark in a 50 mL volumetric flask. Bromate stock solution 0.01 M, was prepared by dissolving 0.167 g of potassium iodate (M = 214) in water and diluting to 100 mL in a 100 mL volumetric flask. Standard stock phenylhydrazine solution (10000 µg/mL) was prepared by dissolving 4.5 mL of phenylhydrazine in water and diluted to 500 mL in a 500 mL volumetric flask. Hydrochloric acid solution was prepared by appropriate dilution of concentrated hydrochloric acid (Merck). Cetyl trimethyl ammonium bromide (CTAB) stock solution 0.0130 M, was prepared by dissolving 1.197 g CTAB (BDH) in water and diluted to the mark with water in a 250 mL volumetric flask. The other surfactants tested, namely, cetylpyridinium chloride (CPC), sodium dodecyl sulfate (SDS) and Triton-X-100 were prepared in a similar way.

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.

Absorption spectra were recorded with 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 630 nm. A thermostate water batch was used to keep the reaction temperature at 25 °C.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 25 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 2-12 µg/mL phenylhydrazine was transferred into a 10 mL volumetric flask and then 0.40 mL 2 M HCl, 2 mL 0.013 M CTAB and 0.4 mL 4.9×10^{-4} M crystal violet were added to the flask. The solution was diluted to *ca.* 8 mL with water. Then, 0.6 mL 0.010 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 630 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 phenylhydrazine solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of bromate. Analytical signal was deference between blank signal and sample signal (ΔA_b-ΔA_s).

RESULTS AND DISCUSSION

In many reactions, suitable micelles can affect the rate of reactions[15-24]. The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface.

Crystal violet undergoes a oxidation reaction with bromate in acidic and micellar medium to from a colorless product at very fast rate. It is found that the trace amount of phenylhydrazine have a inhibitory effect on this reaction. This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of crystal violet (630 nm) (Fig. 1). Therefore, by measuring the decrease in absorbance of crystal violet for a fixed time of 0.5-2.0 min initiation of the reaction, the phenylhydrazine contents in the sample can be measured.

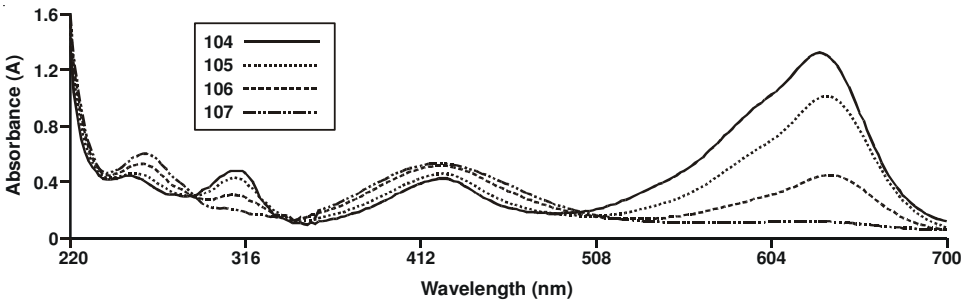

Fig. 1. Variation of the crystal violet-BrO_3^--phenylhydrazine with time. HCl 0.08 M, crystal violet 1.96×10^{-5} M; BrO_3^- 6×10^{-4} M; CTAB 2.6×10^{-3}, phenylhydrazine 1.0 µg/mL; temperature 25 ºC

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

Non-ionic micelles (such as Trition-X-100), anionic micelle (sodium dodecyl sulfate, SDS) and cationic micelle (CTAB) and cetyl pyridinium chloride (CPC) were tested at concentration above their critical micelle concentration (CMC). The results are shown in Table-1. Therefore, between this micelles, CTAB and CPC have a positive effect but CTAB has a more positive effect than CPC, hence CTAB was selected for practical purposes. The results are shown in Table-1. Between this micelles, CTAB and CPC have a positive effect on the analytical signal but CTAB has a more positive effect than CPC, so CTAB was selected for practical purposes.

