Indirect Spectrophotometric Determination of Trace Quantities of Hydrazine

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An indirect, sensitive and accurate method for the determination of trace amounts of hydrazine is described. The method is based on the oxidation of hydrazine by a known excess of iodate in the presence of hydrochloric acid. The unreacted iodate is used in the oxidation of hydroxylamine to nitrite. Sulfanilic acid is diazotized by the nitrite formed. The resulting diazonium ion is coupled with N-(1-naphthyl)ethylenediamine to form a stable azo dye, which shows an absorption maximum at 540 nm. Hydrazine can be determined in the range of 20-400 ng mL^{-1} with a detection limit of 3.1 ng mL^{-1}. The relative standard deviation for 50, 200 and 400 ng mL^{-1} of hydrazine is 2, 1.5 and 1.3%, respectively (n = 10). The method was applied to the determination of hydrazine in water samples.

Key Words : Indirect method, Spectrophotometry, Hydrazine determination

Introduction

Hydrazine and its derivatives have been used in industry, agriculture and other fields, including photographic development, oxygen scavenging, rocketry, explosives, insecticides and blowing agents for plastics.[1] However, hydrazine is a local irritant that is readily absorbed through the skin, and its inhalation results in respiratory tract irritation, bronchitis and pulmonary edema. Furthermore, hydrazine is suspected of being a mutagen and carcinogenic compound.[2] Thus, because of its toxicological effects and industrial significance, development of a sensitive method for the determination of trace quantities of hydrazine is of interest.

Several methods are described in the literature for the determination of hydrazine, using different analytical techniques, such as spectrophotometry,[3-9] spectrofluorimetry,[10,11] voltametry,[12,13] coulometry,[14] amperometry,[15] titrimetry,[16] gas chromatography,[17] chemiluminescence,[18,19] ion selective electrode,[20,21] and indirect methods.[22] However, most of the proposed methods either lack sufficient sensitivity,[16] require complicated and expensive instruments,[17] are time consuming,[3] or provide high detection limits.[10,12] Therefore, the need for a sensitive, simple and reliable method for the determination of hydrazine is well recognized.

In the present paper, an indirect, simple, sensitive and precise spectrophotometric method for the determination of trace quantities of hydrazine based on the diazo-coupling reaction is described.

Experimental Section

Apparatus. Spectral measurements were made with a Jasco Model 7800 double-beam spectrophotometer with 1-cm quartz cuvettes.

Reagents. All reagents were analytical grade and triply distilled water was used throughout. A hydrazine stock solution (1000 μg mL^{-1}) was prepared by dissolving 0.3276 g of hydrazine dihydrochloride (Merck Co., Germany) in 100 mL of water. Work solutions were prepared fresh daily by dilution to the appropriate volume with water. A 1000 μg mL^{-1} potassium iodate solution was prepared by dissolving 0.1 g of KIO_3 (Merck) in water and diluting to 100 mL in a volumetric flask. Suitable dilutions were made to obtain a concentration of 15 μg mL^{-1} of potassium iodate. A 0.25% hydroxylamine hydrochloride solution was prepared by dissolving 0.25 g of hydroxylamine hydrochloride (Merck) in water and diluting to 100 mL in a volumetric flask. A 0.05% (w/v) N-(1-Naphthyl)ethylenediamine dihydrochloride (NEDA) solution was prepared by dissolving 0.05 g of NEDA (Merck) in 100 mL of water. The solution was stored in a brown bottle at 4 ºC. The solution was stable for 2 months. A 0.2% sulfanilic acid solution (w/v) was prepared by dissolving 0.2 g of sulfanilic acid (Merck) and diluting to 100 mL in a volumetric flask. Hydrochloric acid 0.25 mol L^{-1} was prepared by diluting the appropriate volume of concentrated acid (Merck) with water.

Recommended procedure. 1 mL of 0.25 mol L^{-1} hydrochloric acid and 2 mL of 15 μg mL^{-1} potassium iodate were added to the sample or standard solutions containing 0.2-4 μg of hydrazine in a 10 mL volumetric flask. The solutions were diluted to *ca*. 7 mL with water. Subsequently, 1 mL of 0.25% hydroxylamine hydrochloride solution and 1 mL of 0.2% sulfanilic acid were added and the mixtures were allowed to stand for 20 min. Then 1 mL of 0.05% NEDA was added and the solutions were diluted to the mark with water. The blank solution was prepared by the same procedure and the absorbance was measured against water at 540 nm.

