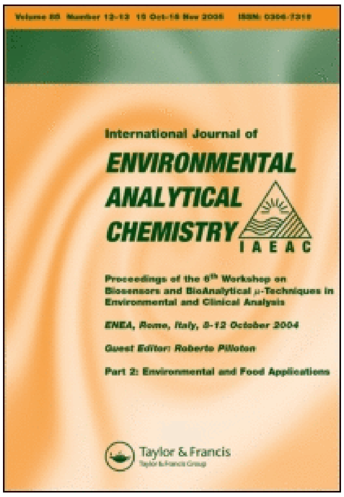

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Spectrophotometric Determination of Nitrite in Aqueous Solution by the Diazotization-Coupling Method with p-Aminoacetophenone-N-(1-Naphthyl)ethylenediamine

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A sensitive spectrophotometric method for the determination of nitrite is worked out. It depends on the reaction of the intended ion with an acidified p-aminoacetophenone solution to form a diazonium cation, which is subsequently coupled with N-(1-naphthyl)ethylenediamine to form a reddish purple colored water-soluble and intense azo dye with maximum absorption at 550 nm. The curve of absorbance versus concentration is linear, indicating that Beer's law is obeyed over the range 1–20 μg of nitrite in a final volume of 25 ml, i.e., 0.04–0.8 ppm, with a molar absorptivity of $5.75 \times 10^4 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$, a relative error of -0.8 to $+1.2\%$ and a relative standard deviation of 0.1–2.7%, depending on the level of determinand concentration. The optimum conditions affecting the color reaction and interference due to foreign ions have been examined.

KEY WORDS: Nitrite determination, aqueous solution, spectrophotometry, diazotization-coupling method, p-aminoacetophenone-N-(1-naphthyl)ethylenediamine.

INTRODUCTION

The determination of nitrite is very important from both the health and pollution points of view. The presence of nitrite, due to microbial oxidation and reduction of ammonia and nitrate in water, indicates pollution.[1] Also, the increasing use of nitrite in foods, fertilizers, detergents, and other industries has caused serious pollution problems. Further, nitrite has been shown[2,3] to play an important role in the formation of N-nitrosamines, many of which are potent carcinogens. The allowable limit of nitrite in potable water as fixed by U.S. Public Health Service is 0.06 ppm.

Because of their sensitivity and simplicity, most of the methods used for the spectrophotometric determination of nitrite are based on the Griess–Ilosavy reaction[4–7] and these are continuously modified by changing the diazotizing reagent as well as the coupling agent for the sake of more favourable results.

In the present investigation, p-aminoacetophenone as the diazotizing reagent, and N-(1-naphthyl)ethylenediamine as the coupling agent have been the choice to form the basis of an analytical method for the determination of nitrite in aqueous solution. The main features of this new method are the use of non-toxic and easily water soluble compounds, i.e., p-aminoacetophenone and N-(1-naphthyl)ethylenediamine (compare p-nitroaniline and azulene),[7] and the fair sensitivity.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade.

Stock nitrite solution, 1 mg ml^{-1}. A 0.1499 g of dried sodium nitrite was dissolved in distilled water containing a pellet of sodium hydroxide to prevent nitrous acid liberation, and 1 ml of chloroform to inhibit bacterial growth,[8] and the volume was diluted to 100 ml with distilled water. This solution was kept in the refrigerator.

Working nitrite solution, 10 μg ml^{-1}. One ml of the stock nitrite solution was diluted to 100 ml, in a volumetric flask, with distilled water. This solution was kept in the refrigerator when not in use.

p-Aminoacetophenone reagent solution, 0.4%. A 0.4 g of the amine was dissolved in distilled water containing 50 ml of 0.5 N hydrochloric acid solution (prepared by dilution of the concentrated BDH volumetric solution), and the volume was made up to 100 ml, in a volumetric flask, with distilled water. This solution was transferred to a brown bottle and kept in a refrigerator when not in use.

N-(1-Naphthyl)ethylenediamine (N-NED) reagent solution, 0.65%. A 0.65 g of the compound ($\text{N-NED} \cdot 2\,\text{HCL} \cdot CH_3OH$) was dissolved in distilled water and the volume was made up to 100 ml, in a volumetric flask, with distilled water. This solution was transferred to a brown bottle and kept in the refrigerator when not in use.

Foreign ion solutions, 1 mg ml^{-1}. These solutions were prepared by dissolving an amount of the compound in distilled water and completing the volume in a volumetric flask.

