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SPECTROMETRIC DETERMINATION OF NITRITE IN AQUEOUS SOLUTION BY THE DIAZOTIZATION-COUPLING METHOD WITH *p*-AMINOBENZOPHENONE-*N*-(1-NAPHTHYL)- ETHYLENEDIAMINE

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Nitrite ion at low concentration is determined spectrometrically by diazotization of *p*-aminobenzophenone and coupling of the resulting diazonium cation with *N*-(1-naphthyl)-ethylene-diamine to form a reddish-violet coloured water-soluble azo dye with maximum absorption at 555 nm. The method is suitable for the determination of nitrite over the range of 0.04–1.00 ppm. Beer's law is obeyed over this range of concentrations. The observed molar absorptivity and Sandell's sensitivity of the azo dye are $7.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $6.5 \times 10^{-4} \mu\text{g cm}^{-2}$, respectively. Interferences due to other ions were studied to test the selectivity.

KEY WORDS: Nitrite determination, aqueous solution, spectrometry, diazotization-coupling method, *p*-aminobenzophenone-*N*-(1-naphthyl)-ethylenediamine

INTRODUCTION

Nitrite is regarded as one of the important pollutants present in water; its formation in water is due to microbial oxidation and reduction of ammonia and nitrate.¹ Nitrites are considered as potentially hazardous compounds due to the formation of carcinogenic *N*-nitroso compounds by the reaction with secondary or tertiary amines and amides² or through the reaction with the biological precursors present in the curing solutions.³ The allowable level of nitrite in potable water was fixed by the US Public Health Service as 0.06 ppm.⁴ Several methods are available for the determination of nitrite, most of which represent modification of the classical Griess–Ilosavy diazo reaction,^{5–9} involving the diazotization of an aromatic amine and coupling of the diazo compound with a naphthalene derivative to form a highly coloured azo dye. In this paper, a new reagent, *p*-aminobenzophenone, is used as the diazotizable amine and *N*-(1-naphthyl)-ethylenediamine (*N*-NED) as the coupling agent. This system gives good results for the determination of nitrite ion in aqueous solutions with high sensitivity, simplicity and rapidity.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade.

Stock nitrite solution, 1 mg ml⁻¹ A 1000 ppm stock solution was prepared by dissolving 0.1499 g of a reagent-grade NaNO₂ in distilled water containing a pellet of sodium hydroxide to prevent nitrous acid liberation; 1 ml of spectroscopic-grade chloroform was added to prevent bacterial growth,¹⁰ and the volume was then made up to 100 ml with distilled water of nitrite ion. Less concentrated solutions were prepared by dilution with distilled water. All solutions were kept in the refrigerator when not in use.

p-Aminobenzophenone, 0.3% Amine (0.3 g) was dissolved in distilled water containing 60 ml of 1 M hydrochloric acid (BDH) and 5 ml of 5 M acetic acid (Fluka), and the volume was made up to 100 ml in a volumetric flask with distilled water. The addition of acetic acid was found to be necessary for dissolving the amine.

N-(1-naphthyl)-ethylenediamine (N-NED) reagent solution, 0.5% The compound (0.5 g N-NED.2HCl.CH₃OH; Fluka) was dissolved in 100 ml of distilled water. The solution was kept in the refrigerator in a brown bottle when not in use.

Foreign ion solutions, 1 mg ml⁻¹ These solutions were prepared by dissolving the calculated amount of the compound in distilled water and making up to volume in a volumetric flask.

Apparatus

Spectral and absorbance measurements were made with a Pye Unicam digital single-beam SP 6-350 spectrophotometer using 1-cm glass cells.

Procedure

Increasing volumes of the working nitrite solution were transferred to a series of 25 ml volumetric flasks to cover the range of 1–25 μg. Before making up the volume to the mark with distilled water, 6 ml of *p*-aminobenzophenone and 5 ml of *N*-NED solution were added. The absorbances of these solutions were measured against a reagent blank containing the same amounts of reagents used except nitrite ion, at 555 nm using 1-cm glass cells. The colour develops immediately and is stable for about 60 min.

RESULTS AND DISCUSSION

Absorption Spectra

When an aqueous solution of *N*-NED was added to a mixture of *p*-aminobenzophenone and hydrochloric acid, in the presence of nitrite (diazotized salt or cation) a reddish-violet dye forms immediately. The azo dye formed shows a maximum

