



The Development of a New Inhibition Kinetic Spectrophotometric Method for the Determination of Phenylhydrazine Based on its Inhibitory Effect on Oxidation of Methyl Red by Bromate in Micellar Medium

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Received 15 January 2010; Accepted 10 March 2010

Abstract: A new, simple, sensitive and selective kinetic spectrophotometric method was developed for the determination of trace amounts of phenylhydrazine over the range of 0.02-0.30 $\mu\text{g/mL}$. The method is based on the inhibitory effect of phenylhydrazine on the oxidation of methyl red by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of methyl red at 518 nm with a fixed-time 0.5–2.0 min from initiation of the reaction. The relative standard deviation of 0.08 and 0.2 $\mu\text{g/mL}$ phenylhydrazine was 1.7 and 2.4%, respectively. The method was applied to the determination of phenylhydrazine in water samples.

Keywords: Phenylhydrazine, Inhibition, Methyl Red, Micellar, Bromate.

Introduction

Phenylhydrazine, hydrazine and its derivatives are important industrial chemicals with many applications. They are used, for example, in the pharmaceutical, polymer and dye industries and in agriculture¹. 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 hydrazin and its derivatives have been described². Contact with phenylhydrazine irritates the skin, eyes, and respiratory tract. Also, it may cause skin sensitization as well as systemic poisoning³. Therefore, the need for a sensitive, simple and reliable method for the determination of phenylhydrazine is clearly recognized. Several methods have been reported for the determination

of phenylhydrazine. These, include titrimetry⁴, spectrophotometry⁵⁻⁷, gas chromatography⁸ and kinetic methods⁹⁻¹³. These methods either lack of sensitivity or time consuming. In order to overcome these problems, we developed and validated a rapid, sensitive and selective kinetic spectrophotometric method for the determination of phenylhydrazine.

In this paper, we developed and validated a rapid, sensitive kinetic spectrophotometric method for the determination of phenylhydrazine. Here, we report a kinetic method for trace determination of phenylhydrazine, based on its inhibitory effect on the oxidation of methyl red 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.

Methyl red solution 3.71×10^{-4} M was prepared by dissolving 0.010 g of the compound (Merck) in ethanol and solution was diluted to the mark in a 100 mL volumetric flask.

Bromate stock solution 0.010 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 $\mu\text{g/mL}$) 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 $\mu\text{g/mL}$) 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.

Apparatus

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 bath at 27 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.20-3.0 $\mu\text{g/mL}$ phenylhydrazine was transferred into a 10 mL volumetric flask, and then 0.3 mL 2.0 M HCl 2.6 mL 0.013 M CTAB and 1.4 mL 3.71×10^{-4} M methyl red were added to the flask. The solution was diluted to ca. 8 mL with water. Then, 0.3 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 518 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 phenylhydrazine. Analytical signal was the difference between blank signal and sample signal ($\Delta A_b - \Delta A_s$).

Results and Discussion

methyl red undergoes a oxidation reaction with bromate in acidic and micellar medium to form a colorless product at very fast rate. We found that trace amount of phenylhydrazine have a inhibitory effect on the this reaction. Therefore, by measuring the decrease in absorbance of methyl red for a fixed time of 0.5-2.0 min initiation of the reaction, the phenylhydrazine contents in the sample can be measured. Figure 1 shows the relationship between A and reaction time and also Figure 2 shows the structure of methyl red.

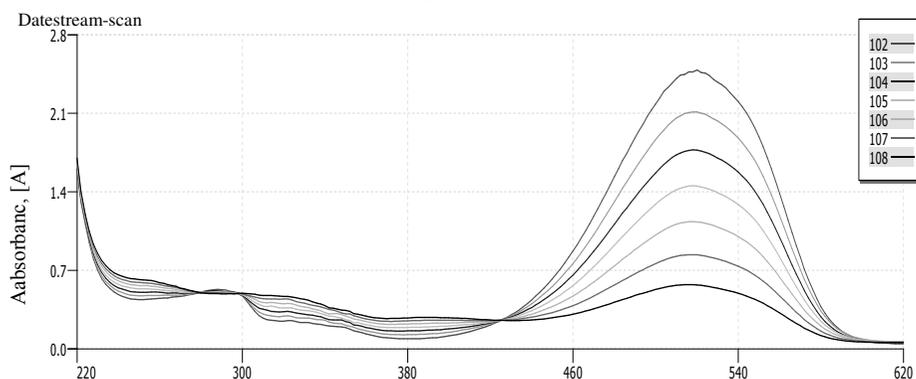


Figure 1. Absorption spectrum for the phenylhydrazine-methyl red- BrO_3 system with time. Conditions: HCl 0.06 M, methyl red 5.1×10^{-5} M; BrO_3^- 2×10^{-4} M; phenylhydrazine, 0.1 $\mu\text{g/mL}$; temperature 27 $^\circ\text{C}$; interval time for each scan, 0.5, 1.5, 2.5, 3.5, 4.5, 5.5 and 6.5 min from initiation of the reaction.