Apparatus

All absorption measurements were carried out on a Pye Unicam SP 30 UV digital double-beam spectrophotometer using 1 cm optical glass cells.

Procedure

To a series of 25 ml volumetric flasks were transferred increasing volumes of working nitrite solution to cover the range of 1–20 μg. Four ml of p-aminoacetophenone reagent solution and 1 ml of N-NED solution were added and final volumes were made up to the mark with distilled water. The absorbances were measured, against a reagent blank prepared in the same manner but without nitrite, at 550 nm using 1 cm cells. The color develops immediately and is stable for at least 5 h. A straight-line calibration curve passing through the origin was obtained, showing that the colored system followed Beer's law over the concentration range of 1–20 μg of nitrite in a final volume of 25-ml, i.e., 0.04–0.8 ppm. The conditional molar absorptivity,[9] calculated in the region of least photometric error at the wavelength of measurement, was found to be $5.75 \times 10^4\ \text{l mol}^{-1}\,\text{cm}^{-1}$ and a sensitivity index[10] of 0.0008 $\mu\text{g cm}^{-2}$.

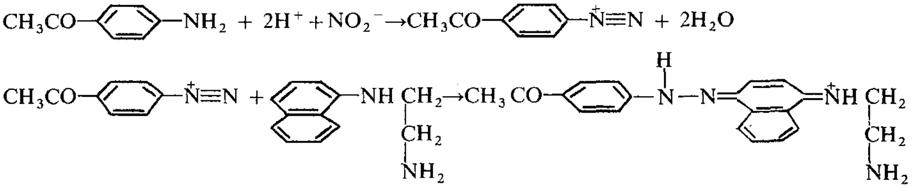
For the subsequent experiments, 10 μg of nitrite were taken and final volumes were made 25 ml.

RESULTS AND DISCUSSION

The couple, p-aminoacetophenone-N-NED, has been the choice of this investigation because, to our knowledge, this couple has been neither used nor suggested previously;[11] moreover p-aminoacetophenone is easily soluble in mineral acids, is rapidly diazotized, and giving a water-soluble azo dye under the conditions of determination thus eliminating the time-consuming extraction process.

Color reaction

The reaction sequence in the procedure involves two steps. In the first, p-aminoacetophenone reacts with nitrite to form the corresponding diazonium cation. In the second step, the diazonium cation is coupled with N-NED to form the reddish purple azo dye. The reactions can be represented as follows:



The electrophilic substitution of the diazonium ion at position 4 is known.[12–14] These reactions are very fast at room temperature and are the basis of the present method.

Absorption spectra

When nitrite ion was treated according to the recommended procedure, the absorption spectrum, shown in Figure 1, was obtained. The maximum absorption occurred at 550 nm and being characteristic of the reddish purple azo dye in contrast to the transparent blank reagent which gave an almost flat absorption in the scanned (450–600 nm) region. The absorbance measurements were made at 550 nm against the reagent blank.

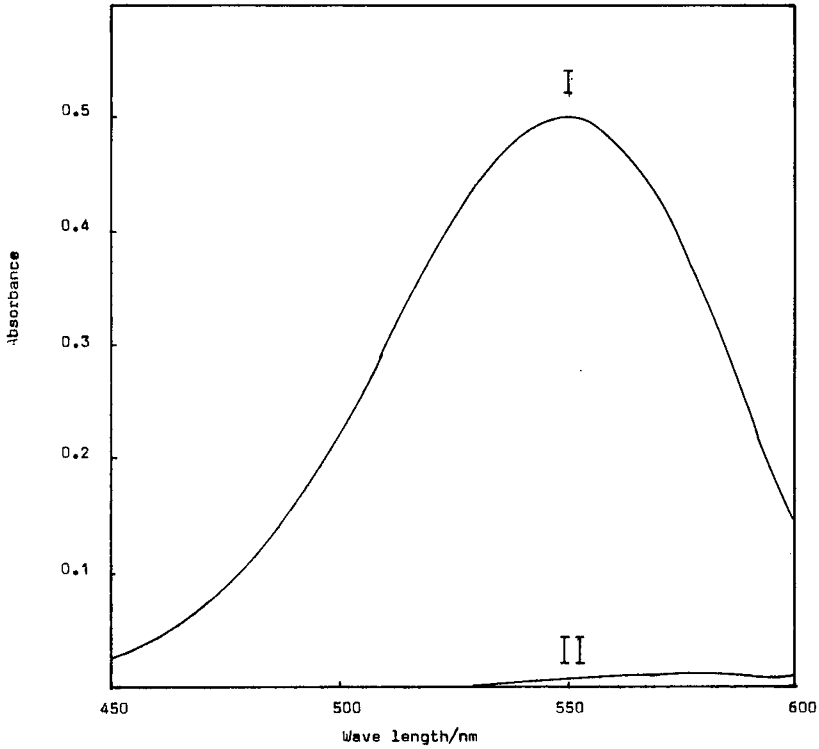


FIGURE 1 Absorption spectra of (I) 10 μg of nitrite, treated as in the procedure, measured against reagent blank, and (II) reagent blank measured against distilled water.

