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Spectrophotometric Determination of Hydrazine

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A spectrophotometric method for the determination of hydrazine, which involves conversion of hydrazine to ammonium sulphate by Zn/H_2SO_4 reductor column, has been developed. The formed ammonium sulphate is determined based on Berthelot reaction using salicylic acid, sodium hypochlorite and sodium nitroprusside. The λ_{max} for the formed dye is at 648 nm and the calculated molar absorptivity is 1.8×10^4 L mol^{-1} cm^{-1}. The method is useful for determining hydrazine in the concentration range 0.25–2.5 ppm with the relative standard deviation of 2% for n = 10 at 1.5 ppm of hydrazine. Response of the proposed method for hydrazine determination in the presence of potential interferents is evaluated. The proposed method has been successfully applied for the estimation of hydrazine in feed waters for high-pressure steam generating boilers. The results obtained in the developed method compare well with the *p*-dimethylaminobenzaldehyde (*p*-DAB) method and by recovery studies of added hydrazine.

Key Words: Hydrazine, Indophenol, Spectrophotometry, Boiler feed water.

INTRODUCTION

Hydrazine is an important industrial chemical with many applications in pharmaceuticals, polymers and dye industries[1]. It is also widely used to remove dissolved oxygen in boiler feed water and as corrosion inhibitor[2]. Hydrazine and its salts have found widespread use as high-energy rocket propellants.

Besides being reactive and explosive, hydrazine is highly toxic. It may cause skin sensitization as well as systemic poisoning[3]. It is also a suspected human carcinogen[4] and the threshold limit value for workroom air is 0.1 ppm in the USA[5]. High toxicity of hydrazine and its potential occurrence in the workplace environment makes the development of reliable and sensitive monitoring methods very important.

Several methods have been suggested for the determination of hydrazine, all of which depend on its basic character or reducing property[6, 7]. Spectrophotometric methods are more useful for the determination of hydrazine at low concentration levels.

A spectrophotometric method was reported[8] for the determination of hydrazine in the UV region after reacting hydrazine with salicylaldehyde. Lin *et al.*[9] synthesized decafluorobenzaldazine from hydrazine, followed by tritium electron capture detection, which was a measure of hydrazine concentration. An extraction spectro-

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photometric method was reported[10] based on reaction of hydrazine with 2-hydroxy-1-naphthaldehyde to form a water-insoluble yellow aldazine. A kinetic spectrophotometric method had been reported[11] based on hydrazine inhibition effect on the reaction between bromate and hydrochloric acid. The decolorization of methyl orange by the reaction products was used to monitor the reaction spectrophotometrically.

The well-known method for the spectrophotometric determination of low concentration of hydrazine is Pesez and Petit method[12]. This method is based on the reaction of hydrazine with *p*-dimethylamino benzaldehyde (*p*-DAB) in acid medium to give a compound with a *p*-quinone structure that is yellow in solution. Many variants of this method have been published and all of them seem to be capable of giving satisfactory results[13].

In this work, a new sensitive spectrophotometric method of determination of hydrazine is reported. The method is based on the conversion of hydrazine to ammonium sulphate by Zn/H_2SO_4 reductor column. The formed ammonium sulphate is determined based on Berthelot reaction[14] using salicylic acid, sodium hypochlorite and sodium nitroprusside to form indophenol dye. The λ_{max} for the formed dye is at 648 nm. Response of the proposed method in the presence of potential interferents was evaluated. In the present method hydroxylamine can be tolerated up to 250 μg and nitrate, nitrite can be tolerated up to 400 μg. The method was successfully applied in feed waters for high-pressure steam generating boilers. The results were validated with *p*-DAB method[12] and also by recovery studies of added hydrazine.

EXPERIMENTAL

All chemicals used were analytical grade reagents. All absorbance measurements were made using Elico SL177 scanning spectrophotometer with 1 cm glass cells.

Zinc reductor column: A glass column (30 cm height and 0.9 cm diameter) was loaded with zinc granules to a height of 5 cm.

