Titrimetric and Polarographic Microdetermination of Nitrite by Amplification Reactions

D. AMIN, S. T. SULAIMAN and MOUAYED Q. AL-ABACHI

Department of Chemistry, College of Science, Mosul University, Mosul, Iraq

Nitrite (5-2000 μg) oxidizes iodide quantitatively to iodine in acidic medium. The liberated iodine is extracted into chloroform and is reduced to iodide by back extraction with 1% sodium hydrogen sulphite solution. The iodide ion is then amplified by bromine oxidation and determined titrimetrically or polarographically by measuring the a.c. polarographic wave of the iodate formed in alkaline medium (pH 12). The coefficient of variation of the two methods does not usually exceed 2% for 2000 μg of nitrite but increases to 3.2% at 5 μg level.

BECAUSE of the widespread occurrence of nitrite ion in the environment, either naturally or because of its use as a food preservative, the development of a sensitive, rapid and accurate method for the microdetermination of this ion is worthwhile.

A number of methods for the determination of nitrite is found in literatue. Cool and Yoe[1] examined more than thirty titrimetric procedures, of which only a few proved relatively satisfactory. Most commonly, nitrite is determined by the Saltzmann modification of the Griess method[a] in which sulphanilic acid is diozotised by free nitrite ion in acidic medium and the diazonium ion is coupled with naphthylethylene diamine to give an azo dye. The intensity of the colour corresponds to the concentration of nitrite in the sample, and is determined spectrophotometrically. Fluorimetry[8,4] has also been used in nitrite determinations. This method, however, suffers from quenching effects due to the presence of some interferants.

Electroanalytical approaches to the determination of nitrite are usually based on oxidation of nitrite to nitrate. An amperometric titration with permanganate was investigated by Stock and Bjork[5] but the errors were not less than a few percent. Constant-current coulometry using excess of manganese(III) as oxidant was proposed by Buck and Crowe[6]. Small samples could be analysed with this method but the use of two intermediates seems rather complicated. A more straight forward method in which nitrite is directly oxidized to nitrate at a platinum electrode by coulometry at controlled potential has been described by Harrar[7]. The accuracy was very good but the time of electrolysis was more than 20 min. Finally, differential-pulse polarography has recently been applied in the determination of nitrite[8,9].

In the present investigation, a new amplification method is described for the determination of nitrite. The method is based upon the reaction of nitrite with excess iodide in acidic medium, removal of the nitrogen oxide with sodium bicarbonate, extraction of the liberated iodine into chloroform, and reduction of the iodine to iodide with 1% sodium hydrogen sulphite solution. The iodide ion in the aqueous solution is oxidized into iodate by bromine water and is determined titrimetrically, or polarographically by measuring the a.c. polarographic wave of iodate at pH 12. As far as we know, no such method has so far been reported in the literature.

Experimental

Apparatus :

A metrohm E506 polarecord, with a three-electrode electrolytic cell is used. The working electrode is a dropping mercury electrode (d.m.e.) connected with a tapping device for controlled drop times of 0.4-0.6 sec. The reference electrode is Ag/AgCl, KCl and the auxiliary electrode is a platinum wire.

Reagents :

All chemicals used were analytical grade reagent except otherwise stated. Standard sodium nitrite solution, (1 mg nitrite/ml), was prepared by dissolving exactly 150 mg sodium nitrite in 50 ml distilled water and 2 ml chloroform as stabilizer, and diluting to 100 ml with distilled water.

Oxygen-free nitrogen was obtained by passing the gas through a train of five bubblers, the first three of which contained alkaline pyrogallol followed by one containing conc. sulphuric acid and an empty one.

