

PHOTOMETRIC DETERMINATION OF TRACE AMOUNT OF NITRATE AND NITRITE WITH 2-HYDROXYBENZOIC ACID – A NEW METHOD

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An improvement was found in the trace level determination of nitrate with 2-hydroxybenzoic acid as compared to 2-(acetyloxy)benzoic and 3-carboxy-4-hydroxy-benzenesulphonic acid which were reported earlier. Spectral interference was also found to be low in this method. Nitrite at trace level was determined indirectly by this method.

Key words: Photometry, Trace level, Nitration.

INTRODUCTION

The reported reagents used in the determination of nitrate at trace level are aromatic in nature, like xylenols [1,2] phenylsulphonic acid [3], 3-carboxy-4-hydroxy-benzenesulphonic acid [4] and 2-(acetyloxy)benzoic acid [5]. Since, nitro-derivative of these compounds absorb light in the visible region, they have been extensively used in the photometric determination of nitrate [6].

Attempts were made to improve the trace level nitrate determination by using 2-hydroxybenzoic acid. A comparative study was made employing 3-carboxy-4-hydroxy-benzenesulphonic acid and 2-(acetyloxy)benzoic acid. This compound was also employed in an indirect method for the estimation of trace amount of nitrite [7,8].

EXPERIMENTAL

Standard solutions of KNO_3 (E. Merck, 10 ppm), KNO_2 (E. Merck, 10 ppm), 3-carboxy-4-hydroxybenzenesulphonic acid (E. Merck, 5.3×10^{-2} mole/dm³), 2-acetyloxybenzoic acid (E. Merck, saturated at 70°C) and 2-hydroxybenzoic acid (E. Merck saturated solution at 70°C) were prepared. A buffer solution of pH 12 was made by mixing equal volumes of disodium hydrogen-phosphate (E. Merck, 5×10^{-1} mole/dm³) and sodium hydroxide (E. Merck, 10^{-1} mole/dm³). All reagents used were of reagent grade and were prepared in double-distilled water.

Photometric studies were done by using Beckman-25 double beam spectrophotometer equipped with two matched quartz cells of 1 cm path length. The Beckman 10" linear chart recorder was used for recording spectra.

Procedure

The reported method [5] was used for these estimations. Standard solutions of KNO_3 (1 – 10 ppm) along with 2 ml of saturated solution of 2-hydroxybenzoic acid and 0.1 ml of 18 mole/dm³ H_2SO_4 were added in a 25 ml volumetric flask. The contents were heated at 250°C for 20 min. When the colour of the reaction mixture became purple, it was allowed to cool down to room temperature. Then 0.7 ml of 8.75 mole/dm³ NaOH and 2 ml of buffer solution (pH 12) were added and the volume of the contents was made upto the mark with distilled water. Absorbance was recorded at 410 nm. Same procedure was followed for the determination of nitrite where standard solutions of KNO_2 (1 – 10 ppm) were used. Estimations were also carried out using 2-(acetyloxy)-benzoic acid and 3-carboxy-4-hydroxybenzenesulphonic acid for the purpose of comparison with the present work.

RESULTS AND DISCUSSION

Spectra obtained for 3-carboxy-4-hydroxybenzenesulphonic acid, 2-acetyloxybenzoic acid and 2-hydroxybenzoic acid for nitrate determination are given in Fig. 1. 3-Carboxy-4-hydroxybenzenesulphonic acid showed a small shoulder of low absorbance at 400 nm, as reported earlier, while for 2-(acetyloxy)benzoic acid and 2-hydroxybenzoic acid intense peaks are observed at 410 nm. Spectra for nitrite show relatively low absorbance at 410 nm as λ_{max} for all these reagents as shown in Fig. 2. Results obtained using these reagents for the determination of nitrate and nitrite are listed in Table 1 and 2. Calibration curves for nitrate and nitrite are plotted in Fig. 3.

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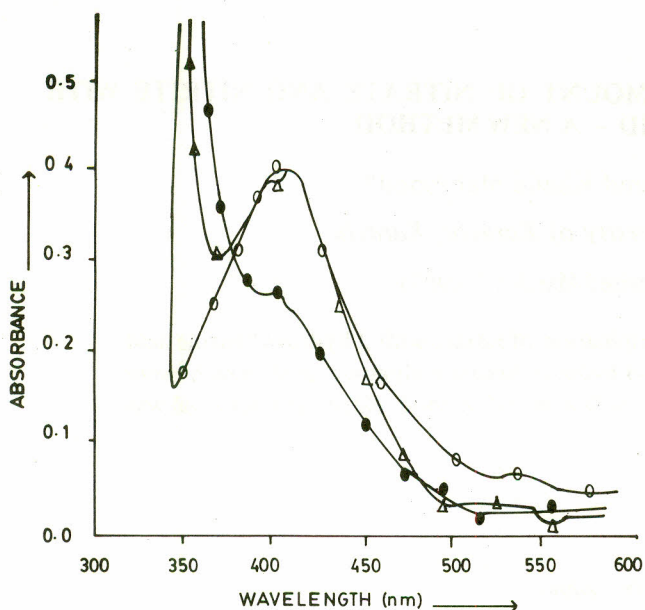


Fig. 1. Absorption spectra of nitrate (2.0 ppm) in

- a) -○-○- 2-hydroxybenzoic acid.
 b) -△-△- 2-(acetyloxy) benzoic acid.
 c) -●-●- 3-carboxy-4-hydroxybenzenesulphonic acid.

