

Spectrophotometric Determination of Nitrite By The Diazotization Coupling With Aniline and 4,6 Dihydroxy-2 Mercaptopyrimidine

H. J. Mohammed, D. S. Hassan and A. Hmood
**Department of Chemistry, College of Education for
women, University of Kufa**

Abstract

A direct spectrophotometric method has been developed for the determination of nitrite in aqueous solution. The method is based on the reaction of the nitrite ion with an acidified aniline solution from diazonium cation, which is subsequently coupled with 4,6 - dihydroxy - 2- mercapto pyrimidine to form yellow colored and water - soluble intense azo dye with maximum absorption at 416nm . A graph of absorbance versus concentration shows that Beer's Law is obeyed over the concentration range of 20 -100 μg of nitrite in final volume of ml (i.e., 2-10 ppm) with a molar absorptivity of $(3.5 \times 10^3 \text{ L.mole}^{-1} .\text{cm}^{-1})$, a Sandall sensitivity of $(0.12 \mu\text{g} .\text{cm}^{-2})$, a relative error of (-0.05%) (-0.65%) and a relative standard deviation $(0.86-1.0\%)$ depending on the concentration.

Key word: Nitrite determination; aniline; diazotization coupling.

Introduction

Most of the methods used for the spectrophotometric determination of nitrite are based on the Griess reaction and these are continuously modified by using different diazotizing reagents as well as the coupling agent to best result (1-5). Pyridylazo and thiazolylazo compounds such as 1- (2-pyridylazo) -2-naphthol and 2-(2-thiazolylazo)- 5- diethylaminobenzoic acid derivatives, (6-8) have been synthesized and proposed as highly sensitive chromogenic in addition to being important complexing agents (9). The determination of nitrite ion at low concentration is very important from both health and Pollution, the presence of nitrite

in a raw water supply usually denotes bacterial activity and is often taken as indicative of the bacterial reduction of nitrite (10). In this paper a Simple and accurate method to determine nitrite is described using aniline as the diazotizing reagent and (DHMP) as the coupling agent has been the choice to from the basic of analytical method.

Experimental

All spectral and absorbance measurements were carried out on a Shimadzu UV-Vis 1700 digital double beam recording spectrophotometer using 1cm optical glass cells.

Reagent and materials

Analytical reagent grade chemicals and distilled water were used throughout. Nitrite ($1000 \mu\text{g/mL}$)

Standard nitrite solution was prepared by dissolving 0.149 gm of sodium nitrite in 100ml distilled water, working standard solution were prepared by simple dilution of the appropriate volume of the standard solution ($1000 \mu\text{g/mL}$) with distilled water.

-Sodium bicarbonate(5%): A 5g of NaHCO_3 was dissolved in 100mL of distilled water.

-Aniline (0.01M)

A 0.1 g of aniline was dissolved in 50 ml of ethanol containing 1.5 ml of concentrated hydrochloric acids, and the volume was made up to 100mL, in a volumetric flask, with distilled water.

4,6- dihydroxy-2- mercaptopyrimidine (5×10^{-3})M

A 0.072 g of (DHMP) was dissolved in 50 ml of ethanol and the volume was made up to 100 ml, in a volumetric flask with distilled water.

-Foreign ion solution (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.

-General Procedure

To a Series of 10ml volumetric flasks were transferred in creasing volumes of nitrite solution to cover the range of 1- 20 μg . A 1.5ml of aniline reagent solution, 2.5 ml of 4,6 dihydroxy -2- marcapto pyrimidine (DHMP) and 0.3 ml of sodium bicarbonate solutions 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 416 nm using 1cm cells. The color developed immediately and was stable for more than 24h. A straight line calibration curve passing through the origin was obtained, Showing that color reaction followed Beer's law over the concentration of 20- 100 μ g of nitrite in a final volume of 10 ml.

Results and discussion

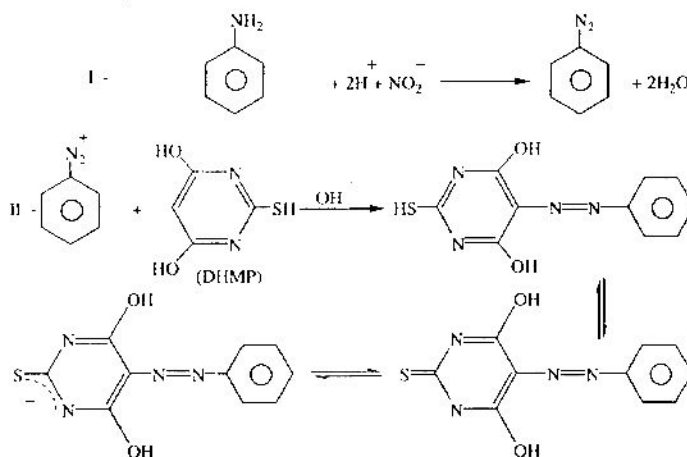
The couple, aniline and DHMP has been the choice of this investigation, this couple has been neither used nor suggested previously diazotised, and giving azo dye under the condition of determination thus eliminating the time consuming extraction Process.