Effect of diazo components

The effect of p-aminoacetophenone concentration on the maximum formation of the colored azo dye was first studied, and a concentration of 0.2–1.6% of the amine was tested. The experimental data revealed that 0.2–0.6% gave maximum and constant absorbance, and 0.4% was recommended for the procedure. Keeping the optimum amount of the amine constant, the effect of mineral acid, which is essential for the diazotization process, was next examined. In this respect, hydrochloric, nitric, sulfuric, phosphoric, and acetic acids were tried. The results showed that the most effective acid was the hydrochloric acid followed by nitric-sulfuric acids, phosphoric acid and the least effective acetic acid. Hydrochloric acid was studied further with respect to its amount effect on the colored azo dye intensity. It was shown that 50 ml of 0.5 N acid per 100 ml of the total volume of the prepared p-aminoacetophenone solution was the optimum amount.

The effect of the volume of the composite reagent (p-aminoacetophenone + hydrochloric acid) was studied. It was found that 4 ml of the composite reagent yielded maximum absorption.

Effect of coupling agent

Keeping the optimum amount of the composite reagent constant, the amount of N-NED was varied. It was found that 0.5–5 ml of 0.65% solution gave maximum and essentially the same absorbance. A 1 ml of the prescribed N-NED solution is kept for use in the procedure.

Color stability

The reddish purple azo dye developed immediately and the intensity of the color remains stable and at its maximum for at least 5 h. The stability of the colored azo dye is sufficient for a large number of measurements to be performed at the same time.

Adherence to Beer's law and sensitivity

The linearity of the change of the absorbance with the changes in the amounts of nitrite present was tested by reacting aliquots of standard solution containing from 1 to 20 μg of nitrite and measuring the abosrbance at 550 nm. Beer's law is obeyed in this range. The sensitivity of the method, expressed as the weight of nitrite corresponding to an absorbance of 0.001 in a 1 cm cell, at 550 nm, is 0.0008 $\mu\text{g cm}^{-2}$. The molar absorptivity is $5.75 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$.

Accuracy and precision of the method

Under the optimum conditions, the accuracy and precision of the present method was checked by measuring nitrite ion at three different concentrations. The results are shown in Table I and indicate that the method is satisfactory.

TABLE I
Accuracy and precision of the method

Nitrite taken/μg	Relative error%[a]	Relative standard deviation%[a]
1	+1.2	2.7
10	−0.8	0.5
20	−0.01	0.1

[a] Of five determinations.

Interferences

In order to realize the possible analytical applications of the proposed method, the effect of foreign ions that may accompany nitrite was examined by performing determinations of 10 μg of nitrite using the recommended procedure. The results are shown in Table II.

TABLE II
Effect of foreign ions on nitrite (10 μg) determination

Interferent	Added as	Amount added/μg	Interference %
Ammonium	NH_4Cl	1000	+0.2
Carbonate	Na_2CO_3	1000	+1.2
Chloride	KCl	1000	+0.3
Fluoride	NaF	100	−0.6
Iodide	NaI	1000	+2.3
Hydrogen carbonate	$NaHCO_3$	100	0.0
Nitrate	KNO_3	100	+1.4
Phosphate	KH_2PO_4	1000	+2.3
Sulfide	$Na_2S \cdot 2H_2O$	100	0.0
Calcium (II)	$CaCl_2$	100	+0.6
Cadmium (II)	$CdCl_2 . 2H_2O$	100	+0.2
Cobalt (II)	$CoCl_2 \cdot 6H_2O$	1000	−1.8
Copper (II)	$CuSO_4 \cdot 5H_2O$	1000	−1.8
Iron (III)	$Fe_2(SO_4)_3$	100	+1.4
Magnesium (II)	$MgSO_4 \cdot 7H_2O$	1000	+0.1
Phenol	—	100	0.0

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