



Reductimetric Determination of Nitrite with Iron(II) in Buffer Medium and in Presence of Oxalate

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A simple, convenient and accurate reductimetric titration method has been developed for the determination of nitrite employing iron(II) as a reductant in buffer medium of pH 1.5-2.0 and in presence of 0.06 M sodium oxalate, using methylene blue as a redox indicator. Nitrite in the range of 3.0-12.0 mg has been determined with an accuracy of $\pm 0.6\%$ by the method. The precision of the method has been determined by computing the pooled standard deviation and 95% confidence limits. In this procedure, nitrite ion is reduced to nitric oxide (NO) by iron(II) in one electron reduction step. The redox reaction has been explained based on the formal redox potential of iron system (iron(III)/iron(II) couple) observed in buffer-oxalate medium. The nature of the species expected to be formed between iron(III) and oxalate under the optimum titration conditions of the medium (pH range 1.5-2.0 oxalate concentration about 0.06 M) have been proposed using a computer programming known as SIMUL. The interference due to diverse ions has been studied.

Key Words: Nitrite, Iron(II), Buffer medium, Oxalate, Methylene blue.

INTRODUCTION

A survey of literature reveals the existence of numerous redox methods for the determination of nitrite. These methods generally utilize oxidants or reductants such as permanganate^{1,2}, chloramine-T^{3,4}, cerium(IV)^{1,5}, bromine¹, bromate^{1,6}, hypochlorite¹, N-bromosuccinimide (NBS)⁷, hexacyanoferrate(III) (HCF)³, manganese(III)³, manganese(IV)⁸, copper(III)⁹, cobalt(III)¹⁰, lead(IV)³, iodide¹, titanium(III)¹, tin(II)¹¹, ascorbic acid¹², hydrazine sulphate³, iron(II) in alkaline triethanolamine (TEA) medium¹³, iron(II) in phosphoric acid medium¹⁴ etc. Redox methods utilizing several other trivial reductants like manganese(II), sulfamic acid, sulphite, bisulphite, urea, *p*-aminobenzoic acid etc., have also been reported. But, these methods do not find much analytical significance, hence the references of the methods have not been cited in the present communication. Recently, a few redox methods have been proposed employing isoniazid¹⁵ and brilliant cresyl blue¹⁶ as redox reagents. But, all these methods are not entirely satisfactory.

The disadvantages associated with the earlier methods may be summarized as follows: several modifications have been suggested to the permanganate method as the reaction velocity diminishes near the end-point. The method recommended with CAT is indirect and tedious. The titrations with cerium(IV) must be carried out at elevated temperatures or in

a bulk volume as high as 300 mL. The method developed with bromine solution is liable for an error due to volatility loss of bromine. The procedures reported using bromate and hypochlorite as oxidants are indirect and tedious. The solutions of N-bromosuccinimide are not very stable, as bromine separates out after a few hours, while those of hexacyanoferrate decompose fairly rapidly. The preparation and preservation of Mn(III), Mn(IV), Cu(III), Co(III), Pb(IV) etc., is a tedious task and most of the methods developed with the reductants are indirect in nature. The iodometric method is tedious and requires the presence of expensive chemicals. The following reductants: titanium(III), tin(II) and ascorbic acid are sensitive to atmospheric oxygen and hence require a special storage apparatus to prevent this. The method with hydrazine sulphate is indirect. In alkaline triethanolamine medium iron(II) undergoes rapid aerial oxidation and the method is less accurate. The procedure developed using iron(II) as a reductant in phosphoric acid medium is indirect. One of the recently reported methods¹⁵ is indirect while the other one¹⁶ requires the use of expensive chemicals as sensitizers.

The present paper describes a direct reductimetric titration method for the determination of nitrite using iron(II) as a reductant in buffer medium and in presence of oxalate using methylene blue as a redox indicator. The method now developed does not suffer from any of the disadvantages associated with the earlier methods. The observed redox reaction has been

explained based on the formal redox potentials of the reductant system [Fe(III)/Fe(II) couple] reported under the optimum conditions and by a computer programming, the nature of the complex species expected to be formed between iron(III) and oxalate in the reaction medium have been presented.

EXPERIMENTAL

All the solutions have been prepared in distilled water and all the chemicals are of AR grade unless and otherwise stated.

Nitrite solution: An approximately 0.025 M solution of nitrite has been prepared by dissolving the required amount of AR grade sodium nitrite in distilled water. The solution is standardized by titrating against a standard solution of cerium(IV) sulphate⁵.

Iron(II) solution: An approximately 0.025 M solution of iron(II) in 0.01 N sulphuric acid medium is prepared from an AR grade ammonium iron(II) sulphate hexahydrate and the solution standardized by titrating against a standard solution of dichromate¹⁷.

Sodium oxalate solution: A 0.2 M solution is prepared by dissolving the required amount of an AR grade anhydrous disodium oxalate in distilled water.

Sodium acetate solution: About 1 M solution of the salt has been prepared from an AR grade sample of sodium acetate.

Acid solutions: An approximately 1 N solutions of hydrochloric acid, sulphuric acid, perchloric and nitric acids have been prepared in distilled water from their respective AR grade samples and the solutions standardized by titrating against a standard solution of sodium carbonate in the usual way.

Buffer solutions of desired pH: Buffer solutions of desired pH have been prepared by mixing suitable volumes of 1 M sodium acetate and 1 N solution of a mineral acid (mentioned above) as described in literature¹⁸.