Oxygen-free water: Prepare the water for the reagents according to the ASTM specification[15] by boiling distilled water and then cooling it under a nitrogen atmosphere to keep it free of dissolved oxygen. Use of oxygen-free water is required till the sample is passed through the reductor column to prevent the loss of hydrazine.0

Sulphuric acid: 2 N and 16 N were prepared by diluting 36 N concentrated sulphuric acid (specific gravity 1.84) with oxygen-free water.

Calibration Graph: Add 1 mL of 2 N sulphuric acid to 10 mL sample containing 0–25 μg hydrazine and pass through the zinc reductor column at the flow rate of 1 mL/min and collect it in a 25 mL standard flask. Wash the column twice with 3 mL portion of distilled water and collect the washings. Add 2 mL of 20% sodium hydroxide, 2 mL of 35% salicylic acid, 1 mL of 0.12% sodium nitroprusside solution and 1 mL of 3% sodium hypochlorite solution and dilute to the mark with distilled water. Measure the absorbance at 648 nm using 1 cm glass cell against reagent blank. Plot the absorbance against the amount of hydrazine to obtain a calibration graph.

Determination of hydrazine in boiler feed waters: Take a sample volume of

10 mL containing not more than 25 μg of hydrazine and follow the procedure described under calibration graph

RESULTS AND DISCUSSION

Hydrazine can be reduced to ammonium sulphate in sulphuric acid medium using zinc[16]. Preliminary experiments to reduce hydrazine to ammonium sulphate using zinc powder and sulphuric acid resulted in 55–60% conversion. To achieve quantitative reduction, a reductor column (Zn/H_2SO_4) using zinc granules was prepared. The flow rate was optimized as 1 mL/min. The formed ammonium sulphate was determined based on the formation of indophenol dye. The quantitative conversion of hydrazine to ammonium salt was established by spectrophotometric measurement of the absorbance of the formed indophenol dye. The absorbance values compare well with the direct colour development using equivalent concentration of ammonium sulphate as standard and indicate quantitative reduction of hydrazine under experimental conditions. The optimized concentrations of salicylic acid, sodium hypochlorite and sodium nitroprusside were incorporated in the working procedure range. The ammonium ion on reaction with salicylic acid, sodium hypochlorite under basic conditions forms blue indophenol dye (Fig. 1) in the presence of sodium nitroprusside as a catalyst[14] with a λ_{max} at 648 nm (Fig. 2).

