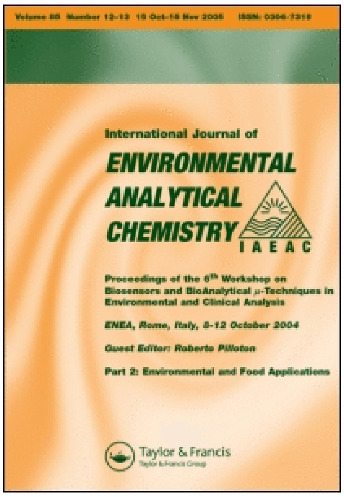

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Indole as A Chromogenic Reagent for Traces of Nitrate in Aqueous Solution

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A sensitive and selective spectrophotometric method for the determination of nitrate in aqueous solution is worked out. In strongly acidic medium, nitrate is reduced to nitrite by chloride ions. The nitrite produced is allowed to react with indole to form a water-soluble and stable compound with an intense absorption at 395 nm and adheres to Beer's law over 0.4–2 ppm of nitrate with a molar absorptivity of $16.15 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

KEY WORDS: Nitrate determination, aqueous solution, indole reagent, spectrophotometry.

INTRODUCTION

The determination of nitrate in trace concentration is of great interest in connection with problems of water pollution, sanitation and allied areas relating to public health.[1] Since spectrophotometric methods permit trace characterization of numerous analytical materials, it is not unexpected that most of the used methods to nitrate determination are based on spectrophotometry, and these are of four types; type 1, relied on the absorption of nitrate in the ultraviolet region,[2,3] type 2, based on the oxidative action of nitrate on organic compounds,[4,5] type 3, dependent on nitration reaction,[6,7] and type 4, based on reduction and diazotization.[8,9] Each of these methods suffers from a common list of disadvantages.

It has been reported that chloride ions reduce nitrate to nitrite in sulphuric acid medium,[10] and this idea has been used for nitrate determination with 4,5-dihydroxycoumarin as the chromogen.[11] However, the color produced with this reagent is unstable unless the highly toxic solvent, benzene, containing some methanol, is used as extractant and the method is not remarkably sensitive.

In this work, use has been made of the above idea[10] but with indole as the chromogen. The main features of the present method is the availability of the reagent (compare reference 11), simplicity of procedure, sensitivity of the color reaction and no need for extraction.

EXPERIMENTAL

Reagents

Chemicals used were of analytical grade.

Standard nitrate solution. Prepared by dissolving 0.1370 g of sodium nitrate in distilled water and completing the volume to 1000 ml with distilled water. This solution, containing 1000 ppm of nitrate ion, was diluted for use.

Indole solution, 0.05% in ethanol.

Sodium chloride solution. 4 M solution was prepared.

Sulphuric acid solution. Concentrated (18 M) solution was used.

Apparatus

Spectral measurement were performed on a Shimadzu UV-210A double-beam recording spectrophotometer and absorbance readings were carried out on a Pye Unicam SP 600 Series 2 single-beam spectrophotometer using matched 1 cm silica cells.

Procedure

To a series of 25 ml volumetric flasks, transfer 1 ml of aqueous sample solution containing 10–50 μg of nitrate. Add 2 ml of chloride solution, 2 ml of concentrated sulphuric acid solution and stopper the flasks. Allow the reaction mixture to stand for 10–15 min then add 5 ml of indole reagent solution and dilute to the mark with distilled water. Measure the absorbances at 395 nm after 5 but not 65 min against the reagent blank using 1 cm cells. A straight line passing through the origin should be obtained, indicating that Beer's law is obeyed over the cited range. The conditional molar absorptivity is $16.15 \times 10^3 \mathrm{mol}^{-1} \mathrm{cm}^{-1}$.

RESULTS AND DISCUSSION

Spectral studies

FIGURE 1 shows the absorption spectrum of the compound formed from the indirect reaction of nitrate (after reduction to nitrite) with indole in acidic medium. The intense yellow-colored species shows

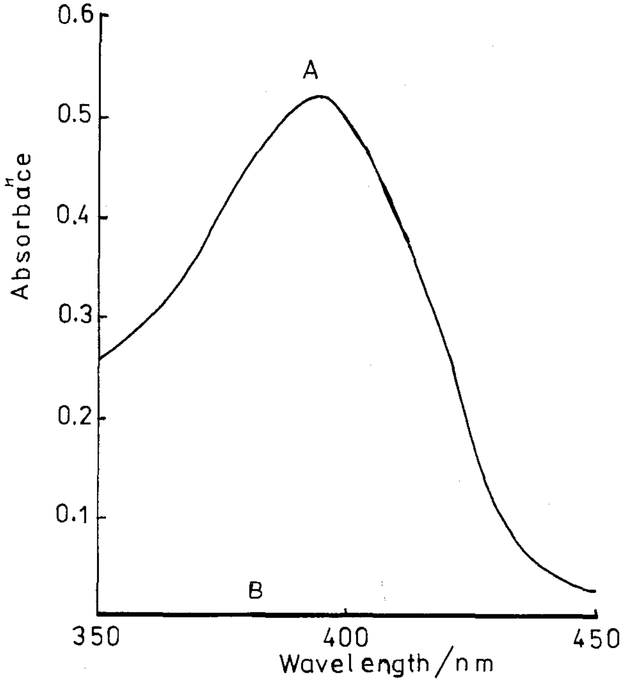


FIGURE 1 Absorption spectra of (A) 50 μg of nitrate, treated according to the recommended procedure, measured against reagent blank, and (B) reagent blank measured against distilled water.

maximum absorption at 395 nm. The flat absorption of the reagent blank at the 395 nm region can allow measurements to be made against distilled water.