Procedure :

1-2 g sodium bicarbonate, 0.5 g potassium iodide, 0.2 ml amyl alcohol and 20 ml water are taken in a 100 ml glass stoppered Erlenmeyer flask and a measured volume (1-2 ml) of nitrite solution containing 5-2000 μg of NO_2^- is added. The

contents are mixed by shaking. After most of the sodium carbonate settled down ∼ 1 ml acetic acid is added in such a way that the acid is distributed through the solution without shaking. The flask is loosely stoppered after carbon dioxide evolution has nearly ceased, gently rotated and 1 ml sulphuric acid solution $(20N)$ is added quickly, without shaking. The flask is gently rotated to mix the solution. The solution is quantitatively transferred to a 100 ml separating funnel and the liberated iodine is extracted with chloroform $(3 \times 20$ ml). The aqueous phase is discarded and the combined extracts is washed with 5 ml water to remove any carried over iodide. The iodine solution is shaken with 10 ml water containing 0.5 ml of sodium hydrogen sulphite solution (1%) to reduce the iodine into iodide. The aqueous layer containing the iodide is transferred to a 50 ml conical flask, 2 ml saturated bromine water added and the solution stirred for 5 min. Excess of bromine is destroyed by addition of 1 ml formic acid solution and stirring for 5 min. The iodate formed is determined titrimetrically or polarographically.

Titrimetric determination :

The iodate solution is acidified with 3 ml sulphuric acid $(2N)$ and ∼ 0.5 g potassium iodide is added. The flask is stoppered and left in the dark for 5 min for complete liberation of iodine. The liberated iodine is titrated with standard sodium thiosulphate solution using starch as indicator. A blank is run. (1 ml of 0.02 N of $S_2O_3^{2-}$=0.1533 mg NO_2^-).

Indirect polarographic determination :

The iodate solution is transferred into a 50 ml standard flask, the pH is adjusted to 12 with $4N$ NaOH solution, 1 ml gelatin solution (1%) is added and the volume is made up to the mark with distilled water. The contents are mixed thoroughly and a portion is taken in the polarographic cell, deoxygenated by purified nitrogen, and the a.c. polarogram of the cathodic reduction wave of iodate is recorded rapidly (starting potential -1.0 V vs the Ag/AgCl reference electrode). The height of the iodate wave is measured and the iodate content is calculated with the aid of a calibration curve constructed with iodate (0.025-75 mg/50 ml).

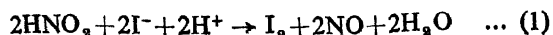The amount of nitrite (mg) is calculated from the following relation :

$$\text{Nitrite (mg)} = \frac{\text{molecular weight of } NO_2^-}{\text{atomic weight of } I^-} \times w$$
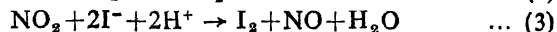$$= 0.3622 \times w$$

where w is the weight of iodide (mg) produced as obtained from the calibration curve.

Results and Discussion

The reaction[1] for the iodometric determination of nitrite is :

$$2HNO_2 + 2I^- + 2H^+ \rightarrow I_2 + 2NO + 2H_2O \quad \dots (1)$$

Air should be carefully excluded because of reactions (2) and (3)

$$2NO + O_2 \rightarrow 2NO_2 \quad \dots (2)$$
$$NO_2 + 2I^- + 2H^+ \rightarrow I_2 + NO + H_2O \quad \dots (3)$$

The main problem in the iodometric methods proposed in the literature[10,11] was the difficulty in preventing reactions (2) and (3). This difficulty can be overcome by evaporating the solution or by addition of organic reagents such as urea or sulphamic acid[12] which reduces the oxides of nitrogen. Alternatively, the nitric oxide liberated can be expelled from the solution by addition of sodium carbonate in acidic medium[13]. In the present investigation a large excess of sodium carbonate was found necessary for removing all the nitric oxide formed. Amyl alcohol has no function other than prevention of over-foaming of the solution during the evolution of carbon dioxide[12].