TABLE-1
SURFACTANT TESTED FOR THE ENHANCED ANALYTICAL SIGNAL OF CRYSTAL VIOLET-BrO_3^--PHENYLHYDRAZINE SYSTEM

Surfactant	Type	CMC (M)	Micellar effect
Trition-X-100	Non-ionic	3.0×10^{-4}	Neutral
SDS	Anionic	8.1×10^{-3}	Neutral
CTAB	Cationic	1.3×10^{-3}	Positive
CPC	Cationic	1.2×10^{-4}	Positive

The effect of hydrochloric acid concentration on the analytical signal was studied in the range of 0.04-0.16 M. (Fig. 2). The results show that the analytical signal increases with increasing hydrochloric acid concentration up to 0.08 M and decreases at higher concentrations. Therefore, a hydrochloric acid concentration of 0.08 M was selected for further study.

The influence of crystal violet concentration on the analytical signal was studied in the concentration range of 9.8×10^{-6}-3.92×10^{-5} M (Fig. 3). The results show that the analytical signal increases with increasing crystal violet concentration up to 1.96×10^{-5} M and decreases at higher concentrations. Therefore, a crystal violet concentration of 1.96×10^{-5} M was selected for further study.

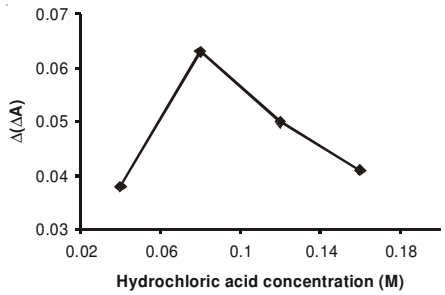

Fig. 2. Influence of HCl concentration on the analytical signal, conditions: Crystal violet 1.96×10^{-5} M; BrO_3^- 4×10^{-4} M; CTAB 1.82×10^{-3} M; phenylhydrazine, 0.8 µg/mL; temperature 25 ºC

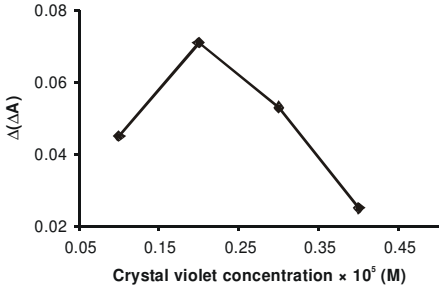

Fig. 3. Effect of crystal violet concentration on the analytical signal. Conditions: HCl 0.08 M; BrO_3^- 4×10^{-4} M; CTAB 1.82×10^{-3} M; phenylhydrazine 0.8 µg/mL; temperature 25 °C

Fig. 4 shows the effect of the bromate concentration on the analytical signal for the range of 2×10^{-4}-10×10^{-4} M. This analytical signal increases with increasing bromate concentration up to 6.0×10^{-4} M and decreases at higher concentrations. Therefore, a final concentration of 6.0×10^{-4} M of bromate was selected as the optimum concentration.

Fig. 5 shows the effect of the CTAB concentration on the analytical signal for the range of 0-2.91×10^{-3} M. Analytical signal increases with increasing CTAB concentration up to 2.6×10^{-3} M and decreases at higher concentrations. Therefore, a final concentration of 2.6×10^{-3} M of CTAB was selected as the optimum concentration.

