

Developed New Procedure for Low Concentrations of Hydrazine Determination by Spectrophotometry: Hydrazine-Potassium Permanganate System

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ABSTRACT

An indirect, sensitive and accurate method for the determination of trace amounts of hydrazine is described. In this proposed the spectrophotometric method is based on its reduction properties of hydrazine with a known concentration of potassium permanganate to reduce the colour. The absorbance of unreduced permanganate is measured the colour difference at different wavelengths 546 and 526 nm which show an absorption spectrum with hydrazine. Hydrazine can be determined in the range of 100 - 700 µg/ml with correlation coefficient of 0.999 and relative standard deviation 1%. The method is successfully applied for the determination of hydrazine in water streams in nuclear reactors/purex process/boiler water and polluted water samples.

Keywords: Hydrazine/Potassium Permanganate; UV-Vis Spectrophotometry; Reducing Property; Water Streams; Nuclear Reactors

1. Introduction

Hydrazine and its analogues have found various applications in many industrial, agriculture and other fields, including the manufacture of metal films, photographic chemicals, antioxidants, insecticides and blowing agents for plastics. In addition, hydrazines and their derivatives are suspected to be carcinogens. Hydrazine is widely used as a scavenger to remove traces of oxygen in boiler feed water system [1]. Several methods have been described for the determination of trace amounts of hydrazine, including spectrophotometry, gas chromatography [2] and ion chromatography [3]. Most of these are based on the reaction of hydrazine with aromatic aldehydes such as benzaldehyde [4], salicylaldehyde [5], p-dimethylaminobenzaldehyde [6], pentafluorobenzaldehyde [7] and 5-nitro-2-hydroxybenzaldehyde [8] to form aldazines. Accordingly, their determination at the micro level is of great importance. Despite the accuracy of most of the redox methods [9,10] used for the determination of hydrazines, only few are suitable for extremely dilute solutions, and some require carefully controlled conditions. Most of the spectrophotometric procedures available so far in the literatures [11-22] are tedious and involve the use of rare and expensive colour reagents. The present work describes a very simple, sensitive and accurate

spectrophotometric procedure for the determination of ppm concentrations of hydrazine salts based on reaction with potassium permanganate and measurement of the decolourisation of permanganate.

2. Experimental

2.1. Instrumentation

Fiber optic aided spectrophotometry with 1 cm path length probe is used for measuring absorbance.

Metrohm make modular Ion-chromatograph equipped with 820 IC separation center, lambda 1010 IC detector (UV-VIS), 818 IC pump (Isocratic), 833 IC liquid handling unit and 830 IC interface and a Metrohm Post column derivatization kit were used. Sample was injected through a 20 µL PEEK loop fitted with injector. IC-net 2.3 metrohm software was used for instrument control and data acquisition.

Ion Chromatographic Conditions

Ion chromatograph: Metrohm modular Ion chromatography system

Eluent concentration: 5 mM Hydrochloric acid

Eluent flow rate: 0.4 ml/min

Pressure: 13.5 MPa

Detector: Lambda 1010 UV-VIS detector.

Analytical mode: Isocratic
Injection loop: 20 μ L
Temperature: Ambient (25°C)
Run time: 10 min

2.2. Reagents

All the reagents used were of analytical grade and double distilled water was always used. A stock solution of hydrazine nitrate (obtained from Orion Chem.Pvt.Ltd., Mumbai) was prepared freshly by dilution to the appropriate volume with water. Fresh work solutions are prepared daily by dilution to the appropriate volume of 3.3×10^{-3} M aqueous solutions. The hydrazine nitrate solutions were standardized by titration with standard potassium iodate solutions [23,24]. The standard potassium permanganate solutions (Prolabo, purity = 98%) were prepared and analyzed by titration with oxalic acid [25].

3. Procedure

Suitable aliquot of hydrazine and permanganate were added into a series of 10 ml volumetric flasks and made up to mark with distilled water. The absorbance changes of the solution were measured from 700 to 400 nm using fiber optic aided spectrophotometry. Blank also was run in the same manner.

Ion-Chromatography

In order to compare the results obtained by spectrophotometric analysis with those of Ion chromatographic technique, experiment were conducted for the determination of hydrazine present in aqueous phase by formation of yellow coloured azine complex by post column derivatization of hydrazine with (pDMAB) *para*-dimethylaminobenzaldehyde and then analyzing by Ion chromatographic technique using UV-Vis detector. Various hydrazine standards of known concentrations (1 - 10 μ g/ml) were prepared by dissolving hydrazine nitrate in Millipore water. 20 μ L of these solutions directly injected into

the ion-chromatography column connected with UV-Vis detector. Hydrochloric acid (5 mM) with a flow rate of 0.4 ml/min was used as mobile phase. A mixture of *p*-dimethylaminobenzaldehyde (42 mM), hydrochloric acid (0.6 M) and methanol (1%) with a flow rate of 0.6 ml/min was used as derivatization reagent. A calibration graph was made for the concentration range of hydrazine from 0.05 to 10 μ g/ml with RSD 0.807% and correlation coefficient of 0.9999. Synthetic aqueous solution containing known concentration of hydrazine was prepared in water, injected 20 μ L aqueous sample in to Ion chromatography.