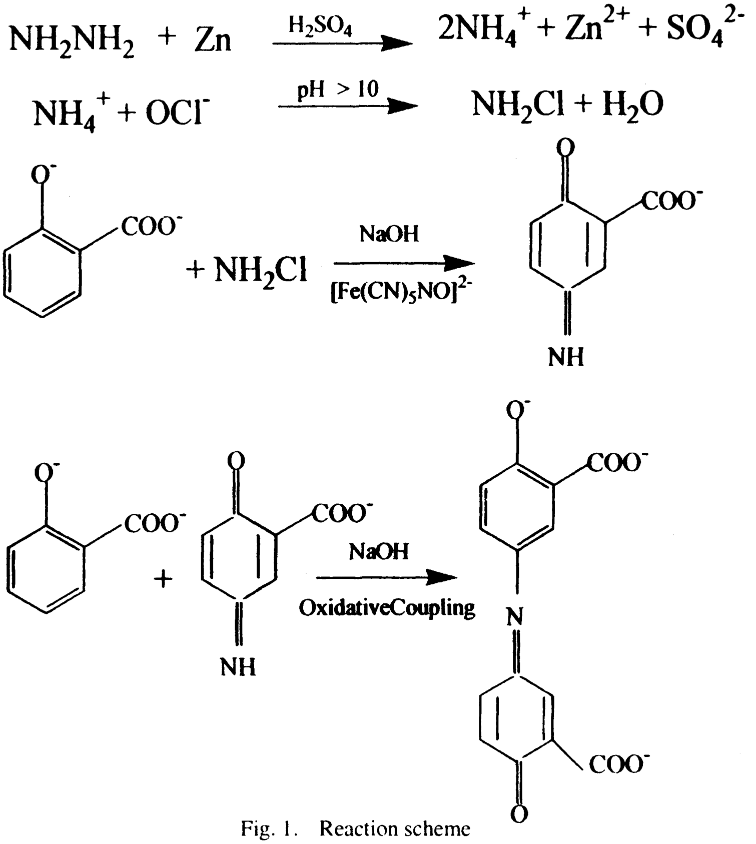

Fig. 1. Reaction scheme

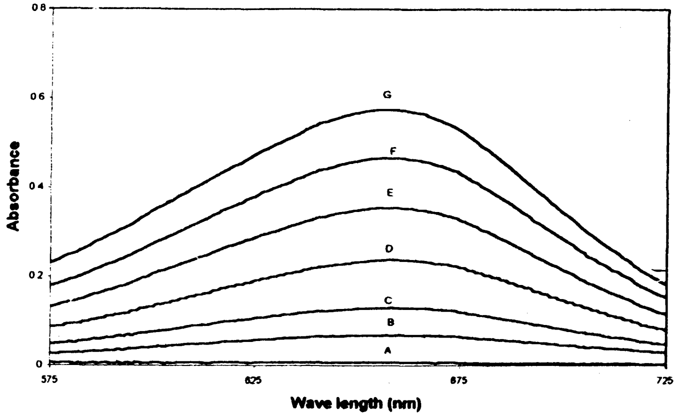

Fig. 2. Absorbance spectra measured against water: (A) reagent blank; (B) 2.5 μg of NH_2NH_2; (C) 5 μg of NH_2NH_2; (D) 10 μg of NH_2NH_2; (E) 15 μg of NH_2NH_2; (F) 20 μg of NH_2NH_2; (G) 25 μg of NH_2NH_2

The proposed method was useful for the determination of hydrazine in the concentration range of 2.5–25 μg in an overall volume of 25 mL. The molar absorptivity of the coloured system was calculated to be 1.8×10^4 L mol^{-1} cm^{-1} and the developed colour remains stable for 24 h. The calibration graph is a straight line with a positive slope and the equation of the line is $Y = 0.0226X$ where Y is the absorbance and X (μg) is the concentration of hydrazine. The relative standard deviation is 2% at 1.5 ppm level of hydrazine ($n = 10$) and the correlation co-efficient is 0.9996. The detection limit of hydrazine in the proposed method is 0.13 ppm.

Effect of interfering species on hydrazine determination: The interfering effect of common anions and cations, which may co-exist with hydrazine, was studied. Any deviation in the absorbance of ±0.01 to that obtained in the absence of other interfering ions in hydrazine determination was taken as a sign of interference. In hydrazine determination, varying concentrations of interfering species were introduced along with 15 μg of hydrazine and the recovery of hydrazine was established following the procedure described under the calibration graph. Tolerance limits of various ions studied in hydrazine determination are summarized in Table-1.

Hydroxylamine is a potential interferent in most of the methods for hydrazine determination. Hydroxylamine when present along with hydrazine also undergoes quantitative reduction to ammonium sulphate and causes positive interference. In the proposed method, formaldehyde solution is added to eliminate hydroxylamine interference. Reaction between formaldehyde and hydroxylamine is very fast to form the oxime, compared to the reaction between hydrazine and formaldehyde. In the present method, hydroxylamine is tolerated up to a concentration of 250 μg in the presence of 1 mL of 6000 ppm formaldehyde solution when present along with 15 μg of hydrazine.