-Absorption spectra:

The absorption spectrum by treating 50 μ g of nitrite ion according to the recommended procedure is shown in fig (1). The maximum absorption occurred at 416nm and being characteristic the yellowish azo dye, in contrast to the reagent blank prepared from aniline reagent which gave almost flat absorption at 416nm against distilled water.

Reaction mechanism of the method:

The reaction sequence in the procedure involves two steps. In the first, aniline reacts with nitrite to form the diazonium ion which is coupled with 4,6 dihydroxy -2-mercapto pyrimidine (DHMP) to form yellow azo dye. This reaction involves the electrophilic attack of diazonium cation at position 5 of (DHMP) and it can be represented as follows:



Scheme 1. Proposed mechanism of the reaction

-Effect of Reagent Concentration:

When various concentration of aniline solution was added to 50 μ g of nitrite, 1.5 ml of 0.01M reagent was found enough to develop the color to its full intensity and give a minimum blank value and was considered to be optimum for the concentration range of (2-10 ppm) of nitrite.

-Effect of mineral acid:

Different acids were examined these include concentrated sulfuric acid, nitric acid, and hydrochloric acid. The results showed that the most effective acid was the concentrated hydrochloric acid from the sensitivity point of view. Therefore, HCl was studied further with respect to its amount effect on the colored azo dye intensity.

It was shown that 1.5 ml of the concentrated (12M) per 100 ml of the total volume of the prepared amine solution was the optimum amount.

-Effect of (DHMP):

Different aliquots of the standard solution, each containing 50 μ g nitrite ion were treated with 1.5ml of concentration acid, and different volumes ranging from 1-5 ml of aniline Solution in of 4,6 dihydroxy 1-2- mercaptoprimidine reagent were added. It was found that 2.5 ml of (DHMP) of this reagent was optimum and gave a maximum absorption

Effect of NaHCO₃ (5%)

In order to obtain a maximum intensity it was found that 0.3-0.5 ml of NaHCO₃ Solution gave a maximum absorption of nitrite. A 0.5ml of NaHCO₃ was recommended for the procedure.

Color Stability

The yellowish azo developed instantaneously and the intensity of the color remained stable at its maximum for more than 24h.

Order of addition of reagent.

For maximum absorbance the sequence cited in the procedure should be followed, otherwise a loss in sensitivity is observed.

Beer's law and sensitivity.

The linearity to the change in absorbance with the variation in amount of nitrite present was tested by reacting aliquots of the standard solution containing (2- 10ppm) of nitrite and measuring the absorbance at 416nm. Beer's law is obeyed in this range with a correlation coefficient of (0.9989) and an intercept of (0.00217). The molar absorptivity and Sandell sensitivity are 3.5×10^3 L. mole⁻¹. cm⁻¹ and 0.12 μ g cm⁻² respectively.

Accuracy and precision

The accuracy and precision of the method were checked by measuring nitrite ion at three different concentrations. The result are shown in table (1) and indicate that the method is reliable.

Interference

In order to realize the possible analytical application of the studied method, the effect of foreign ions that may accompany nitrite was examined by carrying out determination of nitrite using the recommended Procedure. The results are shown in table (2).

Applications

The proposed method are simple and rapid. Results of good recoveries were obtained for the spectrophotometric determination of nitrite in underground waters at AL-Kufa and AL-Sahlla wells. More accurate results were achieved by applying similar experimental conditions standard curves and the samples. To study the possible analytical applications of the proposed method to determine NO₂ in underground water from Kufa wells. The samples were boiled, filtered, left to stand for one hour. The nitrite was estimated using the proposed method and the results are given in table (3).

Conclusion

The method is found to be simple rapid sensitive furthermore it is useful for the trace determination of nitrite. In view of the results obtained and the simplicity of the analytical procedure, the proposed method can be recommended for the determination of nitrite in (e.g waste water).

Acknowledgements

The authors would like to express their thanks to their ex- research Adhraa Abed-Khadem. and Nagham for their help in the experimental work.