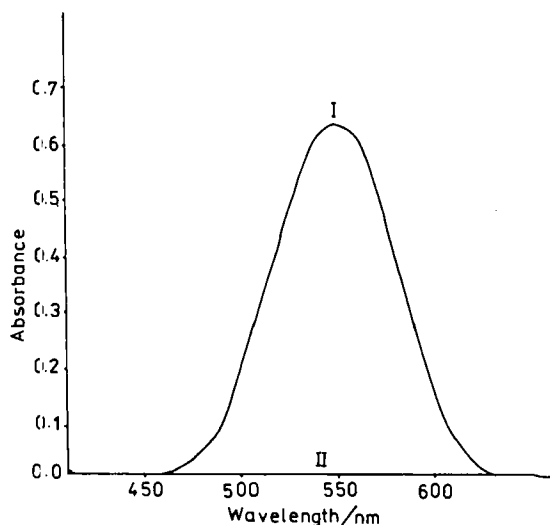
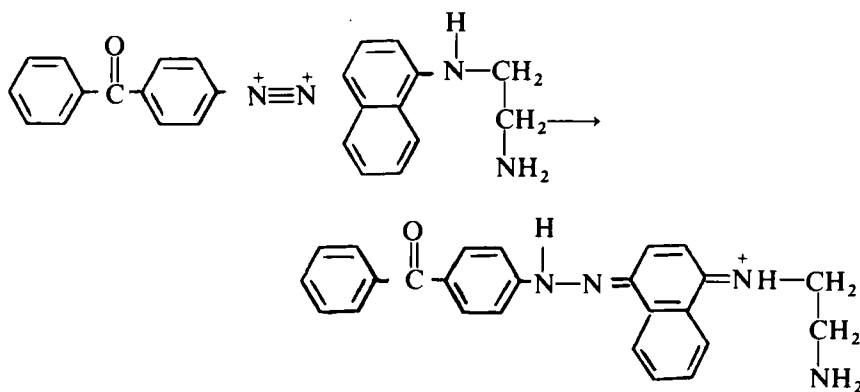
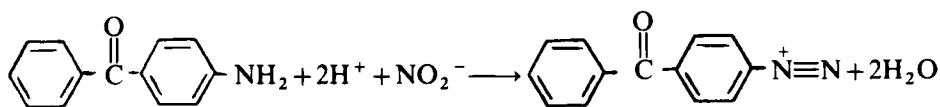


Figure 1 Absorption spectra of (I) 10 μg of nitrite treated as in the procedure, measured against reagent blank, and (II) reagent blank measured against distilled water.

absorption at 555 nm against a reagent blank which shows no absorption in this region (Figure 1).

Colour Reaction

The reaction sequence in the method involves two steps. In the first, *p*-aminobenzophenone reacts with nitrite to form the corresponding diazonium cation. In the second step, the diazonium cation couples with *N*-NED to form the azo dye. The reactions can be represented as follows:



The electrophilic substitution of the diazonium ion at the para position is well known.¹³⁻¹⁴

Study of the optimum reaction conditions

The effect of different parameters on the absorption intensity of the azo dye were studied and the reaction conditions were optimized.

Effect of reagents The amounts of the various reagents were varied to obtain maximum absorbance. The effect of the concentration of the *p*-aminobenzophenone was first studied, and a concentration of 0.1–0.5% of the amine was tested. It was found that 0.3% is the optimum amount, because it shows maximum absorption under the given conditions. A larger amount of the amine causes turbidity which retards any determination. Keeping the optimum amount of the amine constant, the effect of hydrochloric acid was next examined, the range of 5–70 ml of 1 M hydrochloric acid per 100 ml total volume being studied; 60 ml of 1 M acid per 100 ml of the prepared *p*-aminobenzophenone solution was the optimum amount. The effect of the volume of the composite reagent (*p*-aminobenzophenone + hydrochloric acid) was studied next; 6 ml of this reagent gave maximum absorption. Finally, the effect of different amounts of the coupling agent (*N*-NED) on the reaction was studied. At a constant amount of composite reagent, 4.0–6.0 ml of 0.5% solution gave maximum absorption. Five ml of 0.5% solution of *N*-NED was used in our procedure.

Effect of time The azo dye formation was instantaneous and the absorbance remained constant and maximum for about 60 min; after that, a gradual decrease was observed.

Beer's law and sensitivity Beer's law was obeyed in the concentration range 1–25 μg of nitrite in a final volume of 25 ml, i.e., 0.04–1.00 ppm. The calculated molar absorptivity in the region of least photometric error, and the sensitivity of the method in 1-cm glass cells at 555 nm were $7.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $6.5 \times 10^{-4} \mu\text{g cm}^{-2}$, respectively.

Accuracy and precision of the method For determining the accuracy and precision of the method, the procedure was carried out using three different concentrations of nitrite ion. The results, given in Table 1, indicate high accuracy and precision.

Interferences The interferences of various cations and anions which usually accompany nitrite was studied by adding 100–1000 μg of the ions per 25 ml of solution containing 10 μg of nitrite and proceeding as recommended in procedure. Table 2 shows that only Cu(II), Fe(III) and phosphate cause a real, although still slight, interference. A 10 μg amount of nitrite, when added to 10 ml of tap water and determined by the proposed method gave an error of –3.0% (one determination only due to lack of *N*-NED reagent).