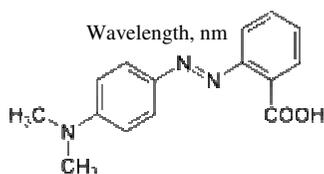


Figure 2. Structure of methyl red.

Influence of variables

In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of acid concentration, methyl red and bromate concentration, type of surfactants and temperature on analytical signal was studied. In many reactions, Suitable micelles can affect the rate of reactions¹⁴⁻²¹. A micelle usually can be formed by aggregation of a charged organic molecules. These micelles have the same charge at the outer sphere. For those reactions which have charged species, these micelles can affect the rate of reaction by increasing the effective collisions. The accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface²². Cationic (CPC, CTAB), anionic (SDS) and nonionic (Triton x-100) micelles were tested at a concentration greater than that critical micelle concentration (c.m.c). The results are shown in Table 1

Table 1. Surfactant tested for enhancement of analytical signal of methyl red - BrO_3^- - phenylhydrazine system

Surfactant	Type	CMC, M	Micellar Effect
SDS	Anionic	8.1×10^{-3}	Neutral
CTAB	Cationic	1.3×10^{-3}	Positive
CPC	Cationic	1.2×10^{-4}	Positive
Triton-x	Nonionic	3.0×10^{-4}	Negative

Between these micelles, CTAB and CPC have a positive effect but CTAB has a more positive effect than CPC, therefore CTAB was selected for practical purpose. The results show that in the presence of CTAB, phenylhydrazine have an inhibitory effect on the oxidation of methyl red by bromate. Thus CTAB was chosen for the study. The effect of hydrochloric acid concentration on the analytical signal was studied in the range of 0.04-0.12 M. (Figure 3).

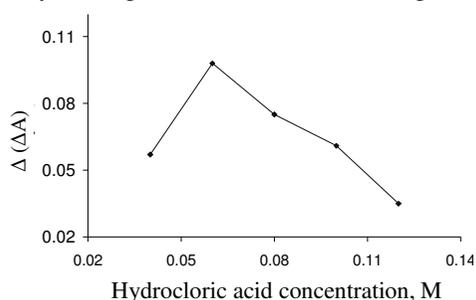


Figure 3. Influence of HCl concentration on the analytical signal, conditions: Methyl red 3.7×10^{-5} M; BrO_3^- 2×10^{-4} M; CTAB 2.6×10^{-3} M; phenylhydrazine, 0.1 $\mu\text{g}/\text{mL}$; temperature 27 °C

The results show that the analytical signal increases with increasing hydrochloric acid concentration up to 0.06 M and decreases at higher concentrations. Therefore, a hydrochloric acid concentration of 0.06 M was selected for further study. The influence of methyl red concentration on the analytical signal was studied in the concentration range of 2.2×10^{-5} - 7.4×10^{-5} M (Figure 4).

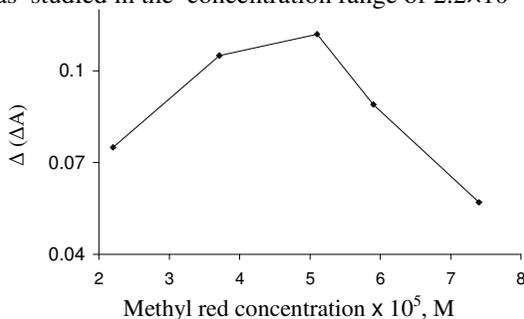


Figure 4. Effect of methyl red concentration on the analytical signal. Conditions: HCl 0.06 M, BrO_3^- 2×10^{-4} M; CTAB 2.6×10^{-3} M; phenylhydrazine, 0.1 $\mu\text{g}/\text{mL}$; temperature 27 °C

The results show that analytical signal increases with increasing methyl red concentration up to 5.1×10^{-5} M and decreases at higher concentrations. Therefore, a methyl red concentration of 5.1×10^{-5} M was selected for further study. Figure 5 shows the effect of the bromate concentration on the analytical signal for the range of 1×10^{-4} - 6.0×10^{-4} M. This analytical signal increases with increasing bromate concentration up to 2.0×10^{-4} M and decreases at higher concentrations. Therefore, a final concentration of 2.0×10^{-4} M of bromate was selected as the optimum concentration.