In subsequent measurements, 1 ml of solution containing 50 μg of nitrate was taken and final volumes were made up to 25 ml.

Effect of acid concentration

The effect of sulphuric acid concentration, which is essential for the reduction of nitrate to nitrite, on the formation of the colored compound is first tested. To a series of nitrate solutions 0.5–4 ml of concentrated sulphuric acid solution are added. The intensity of the colored compound increases with increasing acid concentration and reaches maximum when the volume of added acid is 1.8–2.2 ml, and 2 ml of the concentrated acid is recommended for the procedure.

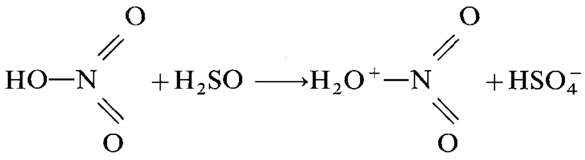
Effect of chloride concentration

Under the above optimum amount of sulphuric acid, the effect of sodium chloride (4 M) solution on the absorbance of the colored compound is next investigated. To a series of nitrate solutions are added 0.5–5 ml of chloride solution. The absorbance values remain maximum in the range 1.5–5 ml, and the addition of 2 ml of the chloride solution was incorporated in the procedure.

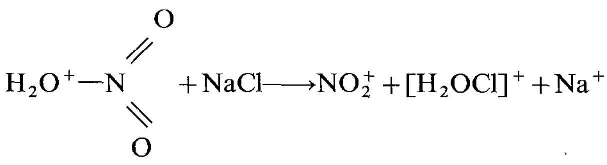
Effect of standing time for reduction

Since the nitrate–nitrite conversion has been observed to be time dependent, we thought that the reduction is not a one-step process and therefore postulated the following scheme:

$$\mathrm{2NaNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + Na_2SO_4} \qquad (1)$$



$$\mathrm{HO{-}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{N}}} + \mathrm{H_2SO} \longrightarrow \mathrm{H_2O^+{-}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{N}}} + \mathrm{HSO_4^-} \qquad (2)\ \text{slow}$$



$$H_2O^+{-}NO_2 + NaCl \longrightarrow NO_2^+ + [H_2OCl]^+ + Na^+ \quad (3)$$

$$NO_2^+ + 2NaCl \longrightarrow NaNO_2 + Cl_2 + Na^+ \quad (4)$$

$$NaNO_2 + H_2SO_4 \longrightarrow HNO_2 + NaHSO_4 \quad (5)$$

$$HNO_2 + H_2SO_4 \longrightarrow H_2NO_2^+ + HSO_4^- \quad (6) \text{ slow}$$

$$H_2NO_2^+ \longrightarrow NO^+ + H_2O \quad (7) \text{ slow}$$

$$NO^+ + \text{indole} \longrightarrow \text{Colored product} \quad (8) \text{ relatively rapid}$$

The minimum standing time required for maximum color development is 10 min, and a time of 10–15 min is adapted for the procedure.

Development time and stability period

The reaction rate, after dilution to the mark with distilled water, for the formation of the colored body is found by measuring the absorbance of the reaction mixture at various intervals of time. The experimental data indicate that maximum formation of the chromophore takes place after 5 min, from dilution to the mark, and remains stable for about 1 hr, after which gradual fading occurs.

Accuracy and precision of the method

Under the above optimum conditions, the accuracy and precision (from eight replicate determinations) of the method are checked. The results are given in Table I.

TABLE I

Accuracy and precision of the method.

Nitrate taken/μg	Relative error, %	Relative standard deviation, %
10	+0.12	1.4
25	+0.19	0.2
50	+0.52	0.6

Study of diverse ions

In order to assess the possible analytical applications of this colour reaction, the effects of foreign ions that may accompany nitrate have been examined by carrying out determinations on 50 μg of nitrate in the presence of each of these ions. The results are compiled in Table II.

The method is more selective for most of the anions tested than for cations. The latter may simply be trapped using ion-exchange procedure.

Comparison with other methods

The method is superior to most of the currently-used methods for nitrate determination. The method is more sensitive than, the most recently published method, i.e. the 4,5-dihydroxycoumarin procedure.[11] Further, the color reaction needs no extraction and is simple and rapid.

CONCLUSION

A sensitive, accurate and precise method has been developed for the determination of nitrate in the range 0.4–2 μg ml^{-1}. Because of its advantageous characteristics, the method will be useful in routine analysis of nitrate. However, some ions commonly present in waters can cause interference. A suitable preliminary ion-exchange clean-up may therefore frequently be required.

TABLE II

Effect of diverse ions on nitrite determination.

Interferent	Permissible amount in the presence of 50 *μg of nitrate/μg*
Acetate	22,500
Ammonium	13,000
Bromide	5000
Carbonate	22,500
Chloride	25,000
Fluoride	45,000
Hydrogen carbonate	20,000
Iodate	75
Iodide	200
Phosphate	5000
Sulphate	17,500
Sulphide	12.5
Sulphite	22.5
Aluminium	12.5
Barium	300
Cadmium	25
Calcium	10,000
Chromium (III)	37.5
Chromium (VI)	25
Cobalt (II)	25
Copper (II)	50
Iron (II)	25
Iron (III)	50
Lead (II)	25
Magnesium	750
Molybdenum (VI)	25
Nickel (II)	25
Vanadium (V)	25
Zinc	2.5

[a] Amount of diverse ions causing an error of more than or equal to ±5% in the absorbance readings.

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