Table 1 Accuracy and precision of the method ($n = 5$)

Nitrite taken ($\mu\text{g}/25\text{ ml}$)	Relative error (%)	Rel. standard deviation (%)
1	+2.4	2.4
10	-0.1	0.43
25	+0.03	0.41

Table 2 Effect of foreign ions on nitrite determination

Interfering	Added as	Amount added (μg)	Interference (%)
Ammonium	NH_4Cl	500	+0.2
Chloride	KCl	1000	-0.2
Fluoride	NaF	500	-0.7
Bromide	NaBr	500	-0.2
Iodide	KI	100	-1.0
Barium (II)	BaBr_2	100	-1.6
Calcium (II)	CaCl_2	1000	-1.3
Cadmium (II)	$\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$	100	-1.6
Copper (II)	CuCl_2	500	-2.5
Cobalt (II)	CoCl_2	500	+0.3
Chromium (III)	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	500	0.0
Hydrogen carbonate	NaHCO_3	500	+1.6
Iron (III)	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1000	+2.1
Lead (II)	$\text{Pb}(\text{NO}_3)_2$	500	-0.2
Magnesium (II)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100	+0.7
Nickel (II)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	500	-1.1
Phosphate	NaH_2PO_4	1000	+3.3
Sulphate	K_2SO_4	1000	+0.3
Sulphite	Na_2SO_3	500	-0.7

Table 3 Comparison of the proposed method with some Griess modifications for the determination of nitrite

Reagent	λ_{max} (nm)	ϵ ($\text{l. mol}^{-1} \cdot \text{cm}^{-1}$)	Determination range (ppm)	Ref.
<i>p</i> -Aminobenzoic acid	519	3.5×10^4	0.1 -1.3	15
Indole	530	9.5×10^3	0.5 -2	16
<i>p</i> -Aminosalicylic acid	520	14.7×10^3	0.1 -3	17
<i>p</i> -Aminobenzoic acid	499	3.2×10^4	0.1 -1.5	18
<i>p</i> -Nitroaniline	550	3.2×10^4	0.08-1.1	19
<i>p</i> -Aminobenzotrifluoride	510	3.9×10^4	0.03-0.8	20
<i>p</i> -Aminobenzophenone	555	7.0×10^4	0.04-1.0	This work

CONCLUSION

Rapid colour development, simplicity, high sensitivity, temperature independence and the elimination of extraction steps make the proposed method superior to most of the Griess modifications. A comparison with some Griess modifications is shown in Table 3. The selectivity of the procedure makes it useful in routine analysis of nitrite in water samples, in which many of the common ions do not interfere.

References

1. C. N. Sawyer and P. L. McCarty, *Chemistry for Environmental Engineering* (McGraw-Hill, New York, 1978), p. 440.
2. P. Magee and J. Barnes, *Brit. J. Cancer* **10**, 114 (1956).
3. R. F. Theiler, K. Sato, T. G. Aspelund and A. F. Miller, *J. of Food Science* **46**, 996 (1981).
4. J. E. McKee and W. Wolf, *Resources Agency of Control Board Publication* **3(A)**, 224 (1969).
5. E. E. Garcia, *Anal. Chem.* **39**, 1605 (1967).
6. F. Celardin, M. Marcantonatos and D. Monnier, *Anal. Chim. Acta* **68**, 61 (1974).
7. K. Tōei and T. Kiyose, *Anal. Chim. Acta* **88**, 125 (1977).
8. G. Norwitz and P. N. Keliher, *Analyst* **109**, 1281 (1984).
9. P. K. Tarafder and D. P. S. Rathore, *Analyst* **113**, 1073 (1988).
10. R. B. Lew, *Analyst* **102**, 476 (1977).
11. I. L. Finar, *Organic Chemistry* (Longman, London, 1963), 4th ed., Vol. 1, p. 718.
12. B. Sulaiman and W. A. Bashir, *Analyst* **109**, 1409 (1984).
13. S. A. Rahim, W. A. Bashir and B. B. Ibrahim, *Analyst* **109**, 955 (1984).
14. K. A. Abdullah, A. G. M. Al-Daher and W. A. Bashir, *Analyst* **110**, 409 (1985).
15. S. Flamerz and W. A. Bashir, *Microchem. J.* **26**, 586 (1981).
16. S. A. Rahim, N. A. Fakhri and W. A. Bashir, *Microchem. J.* **28**, 479 (1983).
17. S. Flamerz and W. A. Bashir, *Analyst* **106**, 243 (1981).
18. W. A. Bashir and S. Flamerz, *Talanta* **28**, 697 (1981).
19. J. Nair and V. K. Gupta, *Anal. Chim. Acta* **111**, 313 (1979).
20. D. Amin, *Analyst* **111**, 1335 (1986).