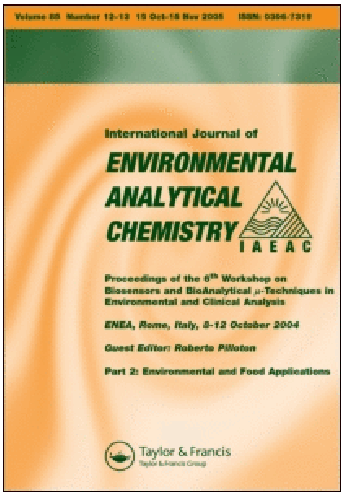

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Spectrophotometric Determination of Nitrite in Aqueous Solution by the Diazotization-Coupling Method with Orthanilic Acid-Resorcinol

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A spectrophotometric method for the determination of nitrite is described. It relies upon the reaction of this ion with an acidified orthanilic acid solution to form a diazonium ion, which is subsequently coupled with resorcinol, in alkaline medium, to form immediately a yellow-colored stable water-soluble and intense azo dye having maximum absorption at 426 nm. The linear absorbance plot with concentration indicates that Beer's law is obeyed over the range of 1–12 μg of nitrite in a final volume of 10 ml, with a molar absorptivity of 38.7×10^3 l mol^{-1} cm^{-1}, sensitivity index of 0.0012 μg cm^{-3}, relative error of -0.5 to $+0.2\%$ and relative standard deviation of 0.43–3.5%, depending on the concentration level. The optimum conditions affecting and related to the color reaction and interference due to foreign ions have been studied.

KEY WORDS: Nitrite determination, aqueous solution, spectrophotometry, diazotization-coupling method, orthanilic acid-resorcinol.

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, orthanilic acid as the diazotizing reagent, and resorcinol 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., orthanilic acid and resorcinol (compare *p*-nitroaniline and oxine),[7] the selectivity, and the fair sensitivity.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade

Standard nitrite solution. A 0.1499 g of sodium nitrite was dissolved in distilled water, containing a pellet of sodium hydroxide to prevent liberation of nitrous acid, and 1 ml of spectroscopic-grade chloroform to inhibit bacterial growth,[8] and the volume was diluted to 1000 ml with distilled water. This solution, which gives 100 ppm of nitrite ion, was diluted for use in construction of the calibration curve.

Orthanilic acid solution. A 0.2 g of the compound was dissolved in distilled water containing 3 ml of concentrated hydrochloric acid, and the volume was diluted to 100 ml with distilled water.

Resorcinol solution. A 0.2%(w/v) aqueous solution was used.

Potassium hydroxide solution. A 2%(w/v) solution was used.

Apparatus

All spectral and absorbance measurements were carried out on a Shimadzu UV-210A double -beam recording spectrophotometer with 1 cm optical glass matched cells.

Procedure

To a series of 10 ml volumetric flasks were transferred from about 1 to 12 μg of nitrite, 1 ml of the orthanilic acid solution, 1 ml of resorcinol solution, 2 ml of potassium hydroxide solution, and distilled water to the mark. The absorbances were measured, against a reagent blank prepared in the same manner but containing no nitrite, at 426 nm using 1 cm cells. The color develops immediately and is stable for 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 1–12 μg of nitrite in a final volume of 10 ml, i.e., 0.1–1.2 ppm. The conditional molar absorptivity, calculated in the region of least photometric error at the wavelength of measurement, was found to be $38.7 \times 10^3 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$.

