

## A Rapid Spectrophotometric Determination of Nitrite in Polluted Water

P. NAGARAJA, M.S. HEMANTHA KUMAR†  
K.S. RANGAPPA\* and A.S. SURESH†  
*Department of Studies in Chemistry*  
*University of Mysore, Manasagangothri*  
*Mysore-570 006, India*

A new sensitive spectrophotometric method is developed for the determination of nitrite with imipramine hydrochloride coupled with 3-methyl-2-benzothiazolinone hydrazone hydrochloride in acid medium. Beer's law obeyed in the range of nitrite concentration of 0.02–7 µg/mL and the molar absorptivity at 640 nm is  $0.49 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ . Results obtained by using the proposed method for water samples agree well with those obtained by Saltzman standard method.

### INTRODUCTION

A great deal of interest has been generated concerning health hazards of nitrites<sup>1</sup>. They oxidize haemoglobin to methaemoglobin, which is unable to transport oxygen<sup>2,3</sup> and they can react with secondary amines present in the body and may form carcinogenic nitrosamines, which are potent carcinogens. So, determination of nitrite is important<sup>4,5</sup>. In view of the increasing interest in the quality of natural and sewage water, a sensitive, rapid and simple procedure for micro determination of nitrite seems desirable. Nitrite is undesirable in water owing to its toxicity<sup>6,7</sup>. The maximum permissible limit in potable water is fixed by the US Public Health Service at 0.06 ppm. Numerous procedures are available for the determination of the nitrite ion in solution. Nitrite can be determined polarographically.

Several authors<sup>8–10</sup> have proposed flow injection analysis for determining nitrite through formation of azo dyes. Most spectrophotometric methods for determination of nitrite in water and waste water are based on the Griss-Ilosvay reaction<sup>11</sup> which was modified several times. Among these, the modifications introduced by Saltzman<sup>12</sup> and Jacobs-Hochheiser<sup>13</sup> are widely used and have been adopted as standard procedures<sup>14</sup> while some include the use of solvent extraction to enhance sensitivity. Use of the coupling agent dibenzoyl methane<sup>16</sup>, having catalytic effect in the reaction between thymol blue and bromate in acidic medium<sup>17</sup> is a worthwhile method. We present here a sensitive colour reaction

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†Department of Studies in Environmental Studies, University of Mysore, Manasagangothri, Mysore-570 006, India.

for nitrite, based on diazotization of imipramine hydrochloride followed by coupling with 3-methyl-2-benzothiazolinone hydrazone hydrochloride in acid media to give a blue azo dye. The interference of sulphide can be eliminated by addition of mercuric chloride.

## EXPERIMENTAL

A JASCO model UV-DEC 910 Spectrophotometer with matched silica cells of 1 cm path length was used for all measurements. All the chemicals used were of analytical reagent grade and solutions were prepared in triply distilled water.

*Standard nitrite solution (1000  $\mu\text{g/mL}$ ):* Dissolve 1.499 g of sodium nitrite in distilled water and dilute to 1000 mL. Add a pellet of sodium hydroxide to prevent liberation of nitrous oxide and 1 mL of spectroscopic grade chloroform to inhibit bacterial growth. Dilute this solution for use in the construction of the calibration curve.

*Imipramine hydrochloride (IMP) solution:* 0.2% w/v solution was prepared in water. This solution is stable for one month, if refrigerated and protected from light.

*3-Methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) solution 0.2%:* Dissolve 0.2 g of MBTH in water and dilute to 100 mL with water.

### Procedure

Transfer an aliquot of the sample solution containing 0.5–175  $\mu\text{g}$  of nitrite into a series of 25 mL calibrated flasks, add 3 mL of 0.2% IMP solution, 1.5 mL of 0.2% MBTH and 2 mL of 10 M hydrochloric acid solution, dilute to the mark with distilled water and mix thoroughly. The colour develops instantaneously and is stable for up to 24 h. Measure the absorbance at 640 nm against a reagent blank prepared in the same manner but containing no nitrite in 10-mm silica cells.

