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Spectrophotometric Determination of Trace Amounts of Hydrazine by the Inhibition of the Alizarin Navy Blue Reaction

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In this proposed method a simple kinetic method is described for the determination of trace amounts of hydrazine, which is based on its inhibition effect on the reaction between alizarin navy blue and sodium nitrite. The reaction was monitored spectrophotometrically by measuring the change in absorbance of alizarin navy blue at 530 nm. The calibration graph was linear in the range of 0.10-1.40 μg/mL hydrazine, with a limit of detection of 0.09 μg/mL. The relative standard deviation for ten replicate measurements of 0.60 and 1.00 μg/mL hydrazine were 2.2 and 1.5%, respectively. The proposed method was applied to the determination of hydrazine in water samples.

Key Words: Spectrophotometric determination, Alizarin navy blue reaction, Hydrazine, Kinetic method.

INTRODUCTION

Hydrazine and its derivatives have found application in industry, agriculture and other fields including the manufacture of metal film, photographic chemicals, explosives, insecticides and blowing agents for plastic. On the other hand, hydrazine is a toxic materials which must be treated with great care. Thus, there has been an increasing demand for a highly sensitive method of determination of hydrazine in samples such as water, industrial and environment materials. Different methods have been used for determination of hydrazine, including spectrophotometric[1,2], electrochemical[3], spectrofluorimetric[4], chemiluminescence[5] and chromatographic[6] methods. Only a few kinetic methods for hydrazines are described in the literature. A kinetic potentiometric method has been described[7] for the determination of hydrazine, based on monitoring its reaction at 25ºC and pH 9.0 with 1-fluoro-2, 4-dinitrobenzene by means fluoride-selective electrode and hydrazine was determined over the rang of 0.5 to 0.0008 M, while the other procedure[8] has been described the determination of 0.0002 to 0.002

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M hydrazine using an iodide-selective electrode. Trace amount of hydrazine (0.02-30 μg/mL^{-1}) determined using modular stopped flow/diode array detection system[9]. Some of these methods require special equipment, others demand carefully controlled conditions and in some complete report on selectivity are not available.

In the present investigation, a kinetic method is described for the determination of trace amount of hydrazine, which is based on its inhibition effect on the reaction between Alizarin navy blue and sodium nitrite. The method is simple, rapid and sensitive.

EXPERIMENTAL

Analytical reagent grade chemical and doubly distilled water were used throughout. A stock solution of hydrazine (1000 μg/mL) was prepared by dissolving 0.100 g hydrazine dihydrocholoride (Merck) in 100 mL water in a volumetric flask. A solution of 2.97×10^{-4} M alizarin navy blue was prepared by dissolving 0.0100 g alizarin navy blue (Merck) in 10 mL ethanol and diluting with NaOH 1.0×10^{-5} M in a 100 mL volumetric flask.

Sodium bromate (0.010 M) solution was prepared by dissolving 0.150 g $NaBrO_3$ (Merck) in water and diluting to 100 mL in a 100 mL volumetric flask. Solution of 1000 μg/mL nitrite was prepared by dissolving 0.1510 g $NaNO_2$ in water in a 100 mL volumetric flask.

Absorption spectra were recorded on a Shimadzu Model 160-A UV-Visible spectrophotometer with 1 cm glass cells. A thermostate bath (Galen Kemp) was used to keep the reaction temperature 30 ± 0.1ºC. A stopwatch was used for recording the reaction time.

The reaction was followed spectrophotometrically by monitoring the change in absorbance of the reaction mixture at 530 nm by a fixed time method for the first 0.5-4.0 min from initiation of the reaction. In a series of 10 mL volumetric flasks an appropriate volume of 1 mL 3.6 M H_2SO_4, 2 mL 20 μg/mL $NaNO_2$, 0.5 mL 0.010 M $NaBrO_3$ and 1.0 mL of hydrazine (up to 0.40 μg/mL) were added. The solution was diluted to *ca*. 8 mL with water. Then 2.0 mL of 2.97×10^{-4} M alizarin navy blue was added and the solution was diluted to the mark with water and mixed well. The mixture was transferred into a 1.0 cm glass cell within 30 sec from initiation of the reaction. The changes in absorbance were measured during the first 0.5-4.0 min from initiation of the reaction (ΔA_s). Time was measured from just after the addition of the last drop of alizarin navy blue. The same measurement in the absence of hydrazine was repeated to obtain the values for the uncatalyuzed reaction (ΔA_b). The net reaction rate was calculated from the difference in the absorbance changes at a fixed time (ΔA_b-ΔA_s). All the solutions were preheated to a working temperature of 30 ± 0.1ºC in a thermostate bath for about 0.5 h before initiation of the reaction.

RESULTS AND DISCUSSION

Alizarin navy blue can be oxidized by strong oxidizing agents such as bromate in the presence of nitrite in acidic media at a fast rate at room temperature, whereas addition of trace amounts of hydrazine acts as an inhibitor. Hydrazine reacts with nitrite and decreases the rate of reaction of oxidation of 5.94×10^{-5} M alizarin navy blue, 4.0 μg/mL nitrite, 0.0005 M sodium bromate, 0.40 μg/mL hydrazine by bromate in the presence of nitrite. Therefore, by increasing in the absorbance of the reaction mixture (at a fix time) is linear with hydrazine concentration. To obtain a best sensitivity, first influence of variables affect the sensitivity must be optimized.