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

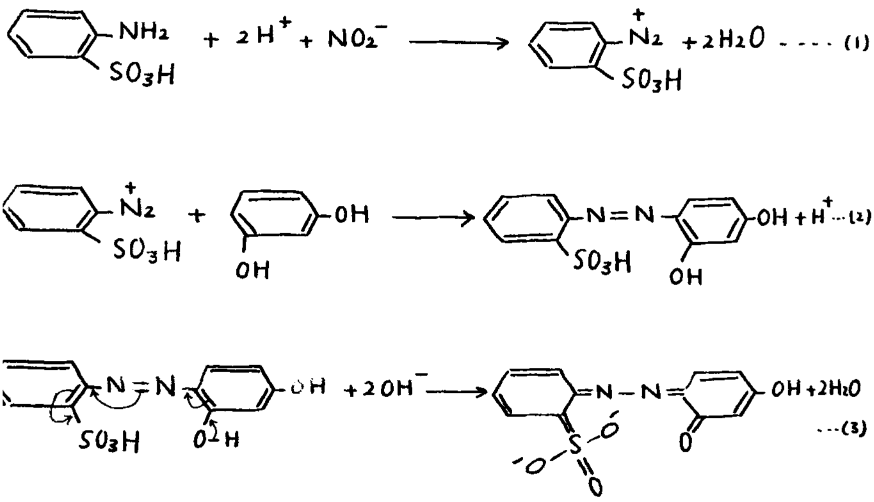
RESULTS AND DISCUSSION

The couple, orthanilic acid-resorcinol, has been the choice of this investigation because, to our knowledge, this couple has been neither used nor suggested previously;[9] moreover orthanilic acid 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. Resorcinol is fairly soluble in water, thus avoiding the use of organic solvents, and is non-toxic.

In the preliminary experiments, the determination of nitrite was attempted under the experimental conditions described previously for the same ion.[4–6] However, the results obtained were not very satisfactory, and optimum reaction conditions were therefore sought.

Color reaction

Nitrite reacts with orthanilic acid, in acidic medium, to form the corresponding diazonium ion. This couples with resorcinol to form, in alkaline medium, intense yellow-colored azo dye which is the basis of the present method. The reaction sequence may be postulated as follows:



Absorption spectra

When nitrite ion was treated according to the recommended procedure, the absorption spectrum, shown in Figure 1, was obtained. The maximum absorption, at 426 nm, characteristic of the azo dye was used in all subsequent measurements. The slight absorption of the reagent blank at 426 nm emphasized the need for measurements to be performed against the reagent blank.

Effect of diazo components

The effect of orthanilic acid concentration on the maximum formation of the colored azo dye was first studied, and a

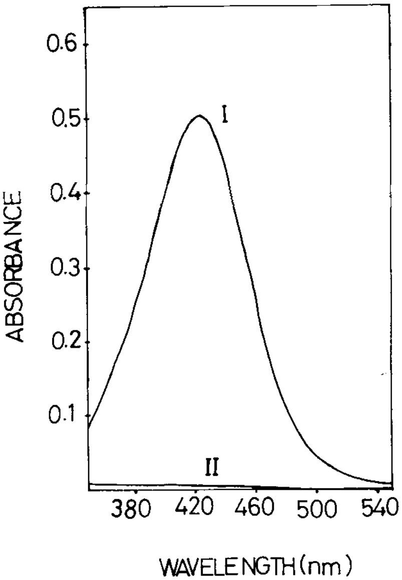


FIGURE 1. Absorption spectra of (I) 6 μg of nitrite, treated as in the procedure, measured against reagent blank, and (II) reagent blank measured against distilled water.

concentration of 0.1–0.3% of the acid was tested. The experimental results showed that 0.17–0.25% was optimum, and 0.2% was recommended in the procedure. Next, the effect of hydrochloric acid concentration, which is essential for the diazotisation process, on the intensity of the colored azo dye was investigated, and 1–4 ml of the concentrated (11.6 M) hydrochloric acid per 100 ml of the total volume of the prepared orthanilic acid solution was used. The data obtained showed that 3–3.2 ml of the hydrochloric acid solution gave maximum absorbance, and 3 ml was incorporated in the procedure. Other acids were not tried.

The effect of the volume of the composite reagent (orthanilic acid + hydrochloric acid) was studied. It was found that 1 ml of the composite reagent yielded maximum absorption.