References

1. Norwite ,G. and Keliher, P. N. (1984). *Analyst*, 109: 1281.
2. Amin, D. (1986). *Analyst*. 111: 1335.
3. Abdul Aziz, K. and Elkhatib, R. (2002), *Natl.J. chem.* 7: 372.
4. Rahim, S. A.; Fakhri, A. A. and Basir, W. A. (1983). *Microchem. J.* 28:479.
5. Nair, J. and Gupta, R. K. (1979). *Anal. Chim. Acta.* 111: 313.
6. Akira, O. and Hitoshi, W. (2001). *J. Analytical. Sci* 17: 1313.
7. Habibollah, E. and Ali, S.G. (2003). *J. Aralytical. Sci* 19: 1513.
8. Furukawa, M. and Shibata, S. (1990). *Banseki. Kogaku* 39: 589.
9. Leonardo, S. T.; Antonio, C. S. Sergio, F. C. and Marcelo, C. S. (1999). *J. Barz. Chem. Soc.* 10: 519.
10. Sawger, C. N. and Mcarty, P. L. (1978). *Ma Graw- Hill, New york* 440.

Table (1) Accuracy and precision of method

Nitrite taken/ mg	Relative error%	R.S.D%	Recovery
2	-0.05	0.86	99.95
4	-0.65	1.09	99.35
8	-0.4	1.06	99.6

Result for five determination.

Table (2) Effect of foreign ions

Foreign ion	Amount added mg	Interference
Cl ⁻	500	+2.5
NO ₃ ⁻	500	+0.73
SO ₄ ⁻	500	+0.95
PO ₄ ⁻³	500	+1.5
Ca ⁺⁺	1000	-2.2
Mg ⁺⁺	1000	+3.2
Na ⁺	1000	+2.9
K ⁺	1000	-1.94

Table (3) Results for determination of nitrite in underground water

Well name	Found* NO ₂ μg/ml
Kufa	3.20
Sahlla	4.09

* A verage of five determinations

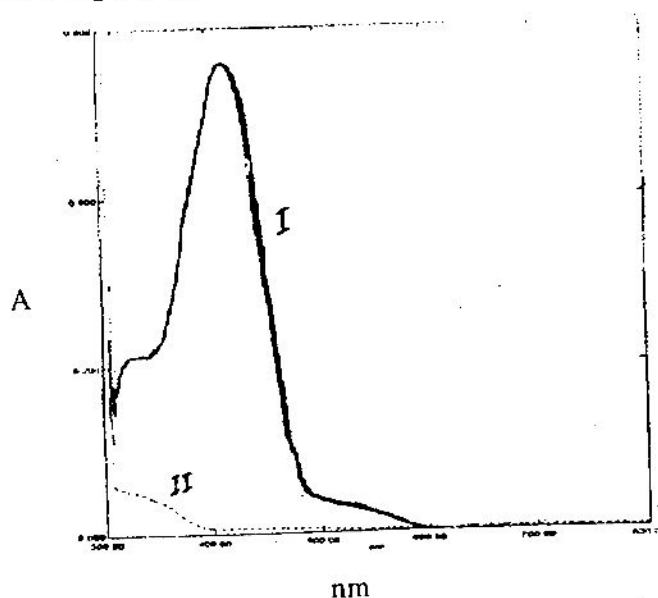


Fig. (1) Absorption spectra of (I) 50μg of nitrite in 10ml Against blank and (II) blank against water

التقدير الطيفي للنائيريت بوساطة ازدواج ديدزة الانلين مع 4 ثنائي هيدروكسي -2- مركبتو بيريميدين، 6،

حسين جاسم محمد، ضياء الدين سالم و عباس حمود الخفاجي
قسم الكيمياء، كلية التربية للبنات، جامعة الكوفة

الخلاصة

طورت طريقة طيفية بسيطة و حساسة لتقدير النتريت.

وتعتمد الطريقة على مفاعلة ايون النتريت مع الانلين في وسط حامضي لتكوين ملح الدايازونيوم الذي يقترن مع 4-6 ثنائي هيدروكسيد 2-مركبتو بيريميدين لتكوين صيغة صفراء اللون لها قابلية للذوبان في الماء وذو امتصاص اقصى عند الطول الموجي 416 نانوميتر. أشار الرسم البياني للامتصاص مقابل التركيز الى ان قانون بير ينطبق ضمن التركيز 20-100 مايكروغرام من النتريت في حجم نهائي 10 مل أي مايكاف في (2-10) جزء في المليون. وكانت قيمة الامتصاصية المولارية مساوية الى $3,5 \cdot 10^3$ لتر. مول⁻¹ سم⁻¹، وقيمة حساسية ساندل 0,12 مايكرو غرام. سم⁻²، وكذلك خطأ نسبي (0,05% & 0,65-8%) وانحراف قياسي نسبي (0,86-1,0%) اعتماداً على مستوى التركيز الذي يراد تقديره.