TABLE-1
EFFECT OF INTERFERING SPECIES IN HYDRAZINE DETERMINATION

Hydrazine = 15 μg)

Species	Amount tolerated (μg)
Carbonate, Phosphate, Borate Oxalate, Tartrate, Citrate	1000
Chloride, Bromide, Iodide, Fluoride	1000
HCHO	6000
K(I), Li(I), Mg(II), Sn(II), Sr(II), Ba(II), Ca(II), Pb(II), Mn(II), Cr(III), As(III), Cd(II), Al(III), Bi(III), Co(II), Ni(II)	1000
NH_2SO_3H	2000
NH_2OH[a]	250
NO_2^-[b]	400
NO_3^-[c]	400
Cu(II), Fe(III), Hg(II)	10

[a] Treated with HCHO solution before passing through the reductor column.
[b] Treated with sulphamic acid before passing through the reductor column.
[c] Treated with HCHO solution, H_2SO_4 followed by sulphamic acid and sodium hydroxide before passing through the reductor column.

Normally nitrate and nitrite are potential interferences in the estimation of hydrazine. Nitrate and nitrite also undergo reduction to ammonium sulphate and cause positive interference. Nitrite is decomposed by the addition of 1 mL of 2000 ppm sulphamic acid to form nitrogen. Nitrate is first reduced to nitrite with HCHO in sulphuric acid medium. The formed nitrite is decomposed by the addition of sulphamic acid. For nitrate interference 4 mL sample containing 15 μg of hydrazine and nitrate (400 μg) was treated with 1 mL of 1000 ppm HCHO solution followed by 5 mL of 16 N sulphuric acid and 1 mL of 2000 ppm sulphamic acid. The solution is neutralized with 10 mL of 8 N sodium hydroxide solution and diluted to 25 mL in a 25 mL calibrated flask before analysis. In the present method both nitrate and nitrite are tolerated up to 400 μg.

Applications

Hydrazine is normally added in small amounts (0.2%) to boiler feed water. Hydrazine is oxidized by dissolved oxygen to nitrogen and prevents the corrosion of boilers.

To demonstrate the applicability of the proposed method, feed water samples were taken from high-pressure steam generating boilers to determine the hydrazine concentration. The results obtained using the proposed method were validated by doing a parallel determination using *p*-DAB method[12]. For this, 10 mL aliquot of the water sample containing not more than 10 μg of hydrazine was taken in a 25 mL calibrated flask. To this, 10 mL of *p*-dimethylamino benzaldehyde solution was added and made up to the mark with 1 M hydrochloric acid. The absorbance was measured at 659 nm against the reagent blank. Recovery of spiked hydrazine was also evaluated. The results obtained are shown in Table-2.

TABLE-2
DETERMINATION OF HYDRAZINE IN BOILER FEED WATER

Sample	Added NH_2NH_2 (μg)	Amount of NH_2NH_2 in samples (μg/mL)[a]	Recovery of added NH_2NH_2 (%)	Amount of NH_2NH_2 in samples (μg/mL)[a]
		Proposed Method		p-DAB Method
Sample 1[b]	—	7.50	—	7.37
	5.0	12.50	100.00	—
	10.0	17.30	98.00	—
Sample 2[c]	—	0.25	—	0.26
	2.5	2.68	97.20	—
	5.0	5.21	99.20	—
Sample 3[c]	—	0.39	—	0.39
	2.5	2.88	99.60	—
	5.0	5.26	97.40	—

[a] Average of three determinations.

[b] Sample taken immediately after the addition of hydrazine to boiler feed water. 1 mL of this is diluted to 250 mL before analysis.

[c] Water sample was withdrawn and analysed at the entry point of the boiler.

Conclusion

The proposed method for the determination of hydrazine is simple, sensitive and reliable. The method is useful for the determination of hydrazine in the concentration range 0.25–2.5 ppm of hydrazine. The molar absorptivity is found to be 1.8×10^4 L mol^{-1} cm^{-1}. The detection limit of hydrazine of the proposed method is 0.13 μg mL^{-1}. The tolerance limit of the potential interfering species hydroxylamine, nitrate and nitrite is higher in the reported method.

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