Studies on Pollutants : Spectrophotometric Determination of Nitrite as "Azoxine Dye"

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Ten new reagent systems for determination of nitrite in water have been studied. A new system for the determination of nitrite using diazotised aromatic amine with 8-hydroxyquinoline as a coupling reagent has been developed. Sulphanilamide was found to be most suited out of the ten amines tried for the determination of nitrite. The λ_{max} of the dye is 500 nm. The Beer's law is followed in the range of 4-30 μg of nitrite per 25 ml. The molar absorptivity and Sandell's sensitivity are 30×10^3 litre mole^{-1} cm^{-1} and 0.0015 μg cm^{-2} respectively. The optimum reaction conditions and other analytical parameters such as, Beer's law, sensitivity and interferences due to foreign species have been studied.

NITRITES occur in water due to bio-degradation of nitrates and organic matter. Their presence in water indicates pollution[1]. Several methods have been suggested for the determination of trace amounts of nitrites in water[2-9]. Most of the methods are based on Griess-Ilosvay diazo reaction[10,11]. These are continuously modified by changing the diazotising reagent as well as coupling reagent[8,4,12,13].

In the present paper 8-hydroxyquinoline proposed recently as a coupling agent[9] has been used for the determination of nitrites in water using ten different amines. The method is based on the diazotisation of aromatic amine by nitrites present in water in acidic medium and coupling the resultant diazonium chloride with 8-hydroxyquinoline in alkaline medium with subsequent measurement of the coloured azoxine dye[14] photometrically. The sulphanilamide and 8-hydroxyquinoline system was found to be the most suitable for nitrite determination. The coloured dye obtained is very stable. The reaction is very sensitive for nitrite determination. Hence, various experimental parameters are evaluated for this reagent system.

Experimental

Apparatus : All the spectrophotometric measurements were done at ECIL spectrophotometer model GS 865 and Carl Zeiss Spekol with 10 mm matched silica cells. *p*H measurements were made on Systronic *p*H meter model 323.

Reagents :

Standard sodium nitrite solution : A standard solution containing 20 μg of nitrite per ml was prepared in deionized water. A few drops of chloroform were added as stabilizer.

Diazotising reagent solution : 0.2% w/v solutions of recrystallized substituted anilines were prepared in 95% alcohol.

Coupling reagent 8-hydroxyquinoline solution : 0.2% w/v solution in 95% alcohol was prepared.

Sodium hydroxide solution : 2N solution was prepared in glass distilled water.

EDTA solution : 10% w/v solution was prepared in water. All the chemicals used were of analytical reagent grade.

Procedure :

An aliquot of water sample containing nitrite (4-30 μg) was taken in 25 ml volumetric flask. To this was added 1 ml of diazotising reagent and appropriate acidity was obtained by adding dilute hydrochloric acid (0.1N). The contents were shaken for 5 minutes (for *p*-anisidine 40-50 minutes are required). Then 1 ml of 8-hydroxyquinoline and 1 ml of EDTA were added and the contents were made alkaline with 3 ml of 2N sodium hydroxide for colour development. The volume was made up to the mark with glass distilled water. The *p*H of the solution was ~11. The absorbance of the coloured dye was measured against the reagent blank at appropriate wavelength.

Results and Discussion

The azoxine dyes formed by coupling the different diazotised aromatic amines with 8-hydroxyquinoline are colourless in the acidic medium while intensely coloured in alkaline medium. The diazotisation reaction is dependent on acidity. It was also found that with *p*-anisidine the colour development is slow.

The coupling of the diazotised amine takes place below 30° at 5 position out of the two possible positions[16] (i.e., at 5 and 7).

Absorption spectra, acidity and molar absorptivity :

The wavelength of maximum absorption against the reagent blanks for 'azoxine' dyes were determined by plotting the graph between wavelength and absorbance. The wavelengths of maximum absorption are given in Table 1.