*Sample preparation:* Place 100 mL of water sample in a beaker and add 2 mL of mercuric chloride solution. Let it stand for 5 min, then filter to remove mercuric sulphides and iodide. Analyze a known volume of the filtrate by the above procedure.

## RESULTS AND DISCUSSION

*Absorption spectra:* Fig. 1 shows the absorption spectrum of the blue azo dye formed by 4  $\mu\text{g/mL}$  of nitrite ion treated by the recommended procedure under the condition of the preliminary investigations and by the prescribed procedure. The coloured azo dye showed maximum absorption at 640 nm.

*Effect of colour reagent concentration:* With MBTH as a coupling agent, dibenzazepine class of compounds like imipramine hydrochloride, clomipramine hydrochloride, desipramine hydrochloride and trimipramine maleate were tested as the substrate for diazotization but only imipramine hydrochloride gave a water-soluble sensitive blue dyestuff under the conditions of the determination, thus eliminating the need for an extraction, a time-consuming procedure. Moreover, it is soluble in water giving a colourless solution. The effect of MBTH and IMP

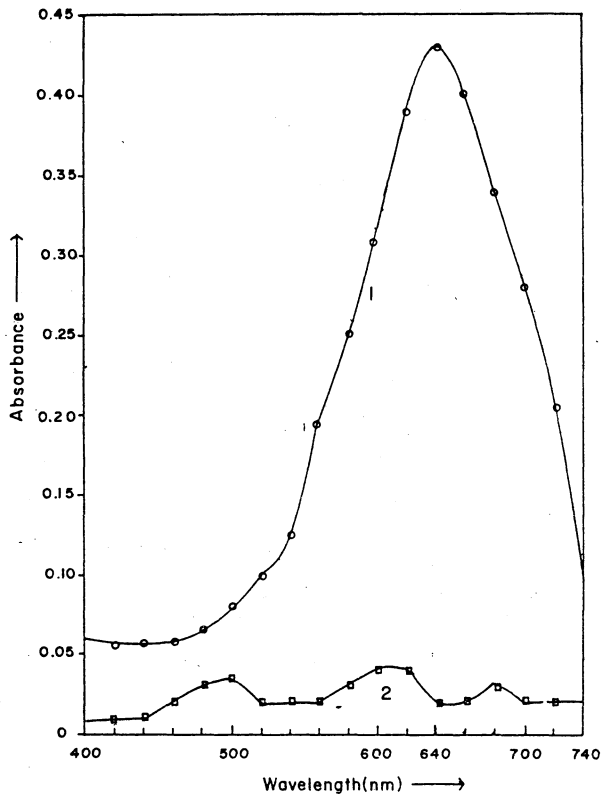


Fig. 1 Absorption of (1) IMP + MBTH +  $\text{NO}_2$  ( $4 \mu\text{g/mL}$ ) product; (2) IMP + MBTH reagent blank

concentration on the colour intensity was studied by using fixed nitrite concentration and varying IMP and MBTH concentration. The result showed that use of 1–6 mL of 0.2% IMP and 1–4 mL of 0.2% MBTH gave constant and maximum absorbance. Therefore the use of 3 mL of 0.2% IMP and 1.5 mL of MBTH is recommended.

*Effect of hydrochloric acid:* Similar experiments were carried out in which hydrochloric acid concentration was varied over the range 1–6 mL of 10 M HCl. Out of these the one having HCl concentration 2 mL of 10 M HCl was found to give maximum colour intensity. Higher acid concentrations have no effect on colour intensity. Other mineral acids were tested and found unsatisfactory.

*Colour stability:* Under the optimized condition, the blue colour azo dye develops instantaneously and remains stable for 24 h, after which there is gradual fading. A temperature range of 10–40°C gives the most useful results. At higher temperature the absorbance value decreases indicating the dissociation of the dye on prolonged heating.

**Analytical characteristics:** The colour system was found to obey Beer's law in the range 0.5–175  $\mu\text{g}$  of nitrite per 25 mL of the IMP-NO<sub>2</sub>-MBTH system. The molar absorptivity was found to be  $0.49 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$ .