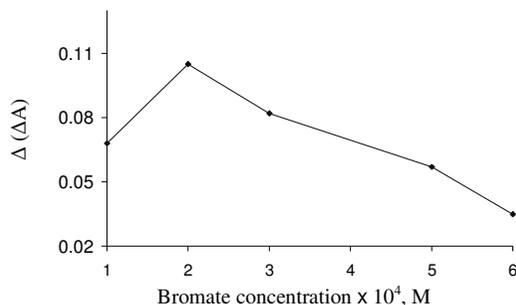


Figure 5. Effect of Bromate concentration on the analytical signal, conditions: HCl 0.06 M, methyl red 5.1×10^{-5} M; CTAB 2.6×10^{-3} M ; phenylhydrazine, 0.1 $\mu\text{g/mL}$; temperature 27 $^{\circ}\text{C}$

Figure 6 shows the effect of the CTAB concentration on the analytical signal for the range of 0- 3.9×10^{-3} M. Analytical signal increases with increasing CTAB concentration up to 3.4×10^{-3} M and decreases at higher concentrations. Therefore, a final concentration of 3.4×10^{-3} M of CTAB was selected as the optimum concentration.

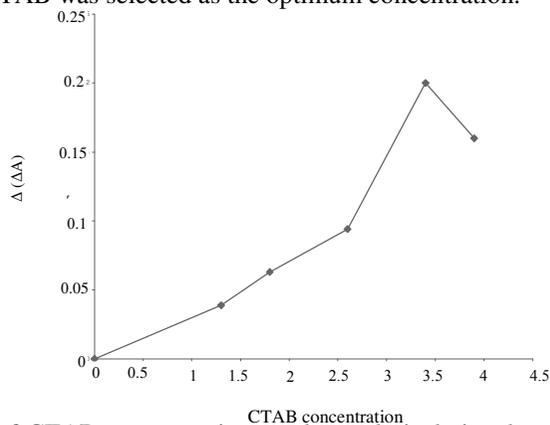


Figure 6. Effect of CTAB concentration on the analytical signal, conditions: HCl 0.06 M, methyl red 5.1×10^{-5} M; BrO_3^- 2×10^{-4} M ; phenylhydrazine, 0.1 $\mu\text{g/mL}$; temperature 27 $^{\circ}\text{C}$

The effect of the temperature on the analytical signal was studied in the range 20-45 $^{\circ}\text{C}$ with the optimum of the reagents concentrations. The results showed that, as the temperature increases up to 27 $^{\circ}\text{C}$, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_b - \Delta A_s$). Therefore, 27 $^{\circ}\text{C}$ 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 initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.020-0.30 $\mu\text{g/mL}$ of phenylhydrazine. The equation of the calibration graph is $\Delta A = 0.4587C + 0.1228$ ($n=7$, $r=0.9997$). The calibration graph was plotted by $\Delta A = \Delta A_b - \Delta A_s$ at a fixed-time method *versus* phenylhydrazine concentration. The experimental 3δ limit of detection was 0.009 $\mu\text{g/mL}$. The relative standard deviation for six replicate determination of 0.08 and 0.2 ng/mL iodide was 1.7 and 2.4 % 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 phenylhydrazine 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 2. The results show that method is relatively selective for Phenylhydrazine determination.

Table 2. Effect of foreign ions on the determination of 0.10 µg/mL phenylhydrazine

Foreign species	Tolerated ratio $W_{\text{species}}/W_{\text{Phenylhydrazine}}$
$\text{C}_2\text{O}_4^{2-}$, HSO_4^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , Tatarate, CH_3COO^- , BO_3^{3-} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Rb^+ , Zn(II) , Ba^+ , Cr(III) , Pb(II) , Pd(II)	1000
Cu(II) , IO_3^- , ClO_3^-	800
SCN^- , $\text{S}_2\text{O}_8^{2-}$, $\text{S}_2\text{O}_8^{2-}$	200
Hg^{+2} , Ni(II) , Co(II)	100
N_2H_4	Inhibited

Sample analysis

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

Table 3. Determination of phenylhydrazine in real samples

Sample	Phenylhydrazine added, µg/mL	Phenylhydrazine found, µg/mL	Recovery %	RSD % n=3
Well water	0.080	0.086	107.5	1.8
Well water	0.140	0.128	91.4	2.1
Well water	0.240	0.253	105.4	2.5

Conclusion

The kinetic method developed for the determination of phenylhydrazine 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. The detection limit of the proposed method in comparison with reported methods was better (Table 4).

Table 4. Comparison of kinetic spectrophotometry methods for the determination of phenylhydrazine with proposed method

Method	DL, µg/mL	LDR, µg/mL	reference no.
Kinetic spectrophotometry	-	3-10	11
Kinetic spectrophotometry	0.05	0.2 -10	12
Kinetic spectrophotometry	0.02	0.05 - 8	13
Kinetic spectrophotometry	0.02	0.05 - 8	13
Proposed method	0.009	0.02 -0.3	-

Acknowledgments

The author are Thankful to the Islamic Azad University-Majlesi Branch for the support of this work.

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