TABLE 1—ACIDITY AND SPECTRAL CHARACTERISTICS

Sl. No.	Reagents	Acidity Range	λ_{max} nm	$\sim \epsilon_{max}$ lit. mol^{-1}cm^{-1}
1.	Aniline	0.09 N and above	480	19×10^3
2.	Sulphanilic acid	0.01 N and above	500	29.5×10^3
3.	Sulphanilamide	0.05 N and above	500	30×10^3
4.	2-5 dimethoxy aniline	0.015 $N - 0.05N$	500-510	21×10^3
5.	o-nitroaniline	0.04 $N - 0.08N$	510	25×10^3
6.	m-nitroaniline	0.02 N and above	500	28.5×10^3
7.	o-anisidine	0.02 $N - 0.06N$	490	23×10^3
8.	p-anisidine	0.01 N and above	490	25.5×10^3
9.	3, 4 dimethyl aniline	0.03 N and above	480	20×10^3
10.	2, 6 dimethyl aniline			General absorption in visible region.

The influence of acidity on diazotisation for obtaining maximum molar absorptivity was determined by varying acidities from 0-4N with dilute hydrochloric acid (0.1N). The acidity ranges for diazotisation and λ_{max} of the dyes for 20 μg of nitrite are given in Table 1.

It is apparent from Table 1 that substituent such as $- NO_2, - CH_3$ etc. when present in ortho position in the diazonium salt, the system is less sensitive. It may be due to steric hindrance or ortho effect. However, more studies in this direction will be useful.

The sulphanilamide was found to be the best out of 10 aromatic amines tried. Hence it was studied in detail.

Effect of Reagent :

It was found that at least 1 : 1 molar ratio of nitrite to sulphanilamide is necessary for complete diazotisation. To achieve the maximum colour development, at least 1 : 10 molar ratio of nitrite to 8-hydroxyquinoline is required. A large excess of both the reagents, can be tolerated without change in absorbance.

Stability and Composition of the dye :

The absorbance of the coloured system was found to be unchanged after keeping it for 3 days at varying temperatures from 20-40°. The composition of dye was determined by Job's method. The results interpreted from the curve plotted with NO_2^-/(NO_2^-)+(sulphanilamide), against absorbance and NO_2^-/(NO_2^-)+(8-hydroxyquinoline), against absorbance indicate that nitrite : sulphanilamide ratio is 1 : 1 and nitrite : 8-hydroxyquinoline ratio is 1 : 1.

Beer's law and Sandell's sensitivity :

The Beer's law is obeyed from 4-30 μg of nitrite

TABLE 2—EFFECT OF FOREIGN SPECIES IN THE DETERMINATION OF NITRITE (10 μg NO_2 in 25 ml)

	Species added	Amount added in ppm	Absorbance		Species added	Amount added in ppm	Absorbance
	NH_4^+	30	0.261		Ni^{2+}	20t	0.261
	As^{3+}	40	0.265		Sn^{2+}	20	0.262
*a	Al^{3+}	40t	0.265		WO_4^{2-}	60t	0.262
*a	Ba^{2+}	240t	0.262		PO_4^{3-}	20	0.261
*b	Bi^{3+}	20t	0.262		CN^-	80	0.265
*a	Ca^{2+}	60t	0.265		I^-	20	0.26
*a	Co^{4+}	130t	0.260		SCN^-	80	0.261
*a	Cr^{3+}	0.8t	0.261		NO_3^-	40	0.262
	Cu^{2+}	0.2	0.263		CO_3^{2-}	50	0.262
*d	Cu^{2+}	16.0	0.260	*c	SO_3	4	0.260
*a	Hg^{2+}	150t	0.260		Aniline	5	0.260
*a	Pb^{2+}	40	0.260		Benzene	10	0.263
	MoO_4^{2-}	20	0.260		Formaldehyde	100	0.265
*a	Mg^{2+}	40	0.260		Phenol	80	0.261
*b	Fe^{3+}	0.4	0.260				
	Fe^{2+}	0.004	0.220				

Note :

*a   In presence of 1 ml of 10% EDTA.

*b   In presence of 1 ml of 10% Sodium Potassium Tartrate.

*c   In presence of 0.5 ml of 1% H_2O_2 (20 volume) H_2O_2.