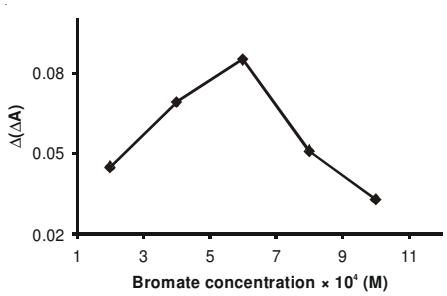

Fig. 4. Effect of bromate concentration on the analytical signal, conditions: HCl 0.08 M; crystal violet 1.96×10^{-5}; CTAB 1.82×10^{-3} M; phenylhydrazine 0.8 µg/mL; temperature 25 ºC

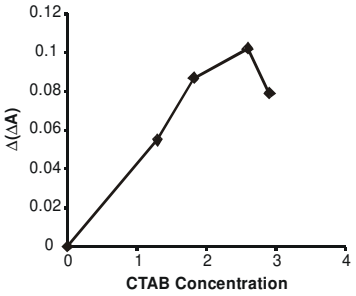

Fig. 5. Effect of CTAB concentration on the analytical signal. Conditions: HCl 0.08 M; crystal violet 1.96×10^{-5} M; BrO_3^- 6 $\times 10^{-4}$ M; phenylhydrazine 0.8 µg/mL; temperature 25 °C

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 temperature increases up to 25 °C, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_b - \Delta A_s$). Therefore, 25 °C was selected for further study.

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 0.20-1.2 µg/mL was obtained of phenylhydrazine.

The equation of the calibration graph is $\Delta A = 0.112C + 0.0166$ ($n = 7$, $r = 0.9995$). The calibration graph was constructed by plotted $\Delta A = \Delta A_b - \Delta A_s$ at a fixed-time method *versus* phenylhydrazine concentration.

The experimental 3δ limit of detection was 0.12. In order to examine the accuracy and precision of the method, standard solutions of 0.5 and 0.8 µg/mL of penylhydrazine were analyzed using the recommended procedure. Six replicate determinations of each concentration gave relative standard deviations (RSD) of 1.9 and 2.5 %, respectively.

Selectivity: Interference study in order to assess the possible analytical application of the proposed method, the effects of various substances present in the real samples on the determination of phenylhydrazine were investigated. A synthetic mixture of a solution containing 0.4 µg/mL of phenylhydrazine and varrious excess amounts of diverse ions were analyzed. The tolerance limit was defined as the concentration of the added ions causing a relative error less than ± 5 %. The results are summarized in Table-2. Many substances did not interfere in 500 fold excess than phenylhydrazine. The results show that method is relatively selective for phenylhydrazine determination.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF
0.4 μg/mL PHENYLHYDRAZINE

Species	Tolerance limit (w_{ion}/w phenylhydrazine)
Na^+, K^+, Ca^{2+}, Mg^{2+}, Rb^+, Ba^{2+}, Sr^{2+}, Cu^{2+}, $C_2O_4^{2-}$ HSO_4^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, CH_3COO^-, Tatarate	1000
ClO_3^-	500
Hg^{2+}	100
NO_3^- Te^{4+}, Se^{4+}, Pb^{2+}, SCN^-	10
Co^{2+}, Ni^{2+}, Mn^{2+}	5
I^-, N_2H_4	Inhibited

Sample analysis: Because of the lack of suitable real samples, analyses of water spiked samples were used to assess the accuracy of the proposed procedure. Replicate determinations were made on well water samples spiked with various amounts of phenylhydrazine using the standard addition method. The results are listed in Table-3. These results show the validity of the proposed method in the determination of phenylhydrazine in water samples.

TABLE-3
DETERMINATION OF PHENYLHYDRAZINE IN WELL WATER

Sample	Phenylhydrazine		Recovery (%)	RSD (n = 5)
	Added (μg/mL)	Found (μg/mL)		
Well water	–	–	–	–
Well water	0.4	0.37	92.5	1.9
Well water	0.8	0.83	102.5	2.6

Conclusion

The results presented clearly demonstrate the inhibition effect of phenylhydrazine on the oxidation of crystal violet by bromate in acidic and micellar medium. The results were applied to develop a simple methodology for the determination of phenylhydrazine at trace level. The validation of method was made by comparing the results obtained using the proposed method and the known spiked amounts in well water samples. Therefore, the method could be proposed for environmental and toxicological analyses.

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