The optimum concentration range evaluated by Ringbom's method is found to be between 1–6  $\mu\text{g mL}^{-1}$  for  $\log I_0/I = 0.001$ . The sensitivity of the reaction as calculated from Beer's law data is  $0.009414 \mu\text{g cm}^{-2}$ . The reproducibility was studied by replicate analysis of a standard nitrite solution over a period of 2 days. The relative standard nitrite solution deviation was found to be 1.2%.

**Effect of foreign ions:** Since the method was developed mainly for the analysis of water samples, the effect of foreign species at the levels commonly present in tap water, river water and tank water was studied. The tolerances shown in Table-1 are the concentrations of foreign species that cause  $\pm 2\%$  error in the determination of 4 ppm of nitrite by this method. SO<sub>2</sub> can be eliminated by oxidizing it to sulphate with hydrogen peroxide. Iron(III) requires masking with tartarate.

TABLE-1  
EFFECT OF DIVERSE SPECIES ON THE DETERMINATION OF (4 ppm) NITRITE

Interferent	Permissible conc. (ppm)	Interferent	Permissible conc. (ppm)
Chloride	300	Bicarbonate	200
Sulphate	220	Phosphate	280
Carbonate	210	Cyanide	150
Nitrate	140	Calcium(II)	200
Cobalt(II)	200	Copper(II)	150
Magnesium(II)	200	Barium(II)	300
Zirconium(IV)	200	Mercury(II)	200
Cadmium(II)	200	Bismuth(III) <sup>x</sup>	300
Iron(III) <sup>x</sup>	100	Iodide <sup>A</sup>	20
Aniline	20	Formaldehyde	20
Sulphite <sup>S</sup>	10	Sulphur dioxide <sup>S</sup>	10
Sulphide <sup>A</sup>	10		

x = Masked with 1 mL of 10% sodium potassium tartrate.

A = Removed by precipitation of HgS or HgI by the addition of 1 mL of 0.2% HgCl<sub>2</sub> solution.

S = Masked with H<sub>2</sub>O<sub>2</sub> (30%) solution.

**Application to Polluted Water:** Samples were collected from the source of industrial effluents. Samples of potable water were collected from different tanks. Mercuric chloride (4 mg per 100 mL of sample) was used to remove any sulphides and iodides may be present in water. Samples were filtered through a Whatman No. 41 paper before analysis.

A set of experiments was performed to check the validity of the method. It was found from the experiment that no water sample can contain nitrite. Therefore recovery of nitrite was checked by adding various amounts of known nitrites to

a fixed volume of test solution. Recoveries were between 98.5 and 100%. The results are given in Tables 2 and 3.

TABLE-2  
TAP WATER ANALYSIS  
(Means of seven analyses, 10 mL sample)

Nitrite added µg/25 mL	Present method		Saltzman standard method <sup>12</sup>	
	Nitrite found µg/25 mL	Recovery %	Nitrite found µg/25 mL	Recovery %
1.25	1.25	100.0	1.26	100.8
5.0	4.97	99.4	5.00	100.0
10.0	9.98	99.8	9.98	99.8
15.0	14.95	99.6	14.96	99.7
20.0	19.95	99.7	19.95	99.7
25.0	24.92	99.6	25.00	100.0
30.0	30.00	100.0	30.00	100.0

TABLE-3  
INDUSTRIAL EFFLUENT\* WATER ANALYSIS BY THE  
STANDARD METHOD  
(Means of five analyses, 10 mL sample)

Sample	Nitrite found (ppm)	
	Present method	Standard method
1.	1.25	1.24
2.	2.50	2.50
3.	3.75	3.76
4.	4.50	4.52
5.	6.25	6.26

\*Water collected from Kukkarahalli lake near University Campus.

## Conclusion

The present method is more sensitive than the standard method. The rapid colour development, excellent reproducibility and freedom from interference by a large group of foreign ions are advantages of the method. This method require neither extraction nor heating.

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