Effect of variables: The influence of acidity, reagent concentration, time of the reaction and temperature on the reaction was studied with 0.40 μg/mL hydrazine within 4.0 min from initiation of the reaction. It gives a good comparison between sensitivity and short analysis time.

Effect of reagents' concentration: The effect of acid concentration on sample and blank reaction in the range of 0.04-0.40 M H_2SO_4 was studied with 5.94×10^{-5} M alizarin navy blue, 2.0 μg/mL nitrite, 0.0005 M sodium bromate, 0.40 μg/mL hydrazine (Fig.1). The results show that the sensitivity increase up to 0.36 M H_2SO_4 and then the sensitivity decreased. Therefore 0.36 M H_2SO_4 was selected for the study.

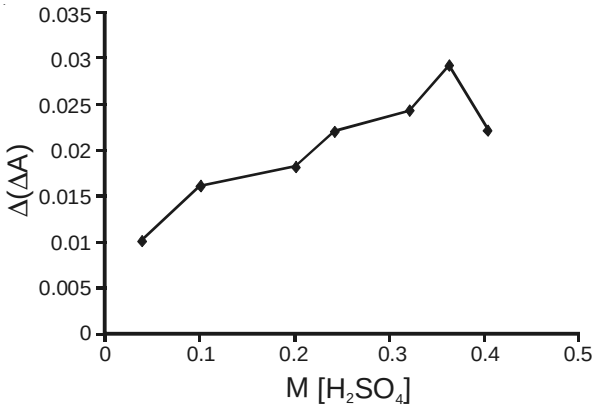

Fig. 1. The influence of acid concentration (H_2SO_4) on the rates of reaction conditions: 5.94×10^{-5} M alizarin navy blue, 2.0 μg/mL nitrite, 0.0005 M sodium bromate, 0.40 μg/mL hydrazine

The influence of nitrite concentration on the sensitivity was studied with 0.36 M sulfuric acid, 0.0005 M sodium bromate, 5.94×10^{-5} M alizarin navy blue and 0.40 μg/mL hydrazine. Fig. 2 shows that the sensitivity increases with increasing nitrite concentration up to 4.0 μg/mL, whereas higher concentration of nitrite causes decreasing the sensitivity. Therefore, 4.0 μg/mL nitrite was selected as the optimum concentration of nitrite.

The effect of bromate concentration on the sensitivity was studied with 0.36 M sulfuric acid, 4.0 μg/mL nitrite, 5.94×10^{-5} M alizarin navy blue and 0.40 μg/mL hydrazine at 30ºC (Fig. 3). The results show that by increasing bromate concentration up to 6.0×10^{-4} M, the sensitivity increases. Higher concentration of reagent causes a decrease in sensitivity. This effect is due to the fact that at higher concentration of bromate ions, the inhibitory effect of hydrazine decreases.

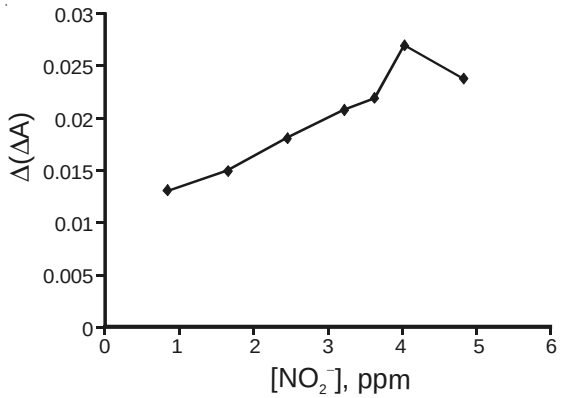

Fig. 2. Effect of nitrite concentration conditions: 5.94×10^{-5} M alizarin navy blue, 0.36 M H_2SO_4, 0.0005 M sodium bromate, 0.40 μg/mL hydrazine

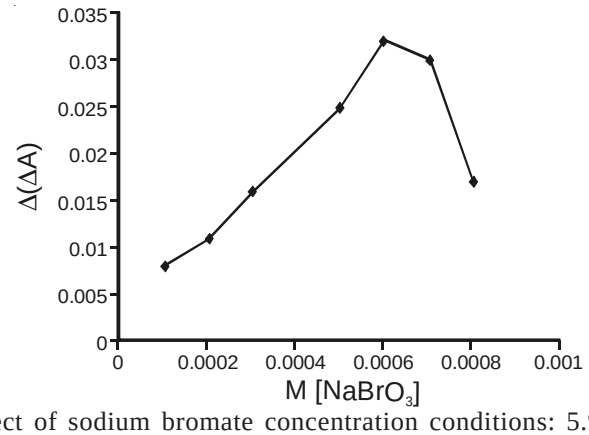

Fig. 3. Effect of sodium bromate concentration conditions: 5.94×10^{-5} M alizarin navy blue, 0.36 M H_2SO_4, 4.0 μg/mL nitrite, 0.40 μg/mL hydrazine

The effect of alizarin navy blue concentration on the rate of reaction in the range of 2.97×10^{-5} to 6.53×10^{-5} M was studied with 0.36 M sulfuric acid, 4.0 μg/mL nitrite, 6.0×10^{-5} M bromate and 0.40 μg/mL hydrazine at 30ºC. Fig.4 shows that the sensitivity increases by increasing alizarin navy blue concentration up to 5.94×10^{-5} M. Therefore, 5.94×10^{-5} M alizarin navy blue concentration was selected.