Results and Discussion

Diazotizaton-coupling reactions followed by spectrophotometric methods have been used routinely for the determination of nitrite.[23,24] These methods are based on the

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reaction of nitrite with various aromatic amines in an acidic medium to form a diazonium salt, which is used with a coupling agent to produce a highly colored azo compound. Spectrophotometric determination of hydroxylamine by oxidation to nitrite and the formation of azo dye has also been reported.[25]

The aim of this study is to establish a highly sensitive method for the determination of hydrazine. The method is based on the combination of three well-known reactions as follows:

1. Oxidation of hydrazine with a known excess of iodate in hydrochloric acid medium

$$N_2H_4 + KIO_3 + 2HCl \rightarrow KCl + ICl + N_2 + 3H_2O$$

2. Oxidation of hydroxylamine to nitrite by the excess of iodate

$$2KIO_3 + 3NH_2OH \rightarrow 3NO_2^- + 3H^+ + 2KI + 3H_2O$$

3. Diazotization of sulfanilic acid by the nitrite formed and the coupling of the resulting diazonium ion with NEDA

The red-violet product, N-{1-[4-(4-sulfophenylazo)naphthyl]}ethylenediamine dihydrochloride, has an absorption maxima at 540 nm.

When hydrazine was added in increasing amounts, it consumed more iodate, and thus the concentration of excess iodate was decreased, which resulted in a concomitant fall in nitrite generation. This caused a proportional decrease in the concentration and absorbance of the azo dye formed in the mixture by an increase in concentration of hydrazine (Fig. 1).

Effect of variables. To establish the best conditions for the formation of azo dye the procedure was optimized by an univariable method (keeping all variables constant except one).

The effect of hydrochloric acid concentration on the absorbance of azo dye was studied. The results show (Fig. 2) that the absorbance increased by an increase in hydrochloric acid concentration up to 0.02 mol L^{-1} and then leveled off. A 0.025 mol L^{-1} hydrochloric acid solution was selected to ensure maximum sensitivity.

To optimize the concentration of hydroxylamine, different volumes of hydroxylamine solution (0.25%) were added to the mixture under study. It was found that 1 mL of hydroxylamine solution was sufficient for maximum color

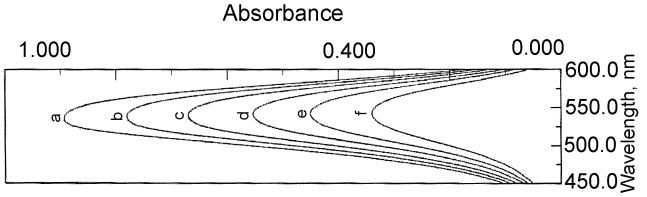

Figure 1. Absorption spectra of the reaction mixture against water in the presence of different concentration of hydrazine: potassium iodate, 3 μg mL^{-1}; hydrochloric acid, 0.025 mol L^{-1}; hydroxylamine, 0.25 mg mL^{-1}; sulfanilic acid, 0.2 mg mL^{-1}; NEDA, 0.05 mg mL^{-1}; hydrazine: a, 0.0; b, 0.1; c, 0.2; d, 0.3; e, 0.4 and f, 0.5 μg mL^{-1}.

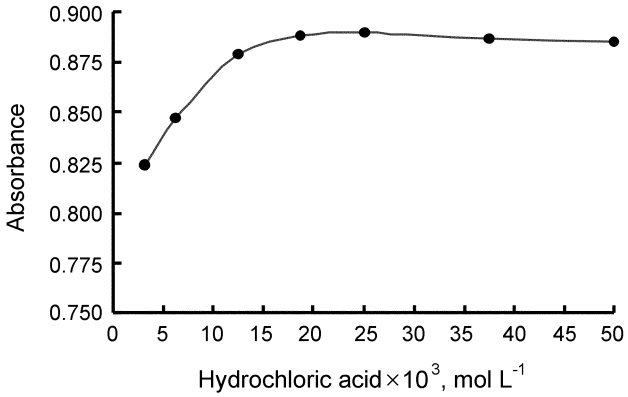

Figure 2. Effect of hydrochloric acid concentration on the absorbance: potassium iodate, 3 μg mL^{-1}; hydroxylamine, 0.1 mg mL^{-1}; sulfanilic acid, 0.3 mg mL^{-1}; NEDA, 0.03 mg mL^{-1}.

development. There was a decrease in absorbance at lower concentration of hydroxylamine, whereas no change in absorbance was observed at higher concentration.

