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MICRODETERMINATION OF NITRITE IN PRESENCE OF NITRATE

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Abstract. *N*-Bromosuccinimide has been used for the estimation of nitrite. An excess of *N*-bromosuccinimide was used and then the residual amount was back titrated against standard sodium thiosulphate. The method was quite precise and accurate, the maximum standard deviation being 0.05 mg when a 3.4 mg sample was titrated.

A careful survey of the literature indicates that not very many satisfactory methods for the estimation of nitrite–nitrate couple are available. Flitman and Miriam[1] used standard solution of 4,4′-sulphonyldianiline using diphenylamine as an internal indicator. In this method numerous stringent conditions are required, i.e. it has to be performed exactly at 45°C, which is quite cumbersome. Singh and Singh[2] determined nitrite with $KMnO_4$ but no interference was checked. Whiteman[3] employed excess of Ce(IV) solution for the estimation of nitrite in presence of nitrate. But Ce(IV) standard solutions are not easy to prepare. Excess of this reagent was then back-titrated with Fe(II) standard solution. The method is time-consuming because two standard solutions are required for this estimation. Nitrite in presence of nitrate has also been estimated iodometrically[4] but bubbling of CO_2 through the test solution was required, thus making the method little laborious.

We have used *N*-bromosuccinimide for various estimations in which selective as well as general oxidations were tried.[5–14] We thought of employing this reagent for the estimation of nitrite in presence of nitrate.

In this method only standardization of sodium thiosulphate against standard *N*-bromosuccinimide, a primary standard, was required.[15] In this method an excess of *N*-bromosuccinimide is used and the residual amount is back-titrated with standard sodium thiosulphate. The method is quite precise and rapid. Nitrate does not interfere in this procedure.

Experimental

N-Bromosuccinimide. Exactly 89.00 mg recrystallized product was dissolved in water and diluted to exactly 100 ml to make 0.01N solution. This was used as primary standard.

Sodium Thiosulphate. A.R. grade substance was used for the preparation of 0.01N solution, which was standardized with *N*-bromosuccinimide.[8]

Potassium Nitrite. A.R. grade chemical was taken and standardized by conventional methods.

Potassium Iodide. KI solution (4%, w/v) was prepared in distilled water.

Acetic Acid. Acetic acid 2N was prepared in distilled water.

All other chemicals used were of comparable purity.

Procedure

A definite volume (2 ml) of nitrite was taken in Erlenmeyer flask and to this was added about 2 ml acetic acid. Then a known excess of standard *N*-bromosuccinimide solution was added to the contents of the flask. After shaking the flask for few seconds 1 ml KI solution was added. The liberated iodine was then titrated against standard sodium thiosulphate solution using starch solution as an indicator. About 2 ml starch solution were added near the end-point. This titer gave the residual amount of *N*-bromosuccinimide. From this, the amount of *N*-bromosuccinimide used for the titration was calculated.

Results and Discussion

It has been found that *N*-bromosuccinimide reacts with nitrite in acid medium to convert it to nitrate. The stoichiometry of the reaction is shown below:

$$H_2O + NO_2^- \xrightarrow{-2\,e} NO_3^- + 2H^+$$

$$Br^+ + 2\,e \longrightarrow Br^-$$

It can be seen from the first half reaction that nitrogen in NO_2^- is at + 3 oxidation state, which after reaction with *N*-bromosuccinimide goes to +5 oxidation state with the loss of two electrons. In the second half reaction bromine in *N*-bromosuccinimide is at +1 oxidation state which after reduction goes to —1 oxidation state with the gain of two electrons. The equivalent weights or normalities of the respective substances were calculated taking these electronic changes into consideration.

This property of *N*-bromosuccinimide to oxidize NO_2^- has been used to estimate this compound quantitatively. The results in Table 1 clearly show that nitrite can be quantitatively determined by using *N*-bromosuccinimide. The results show that the

TABLE 1. DETERMINATION OF NITRITE.

Amount of NO_2^- taken (mg)	Amount of NO_2^- found (mg)	Standard deviation*
0.56	0.56	0.00
1.13	1.14	0.03
1.70	1.70	0.04
2.27	2.28	0.02
3.40	3.40	0.05

*Every result is the average of five determinations.

method is quite precise and accurate. The maximum standard deviation is 0.05 mg when 3.4 mg sample was taken.

Effect of Diverse Ions

The interference in the determination of nitrite was checked due to certain ions and it has been found that, NO_3^-, $PO_4^{\equiv}$, citrate, Cl^-, $SO_4^{=}$, Al^{+++}, Zn^{++} and NH_4^+ do not interfere in acid medium.

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