The two methods give satisfactory results (Tables 1 and 2), the relative percentage error being 0-2%

TABLE 1—RESULTS FOR THE TITRIMETRIC MICRODETERMINATION OF NITRITE AFTER AMPLIFICATION REACTION

Amount of NO_2^- (μg)		Relatie percentage error	Coefficient of variation %[b]
Taken	Found[a]		
10	9.8	−2.0	2.2
30	29.6	−1.3	
50	49.9	−0.2	
80	79.9	−0.1	
100	100.5	+0.5	1.2
500	500	0.0	
1000	1000.2	+0.02	
2000	1997.6	−0.1	1.7

a = Mean of three determinations ;

b = coefficient of variation of five determinations.

TABLE 2—RESULTS FOR THE INDIRECT POLAROGRAPHIC MICRODETERMINATION OF NITRITE

Amount of NO_2^- (μg)		Relative percentage error	Coefficient of variation %[b]
Taken	Found[a]		
5	4.9	−2.0	3.2
10	9.9	−1.0	
50	49.6	−0.8	
100	101.0	+1.0	1.3
500	500.5	+0.1	
1000	1000.5	+0.05	
2000	1996.4	−0.18	1.9

a = Mean of three determinations ;

b = Coefficient of variation of five determinations.

for the titrimetric method (10-2000 μg nitrite) and 0.05-2% for the indirect polarographic method (5-2000 μg nitrite). The recoveries were 1-2% low for lower amounts of nitrite and this may be due to loss of iodine during extraction. The titrimetric method seems simpler and less time consuming than the other. The coefficients of variation for the titrimetric method were 2.2, 1.2 and 1.7% for 10, 100 and 2000 μg nitrite, respectively (Table 1). It can be used to determine 10-

983

2000 μg nitrite. Higher amounts of nitrite can be determined provided the liberated iodine can be extracted with three 20 ml portions of chloroform. The indirect polarographic method is applicable for the determination of 5-2000 μg nitrite and the coefficients of variation were 3.2, 1.3 and 1.9% for the detemination of 5, 100 and 2000 μg nitrite, respectively (Table 2).

According to our investigation the a.c. polarographic wave for iodate is best recorded at pH 12, readily attainable by the addition of $4N$ sodium hydroxide.

The iodate calibration curve is linear and passes through the origin. 25-7500 μg iodate per 50 ml is selected for the calibration as it covers the expected nitrite content of 5-2000 μg in a sample.

Cations and anions (Ce^{4+} or Fe^{3+}) which oxidize iodide to iodine and those which yield polarographic waves in hydroxide medium (e.g. Zn^{2+}) with half-wave potentials close to that of iodate would interfere in the methods.

References

1. R. D. COOL and J. H. YOE, *Ind. Eng. Chem. Anal. Ed.*, 1935, 5, 112.

2. B. E. SALTZMANN, *Anal. Chem.*, 1954, 26, 1949.

3. E. D. COPPLA, A. F. WICKROSKI and J. HANNA, *J. Assoc. Off. Anal. Chem.*, 1976, 59. 783.

4. E. D. COPPLA, A. F. WICKROSKI and J. HANNA, *J. Assoc. Off. Anal. Chem.*, 1975, 58, 469.

5. J. T. STOCK and R. G. BJORK, *Microchem. J.*, 1962, 6, 219.

6. R. P. BUCK and T. J. CROWE, *Anal. Chem.*, 1963, 35, 697.

7. J. E. HARRAR, *Anal. Chem.*, 1971, 43, 143.

8. S. W. BOESE and V. S. ARCHER, *Anal. Chem.*, 1977, 49, 497.

9. S. K. CHANG, R. KOZENIANSKAS and G. W. HARRINGTON, *Anal. Chem.*, 1977, 49, 1272.

10. B. S. DAVISSON, *J. Amer. Chem. Soc.*, 1910, 38, 1683.

11. F. M. LANG and G. AUNIS, *Chim. Anal. Paris*, 1950, 32, 139.

12. I. M. KOLTHOFF and R. BELCHER, "Volumetric Analysis", Interscience, New York, 1957, Vol. 3, p. 203-311.

13. C. A. ABELEDO and I. M. KOLTHOFF, *J. Amer. Chem. Soc.*, 1931, 53, 2893.