The effect of sulfanilic acid concentration in the range of 0.05-0.6 mg mL^{-1} on the absorbance was studied. The results show that 1 mL of a 0.2% sulfanilic acid solution gave satisfactory results.

The influence of NEDA concentration on the coupling reaction was studied. The results of Figure 3 indicate that the best absorbance is obtained in the range of 0.03-0.075 mg mL^{-1}. Therefore, a concentration of 0.05 mg mL^{-1} was selected for further work.

The absorbance was found to be independent of temperature in the range of 15-50 °C. Therefore, as it was more convenient, the procedure was carried out at room temperature. The maximum time required for nitrite generation and diazotization was 20 min.

Analytical performance. Under optimum conditions, a linear calibration graph was obtained over the range of 20-400 ng mL^{-1} of hydrazine. The regression equation was A = 0.894-0.001C (C being the hydrazine concentration, ng mL^{-1}), with a correlation coefficient of -0.9997.

The relative standard deviation for ten replicate analyses

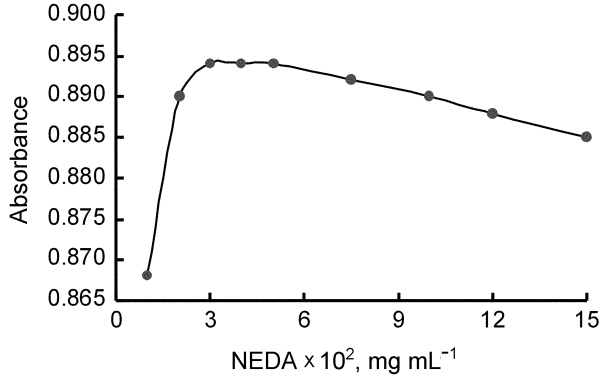

Figure 3. Effect of NEDA concentration on the absorbance: potassium iodate, 3 μg mL^{-1}; hydrochloric acid, 0.025 mol L^{-1}; hydroxylamine, 0.25 mg mL^{-1}; Sulfanilic acid, 0.2 mg mL^{-1}.

Table 1. Tolerance limit of diverse ions on the determination of 100 ng mL^{-1} hydrazine by the proposed method

Interfering ion	Tolerance limit (μg mL^{-1})
Na^+, K^+, Li^+, Ca^{2+}, Pb^{2+}, F^-, Cl^-, Br^-, I^-, NO_3^-	≥ 100
SO_4^{2-}, ClO_4^-, CH_3COO^-, Mg^{2+}, tartrate	
Mn^{2+}, NH_4^+, Al^{3+}, citrate	50
Cd^{2+}, Ni^{2+}, Sn^{2+}, Zn^{2+}, PO_4^{3-}	10
Co^{2+}, Fe^{3+}, CN^-	1
Cu^{2+}, Cr^{3+}, SCN^-, $S_2O_3^{2-}$	0.2

Table 2. Determination of hydrazine added to water samples (n = 5)

Sample	Hydrazine (μg)		Recovery (%)
	Added	Found	
Tap water	0.40	0.39	97.5
	1.00	0.99	99.0
	1.50	1.49	99.3
River water	0.40	0.41	102.5
	1.00	1.00	100.0
	2.00	1.99	99.5
Well water	0.40	0.38	95.0
	1.00	0.98	98.0
	2.00	2.01	100.5

of standard solution containing 50, 200 and 400 ng mL^{-1} of hydrazine was 2, 1.5 and 1.3%, respectively. The experimental limit of detection calculated as three times the standard deviation of a blank (3s criterion) was 3.1 ng mL^{-1} of hydrazine.

Interference. The effects of other ions on the determination of 100 ng mL^{-1} of hydrazine were studied. The tolerance limit was defined as the concentration of added species that causes a relative error less than 3%. The results are summarized in Table 1. At the given concentration no interference was observed in the determination of hydrazine.

Application. The feasibility of the technique for the determination of hydrazine in water samples was examined. 4 mL of tap, river and well water were spiked with different amounts of hydrazine and the procedure given above was followed. The results are given in Table 2. The recoveries were close to 100%, indicating that the present method is suitable for the analysis of water samples.

Conclusion

Hydrazine can be determined with a good accuracy and precision at levels as low as 20 ng mL^{-1} without the need for a preconcentration step. The proposed method is simple and more sensitive than most previously reported spectrophotometric methods.

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