*d   In presence of 1 ml of 1% KCN.

*t   Tolerance limit.

per 25 ml at 500 nm. The optimal concentration range evaluated from a Ringbom curve[16] is 7-26 μg nitrite/25 ml. The Sandell's sensitivity is 0.0015 μg cm^{-2} at 500 nm.

Effect of foreign species :

To evaluate the analytical potentiality of the reagent, the interferences due to different species present in water were studied. The foreign species were added in known amounts to nitrite solution (10 μg) before diazotisation and the absorbance was measured after developing the colour as described in general procedure. The data is presented in Table 2. The interferences of certain ions were corrected by adding EDTA (marked with *a), sodium potassium tartrate (marked with *b), hydrogen peroxide (marked *c) and potassium cynide (marked *d).

When all the ions excluding Cu^{2+} and KCN are added simultaneously to nitrite solution, the turbidity is obtained making determination unreliable. A synthetic sample containing 20 ppm of Mg^{2+}, Pb^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, SO_4^{2-}, NO_3^- in tap water caused no interferences in the determination of nitrite.

Precision and reproducibility :

The precision of the method is high. The standard deviation and relative standard deviation were found to be ± 0.06 and ± 0.6 respectively.

The above method is suitable for determining trace amount of nitrites in water. The proposed method has following advantages over the α-napthylamine method, which is widely accepted as standard method for determination of nitrite.

Note : The present system has been found to be suitable for the determination of nitrogen dioxide in air. The collection efficiency of the alkaline 8-dydroxyquinoline reagent is found to be around 95% and NO_2/NO_2^- factor is found to be 0.75 which is in good agreement with the finding of Nash[17] (0.74).

The nitrogen dioxide is absorbed in 8-hydroxyquinoline. In this system nitrogen dioxide was converted to nitrite which was then used to diazotise the acidified amine and the colour was developed as described in procedure[18].

1. It requires less time for analysis.

2. The stability of the reagent and the dye is higher.

3. It is free from rigorous control of pH and temperature.

Acknowledgement

References

1. Standard Methods for the Examination of Water, Sewage and Industrial Waste, American Public Health Association Inc. 14 Ed., 1975.

2. H. BARNES, *Analyst*, 1950, **75**, 388.

3. K. TOEI and T. KIYOSE, *Anal. Chim. Acta*, 1977, **88**, 125.

4. E. SAWICKI, T. W. STANLEY, J. PFAFF and H. JOHNSON, *Anal. Chem.*, 1963, **35**, 2183.

5. E. SAWICKI, T. W. STANLEY, J. PFAFF and A. D' AMICO, *Talanta*, 1963, **10**, 641.

6. M. ROMAN, A. FERNADEZ-GUTIERREZ and M. C. MAHEDERO, *Bull. Soc. Quim* (Peru), 1977, **43**, 16.

7. E. GRACIA, *Anal. Chem.*, 1967, **39**, 1605.

8. A. K. BABKO and A. T. PILIPENKO, Phometric Analysis, Methods of Determination of Non-metals, Translated from Russian by A. Rosinkin, Mir Publishers, Moscow, 1975.

9. J. NAIR and V. K. GUPTA, *Anal. Chim. Acta*, 1979, **111**, 311.

10. P. GRIESS, *Chem. Ber.*, 1879, **12**, 427.

11. M. L. ILOSVAY, *Buil. Soc. Chim.* (France), 1889, **3**, 317.

12. B. E. SALTZMAN, *Anal. Chem.*, 1954, **26**, 1949.

13. M. B. JOCOBS and S. HOCHHEISER, *Anal. Chem.*, 1958, **30**, 426.

14. J. S. FRITZ, W. J. LANE and A. BYSTROFF, *Anal. Chem.*, 1957, **29**, 821.

15. A. BADRINAS, *Talanta*, 1963, **10**, 704.

16. A. RINGBOM, *Z. Anal. Chem.*, 1938, **115**, 332.

17. T. NASH, *Atmos. Environ.*, 1970, **4**, 661.

18. J. NAIR and V. K. GUPTA, *Atmos. Environ.*, In Press.