Choice of coupling agent

Tiron (disodium salt), 8-hydroxyquinoline, 1-naphthol, 2-naphthol, and resorcinol were tried as coupling agents. Only resorcinol gave maximum color formation. Tiron, for example, although water soluble, gave a very pale yellow color. 1- and 2-Naphthols coupled but with a lower intensity as it is with oxine and which is water insoluble and highly toxic (carcinogen). Therefore, only resorcinol was studied further.

Effect of resorcinol concentration

Resorcinol has the further advantage, over the naphthols and oxine, in being highly water soluble. A resorcinol concentration of 0.1–0.4% was studied, and a concentration of 0.1–0.3% gave maximal absorbance. A 1 ml of 0.2% resorcinol solution was kept for use in the procedure.

Effect of potassium hydroxide solution

The presence of alkali is essential for developing the intense yellow color. The alkalis tested were sodium carbonate, sodium hydroxide, and potassium hydroxide. Sodium carbonate solution showed two but less intense bands in the absorption spectrum. Sodium hydroxide showed a single band with a lower molar absorptivity than that with a potassium hydroxide solution. Consequently, potassium hydroxide was selected and 2 ml of 2% solution gave the optimum results.

Color stability

The yellow color of the azo dye formed develops instantaneously and remains stable for 5 h, after which there was a gradual deterioration.

Accuracy, precision, and sensitivity of the method

Under the optimum conditions, the accuracy and precision (five replicates) of the method were checked. The results, shown in Table I, indicates a reliable method. The sensitivity of the method according to Sandell[10] in 1 cm cell at 426 nm is 0.0012 μg cm^{-2}.

Interferences

In order to realize the possible analytical applications of the

TABLE I

Accuracy and precision of the method

Nitrite taken/μg	Relative error %	Relative standard deviation %
1	−0.5	3.5
5	+0.9	2.3
12	+0.2	0.43

proposed method, the effect of foreign ions that often accompany nitrite is examined by performing determinations of 10 μg of the ion in the presence of each of these ions, in a final volume of 10 ml, i.e., 1 ppm nitrite. The tolerable amounts are: bicarbonate (230 ppm), carbonate (110 ppm), chloride (550 ppm), cyanide (120 ppm), fluoride (440 ppm), nitrate (180 ppm), oxalate (900 ppm), phosphate (140 ppm), sulfate (1300 ppm), sulfide (6 ppm) sulfite (800 ppm), barium (90 ppm), cadmium (41 ppm), calcium (85 ppm), cobalt(II) (4 ppm), copper(II) (35 ppm), lead(II) (93 ppm), magnesium (55 ppm), manganese (30 ppm), mercury(II), nickel(II) (110 ppm), and zinc (120 ppm). These figures correspond to the amount of diverse ions causing an error equal to or better than ±2% in the absorbance reading.

The present method is generally more selective and far more sensitive than the methods[4–6] published from this laboratory. Also, it compares very favourably with the oxine method[7] from both the sensitivity and selectivity points of view.

References

1. C. N. Sawyer and P. L. McCarty, "Chemistry for Environmental Engineering", (McGraw-Hill, New York, p. 440, 1978).
2. W. Lijinsky and S. S. Epstein, *Nature* **225**, 21 (1970).
3. I. A. Wolff and A. E. Wasserman, *Science* **177**, 15 (1972).
4. S. Flamerz and W. A. Bashir, *Analyst* **106**, 243 (1981).
5. W. A. Bashir and S. Flamerz, *Talanta* **28**, 697 (1981).
6. S. Flamerz and W. A. Bashir, *Microchem. J.* **26**, 586 (1981).
7. J. Nair and V. K. Gupta, *Anal. Chim. Acta* **111**, 311 (1979).
8. R. B. Lew, *Analyst* **102**, 476 (1977).
9. E. Sawicki, T. W. Stanley, J. Pfaff and A. D'Amico, *Talanta* **10**, 641 (1963).
10. E. B. Sandell, "Colorimetric Determination of Traces of Metals", (Interscience, New York, p. 83, 1959).