4. Result and Discussion

In this method determination of hydrazine, the reduction of potassium permanganate with hydrazine has been thoroughly studied and hence, no significant changes were done to adapt the experimental conditions for the determination of hydrazine. The absorption spectrum of potassium permanganate in water shows two absorption maxima at 546 and 526 nm (Figure 1) for which the molar absorptivities are 2192.18 and 2279.27 $\text{L}\cdot\text{Mol}^{-1}\cdot\text{cm}^{-1}$ respectively. The experimental conditions for the quantitative reduction of potassium permanganate with hydrazine are well established. Similar results were obtained for hydrazine determination with permanganate. The most commonly used *p*-dimethylaminobenzaldehyde procedures are tedious and suffer from interferences particularly by amines, urea and semicarbazides. High purity and fresh preparation of the colour reagent are essential. Therefore, it was of interest to investigate the possibility of developing a procedure for the determination of hydrazine covering a reasonably wide concentration range and keeping in mind sensitivity, availability and stability of the colour reagent as well as reducing the number of interfering species encountered in the *p*. dimethylaminobenzaldehyde methods. Standard absorption spectrum and calibration graph for potassium permanganate are shown in Figures 1 and 2. Beer's law was obeyed within

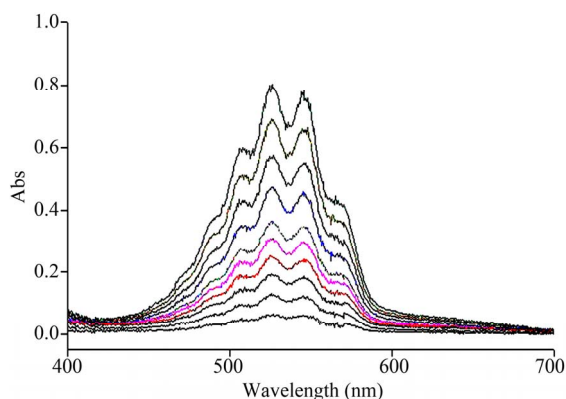


Figure 1. Typical absorption spectrum of KMnO_4 .

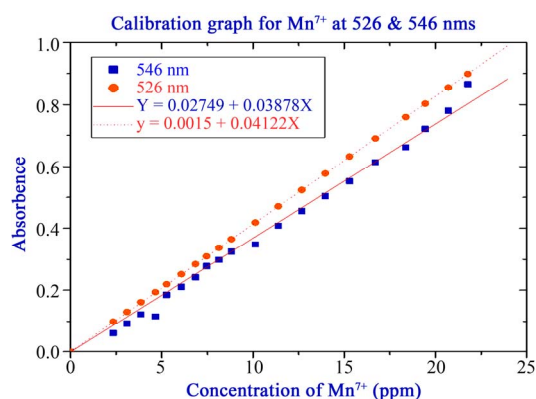


Figure 2. Calibration graph for KMnO_4 at 526 & 546 nm.

the concentration range investigated. The calculated molar absorptivity of potassium permanganate at 546 and 526 are 2192.18 and 2279.27 $L \cdot Mol^{-1} \cdot cm^{-1}$ respectively. **Figure 3** shows that typical absorption spectrum of different concentration of hydrazine with permanganate. **Figure 4** shows that calibration graph was made for hydrazine concentration rang of 15 - 125 $\mu g/ml$ with correlation coefficient of 0.99549 and RSD 1% at different wavelengths with potassium permanganate. The accuracy of the present method was checked by determining hydrazine in various samples by both the present method and by an independent technique, namely, Ion chromatography (IC). A typical chromatogram and a calibration curve are shown in **Figures 5-6**. The results obtained for hydrazine by the proposed and by the ion IC method agreed well within the limits of experimental error and represented in **Table 1**. Typical results obtained by using this methodology and instrumentation for the determination of hydrazine in water samples are reported in **Table 2**.

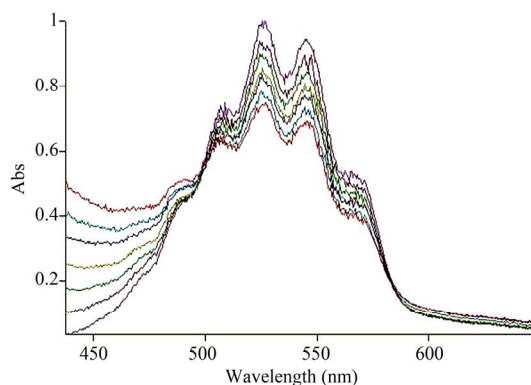


Figure 3. Typical absorption spectrum of hydrazine with $KMnO_4$.