The influence of temperature on the sensitivity was studied in the temperature range of 5-55ºC in the presence of optimum reagents concen-

tration. The results (Fig. 5) showed that increasing temperature up to 30ºC, the sensitivity increases, whereas higher causes decreasing the sensitivity.

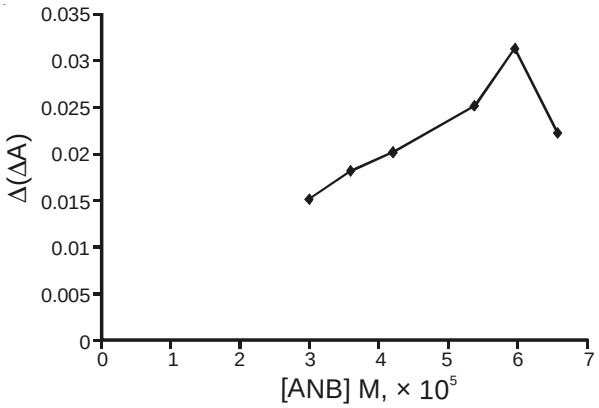

Fig. 4 Effect of alizarin navy blue concentration conditions: 0.36 M H_2SO_4, 4.0 μg/mL nitrite, 0.0006 M sodium bromate, 0.40 μg/mL hydrazine

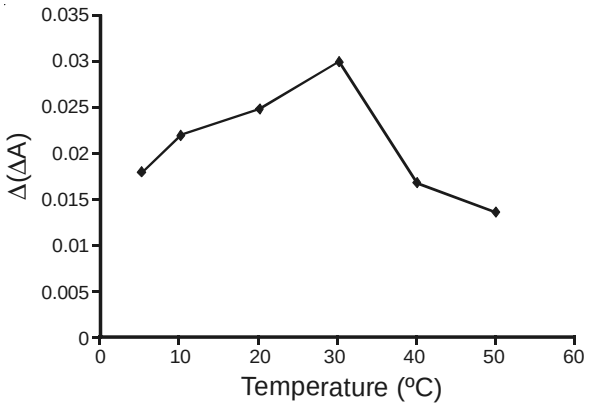

Fig. 5. Effect of temperature on reaction conditions: 5.94×10^{-5} M alizarin navy blue, 0.36 M H_2SO_4, 4.0 μg/mL nitrite, 0.0006 M sodium bromate, 0.40 μg/mL hydrazine

Calibration graph: The calibration graph was obtained under the optimum working conditions and 530 nm with fixed-time method as described above. Measurements were made from 0.5 to 4.0 min from initiation of the reaction because it provided the best regression and sensitivity and reaction time. Under the optimum condition described above, hydrazine can be determined in the concentration range of 0.10-4.0 μg/mL, with a limit of detection of 0.09 μg/mL. The relative standard deviations for ten replicate measurements of 0.60 and 1.00 μg/mL was 2.2% and 1.5%, respectively. The following regression equation was obtained $\Delta A = 0.021 + 1.021 \times 10^{-2}$ C (r = 0.9934 and n = 10).

Interference study: The influence of foreign ions on the system was examined with 0.40 μg/mL hydrazine. The tolerated limits for the ions

assayed are shown in Table-1 (with relative errors less than 5%). As can be seen, most ions used have no considerable effect on the determination of hydrazine. The results show that the method is relatively selective for hydrazine determination.

TABLE-1
EFFECT OF FOREIGN SPECIES IN THE DETERMINATION OF 0.40 μg/mL HYDRAZINE

Species	Tolerance level (μg/mL)
SO_4^{2-}, glucose, sucrose, Co^{2+}, Mn^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, K^+, CH_3COO^-, $C_2O_4^{2-}$, CO_3^{2-}, Na^+, NH_4^+	1000
Ag^+, $S_2O_4^{2-}$	800
ClO_3^-	80

Analysis of real sample: The method was applied to determination of hydrazine in radiator water and boiler water. The samples were analyzed by the method of standard addition. Table-2 shows the results of analysis of real samples. Recovery tests for the analyzed samples were satisfactory with relative standard deviations of 3.4% for radiator water.

TABLE-2
DETERMINATION OF HYDRAZINE IN WATER SAMPLES

Sample	Hydrazine found (μg/mL)	RSD (%)
Radiator water	1.50	3.4
Boiler water	1.85 ± 1	7.8

Conclusion

A kinetic-spectrophotometric method is proposed for trace amounts of hydrazine. The method is simple, highly sensitive, inexpensive and rapid and was used for the determination of hydrazine in real water samples.

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