Methylene blue solution: A 0.05 % (50 mg in 50 mL) aqueous solution of methylene blue is prepared.

Recommended procedure: To 3-10 mL of nitrite solution (0.025 M) is taken in a 150 mL beaker fitted with a three holed rubber stopper (one for accommodating the inlet tube for passage of purified nitrogen gas, the second one for accommodating the tip of the micro-burette, the third one serves as an out-let for nitrogen gas). To this solution about 10 mL of sodium acetate (1 M), 12 mL of hydrochloric acid or any one of the mineral acids mentioned above (1 M) and 15 mL of sodium oxalate (0.2 M) are added. Now the solution is diluted to about 50 mL and the pH of the solution is found to be about 2.0 units. After adding 3-4 drops of methylene blue solution, the contents are titrated against iron(II) solution (0.025 M) while it is being stirred by a magnetic stirrer and passage of inert gas is maintained throughout the titration with the help of the arrangements described above. The iron(II) solution must be added drop-wise near about the end-point. The colour transition of the indicator at the end-point is from blue to colourless and it is sharp and reversible. No indicator correction need be applied. Some of the typical results obtained by the above procedure have been shown in Table-1.

TABLE-1
DETERMINATION OF NITRITE WITH
IRON(II) IN BUFFER-OXALATE MEDIUM

Nitrite found* (mg)		Pooled standard deviation, S _g Mg	$\frac{1.96 \times S_g}{\sqrt{n}}$	95 % Confidence limits (mg)
Reference Method	Present method			$\bar{X} \pm \frac{1.96 \times S_g}{\sqrt{n}}$
3.43	3.41			3.39-3.43
5.24	5.26			5.24-5.28
6.85	6.82	0.02	0.02	6.80-6.84
8.67	8.70			8.68-8.72
10.34	10.39			10.37-10.41
11.46	11.40			11.38-11.42

*Average of six determinations.

RESULTS AND DISCUSSION

The accuracy of the method is found to be ± 0.6 %. The precision of the method has been determined by computing the pooled standard deviation and 95 % confidence limits and the values are included in the same table. In this redox reaction iron(II) reacts with nitrite in equimolar ratio (1:1). Hence, it has been concluded that, nitrite ion is reduced to nitric oxide in one electron reduction step as per the following equation cited in literature¹⁹:



Circulation of inert atmosphere during the titration helps in rapid expulsion of nitric oxide formed and thus avoids the risk of formation of further oxidation products by reaction of nitric oxide (NO) with atmospheric oxygen¹⁹. It also helps to prevent the aerial oxidation of leuco- dye of methylene blue obtained by its reduction with iron(II) at the end point.

Attempts to develop a potentiometric method for the determination of nitrite did not succeed, because the potentials show considerable drift and steady values have not been obtained even after a long period of waiting.

In order to explain the conditions necessary for the observed redox reaction, the formal redox potentials of the reductant system [iron(III)/iron(II) couple] and those of the oxidant system [NO₂⁻/NO] at different pH values of the buffer medium and at different oxalate ion concentrations are necessary. From the earlier work of the present author, the data of the former couple are available in literature²⁰, but those of the latter are not available in literature. But, the author could not measure these potentials *i.e.*, the potentials of the oxidant system [NO₂⁻/NO couple]. This is because, the preparation of pure NO gas and to keep it in equilibrium with NO₂⁻ ions in solution is a difficult task. Further, as stated above, potentials of the system did not get stabilized even after a long period of waiting.

The formal redox potentials of iron system [or iron(III)/iron(II) couple] decrease in buffer medium (pH 1-6) and in presence of oxalate which binds iron(III) in form of a complex, causing considerable decrease in the potential of iron system, thus the reducing ability of iron(II) is enhanced. Raju and co-workers²⁰ measured the formal redox potentials of iron system [or iron(III)/iron(II) couple] at different pH and oxalate ion concentrations and observed them as follows: at a fixed pH (*ca.* 4.0) the potential decreases from about 470 to *ca.* 80 mV

with increase in oxalate ion concentration from 0 to 0.06 M and at fixed oxalate ion concentration (0.06 M), the potential decreases from about 370 mV to *ca.* 85 mV with increase in pH of the buffer medium from about 0.80 to 5.30 units. The present redox reaction, however, has been found feasible in the buffer medium of pH 1.5 to *ca.* 2.0 units and in presence of about 0.06 M sodium oxalate where the redox potential of iron system has been reported to be about 180 mV. It is presumed that the redox potential of iron system under the above optimum conditions is sufficiently low such that iron(II) functions as a power reductant causing rapid reduction of nitrite ion by iron(II).

The author successfully attempted to determine the nature of the species expected to be formed between iron(III) and oxalate in solution in the reaction medium through a computer programme-SIMUL which worked out the data showing the percentage distribution of various complexes (such as *mono-bis-* and *tris-*oxalate complexes) expected to be formed at different pH values of the medium. From the data it has been found that under the above mentioned optimum titration conditions of the medium (pH of the buffer 1.5-2.0 and in presence of 0.06 M oxalate), *tris-*oxalato ferrate(III) are found to be the predominant species.

Study of interferences: A study of interferences due to different ions has been carried out and found that among anions:chloride, acetate, sulphate, nitrate and perchlorate and among cations:iron(III), aluminium(III), manganese(II) *etc.*, do not interfere. However, copper(II) is found to interfere at all concentrations.

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