

4. Nitrite, Nitrogen

4.1 General — Prescribes a method for determination of nitrite nitrogen using Nessler's cylinders or spectrophotometer. Spectrophotometric method shall be the referee method.

4.2 Principle — Nitrite is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulphanilic acid with N-(1 naphthyl)-ethylene diamine dihydrochloride (NED dihydrochloride). The colour obeys Beers' law up to 180 $\mu\text{g/l}$ with 1 cm path length at 543 nm.

4.3 Interference — Nitrogen trichloride (NCl_3) imparts a false red colour when normal order of reagents addition is followed. It can be minimized by adding NED dihydrochloride first and then sulphanilic acid. Ions like Sb^{3+} , Au^{3+} , Fe^{3+} , Bi^{3+} , Pb^{2+} , Hg^{2+} , Ag^+ , PtCl_6^{2-} interfere. Cupric ions cause low results.

4.4 Apparatus

4.4.1 Spectrophotometer or photometer — for use at 543 nm in case of spectrophotometer or photometer having a green filter and having maximum absorbance near 540 nm.

4.4.2 Nessler tubes — matched, 50 ml capacity.

4.5 Reagents

4.5.1 Nitrite-free water — If the distilled water is not nitrite free, prepare as follows:

- Add to 1 litre of distilled water, a small crystal each of potassium permanganate and barium hydroxide or calcium hydroxide. Redistil in an all borosilicate glass bottle.
- Add 1 ml of concentrated sulphuric acid and 0.2 ml of manganese sulphate (36.48 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ /100 ml) solution to each 1 litre of distilled water and make pink with 1 to 3 ml of potassium permanganate solution (400 mg/l). Redistil as in (a) above. Use this water in making all reagents and dilutions.

4.5.2 Sulphanilamide reagent — Dissolve 5 g of the material in a mixture of 50 ml of concentrated hydrochloric acid and 300 ml of water. Dilute to 500 ml with water. The reagent is stable for several months.

4.5.3 NED dihydrochloride — Dissolve 500 mg of the material in 500 ml of water. Store in coloured bottle in dark. Replace monthly or when it turn dark brown in colour.

4.5.4 Hydrochloric acid — 1 : 3.

4.5.5 Sodium oxalate — 0.05 N. Dissolve 3.350 g of sodium oxalate (primary standard grade) in 1 000 ml of water.

4.5.6 Ferrous ammonium sulphate — 0.05 N. Dissolve 19.607 g of ferrous ammonium sulphate in 20 ml of concentrated sulphuric acid and water and dilute to 1 litre. Standardize with standard dichromate.

4.5.7 Stock nitrite solution — Dissolve 1.232 g of sodium nitrite in water and dilute to 1 000 ml (1 ml = 250 μg of N). Preserve with 1 ml of chloroform. Standardize using sodium oxalate (4.5.5) and standard potassium permanganate solution.

4.5.7.1 Intermediate nitrite solution — Calculate the volume, G , of stock nitrite solution required for intermediate nitrite solution from $G = 12.5/A$, where A is the stock solution in mg/l. Dilute the volume G to 250 ml with water (1.00 ml = 50.0 μg N).

4.5.7.2 Standard nitrite solution — Dilute 10.00 ml of intermediate nitrite solution to 1 000 ml with water (1.00 ml = 0.500 μg N).

4.6 Procedure

4.6.1 If the sample is turbid, filter through a 0.45 μg membrane filter. To 50.0 ml of clear sample neutralized to pH 7 or to a portion diluted to 50 ml, add 1 ml of sulphanilamide solution. Let the reagent react for 2 to 8 minutes. Add 1.0 ml of NED dihydrochloride solution and mix immediately. Let stand for at least 10 minutes but not more than 2 hours. Measure absorbance at 543 nm. As a guide, use the following light paths for the indicated nitrite nitrogen concentrations:

Light Path Length, cm	Nitrite Nitrogen, $\mu\text{g/l}$
1	2 - 25
5	2 - 6
10	2

Run parallel checks frequently against nitrite standards.

4.6.1.1 Colour standards for visual comparison — Prepare a suitable series of visual colour standards in Nessler tubes by adding the following volumes of standard nitrite solutions and diluting to 50 ml with water: 0, 0.1, 0.2, 0.4, 0.7, 1.0, 1.4, 1.7, 2.0 and 2.5 ml, corresponding, respectively to 0, 1.0, 2.0, 4.0, 7.0, 10, 14, 17, 20 and 25 μg of nitrite per litre. Develop colour as described in 4.6.1. Compare samples to visual standards in matched Nessler tubes between 10 and 120 minutes after adding NED dihydrochloride reagent. Select the concentration where the sample tube colour matches the standard tube colour.

4.7 Calculation

4.7.1 Calculate nitrite nitrogen from the following:

$$\text{Nitrite nitrogen (as } \text{NO}_2\text{-N) per litre} = \frac{\mu\text{g NO}_2\text{-N (in 52 ml final volume)}}{\text{ml of sample}}$$