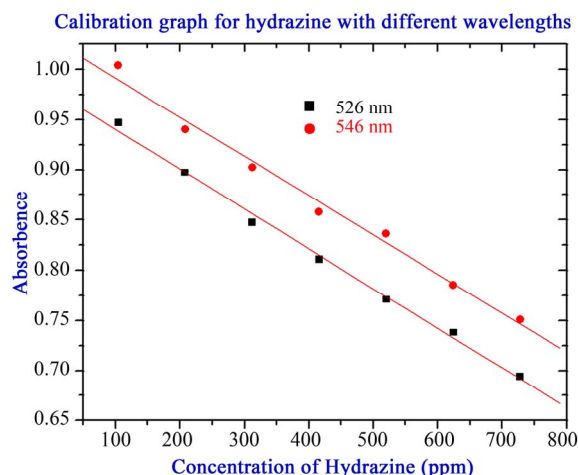


Figure 4. Calibration graph for Hydrazine with potassium permanganate at different wavelengths.

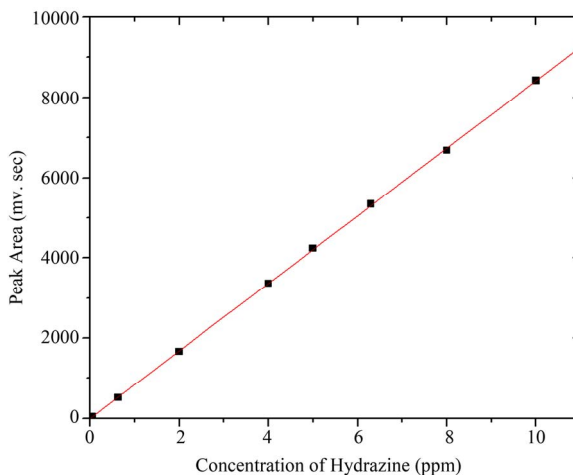


Figure 5. Calibration graph of hydrazine.

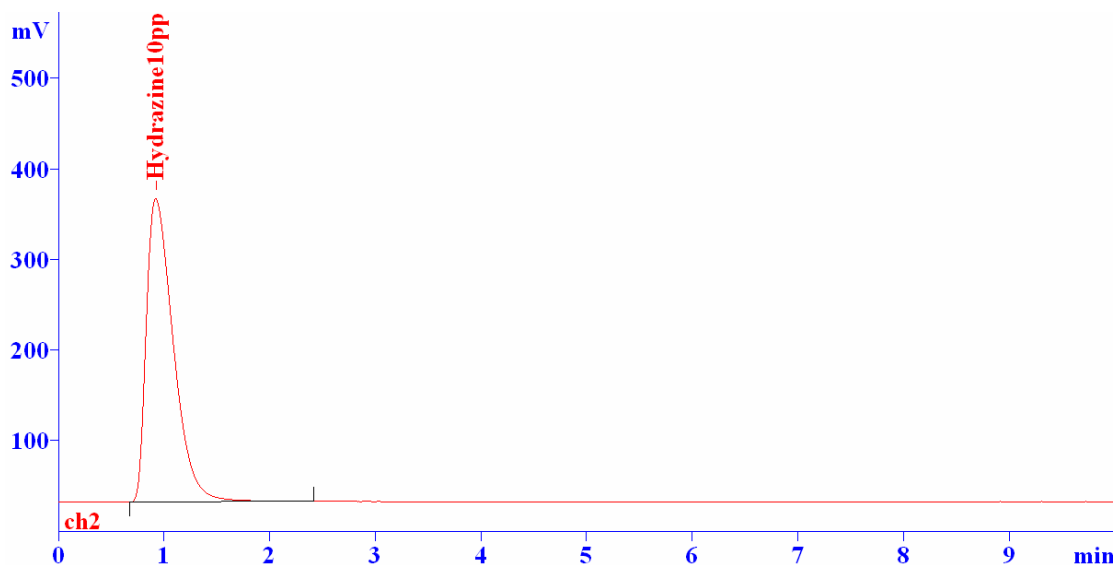


Figure 6. Ion Chromatogram of hydrazine standard.

Table 1. Comparison of two different analytical technique.

S.No.	Concentration of hydrazine ($\mu\text{g/ml}$)	
	Spectrophotometry	Ion-chromatographic Technique
1	6.24	6.303
2	10.80	10.01
3	25.30	24.80
4	12.28	12.10

5. Conclusion

A simple, rapid and sensitive spectrophotometric procedure is described for ppm determination of hydrazine salts. It is based on reduction of potassium permanganate and measurement of the absorbance at 546 and 526 nm. When compared with other procedures, this method was proved to be of comparable sensitivity and has less interference.

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Table 2. Typical results of hydrazine in water samples (Water samples were collected from various located in Chhatisgarh state, India).

S.No	Absorbance	Conc. of Hydrazine ($\mu\text{g/ml}$)
S1	0.814	534.054
S2	0.660	828.375
S3	0.528	1035.469
S4	0.878	406.524
S5	1.542	67.714
S6	0.971	107.534
S7	0.918	113.743

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