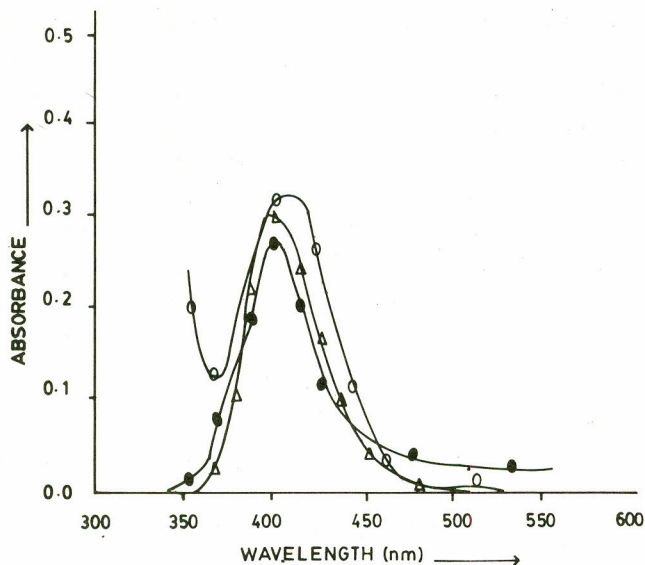


Fig. 2. Absorption spectra of nitrite (2.0 ppm) in

- a) -○-○- 2-(acetyloxy)benzoic acid.
 b) -△-△- 2-hydroxybenzoic acid.
 c) -●-●- 3-carboxy-4-hydroxybenzenesulphonic acid.

While considering nitrate determination with 3-carboxy-4-hydroxybenzene sulphonic acid, according to Sandell [9], the optimum limit of detection was reported to be 3-10.3 ppm but in this method the detection limit is found to be 0.2 – 10 ppm which is similar to that with 2-(acetyloxy)-benzoic acid. However, spectral interference is found to be relatively low in 2-hydroxybenzoic acid as compared

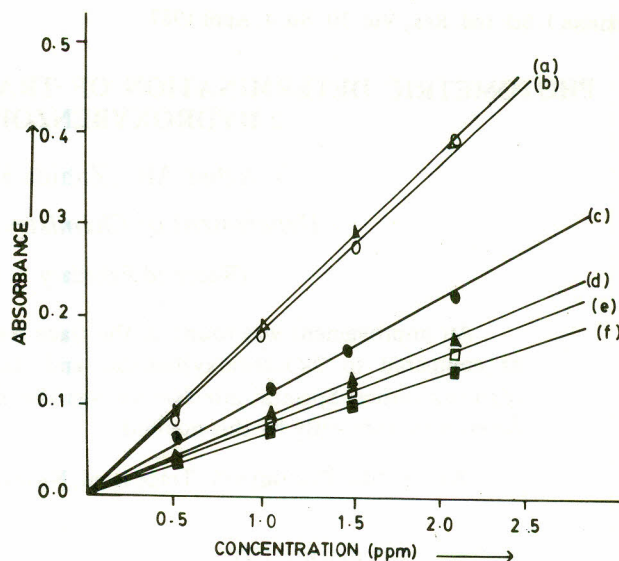


Fig. 3. Calibration curves of nitrate and nitrite.

- a) -△-△- Nitrate in 2-(acetyloxy)benzoic acid.
 b) -○-○- Nitrate in 2-hydroxybenzoic acid.
 c) -●-●- Nitrate in 3-carboxy-4-hydroxybenzenesulphonic acid.
 d) -▲-▲- Nitrite in 2-(acetyloxy)benzoic acid.
 e) -□-□- Nitrite in 2-hydroxybenzoic acid.
 f) -■-■- Nitrite in 3-carboxy-4-hydroxybenzenesulphonic acid.

Table 1. Concentrations and absorbance of nitrate in various systems for calibration.

S. No.	Concentration on nitrate (ppm)	Absorbance in 2-hydroxybenzoic acid	Absorbance in 3-carboxy-4-hydroxybenzenesulphonic acid	Absorbance in 2-(acetyloxy)benzoic acid
1.	0.00	0.000	0.000	0.000
2.	0.50	0.095	0.065	0.100
3.	1.00	0.195	0.125	0.200
4.	1.50	0.295	0.170	0.300
5.	2.00	0.410	0.220	0.390

Table 2. Concentrations of nitrite and absorbance in various systems for calibration.

S. No.	Concentration on nitrite (ppm)	Absorbance in 2-hydroxybenzoic acid	Absorbance in 3-carboxy-4-hydroxybenzenesulphonic acid	Absorbance in 2-(acetyloxy)benzoic acid
1.	0.00	0.000	0.000	0.000
2.	0.50	0.035	0.035	0.040
3.	1.00	0.080	0.073	0.083
4.	1.50	0.125	0.110	0.143
5.	2.00	0.145	0.147	0.185

to 2-(acetyloxy)-benzoic acid.

Furthermore, this method has an advantage over the reported methods, i.e. at reaction temperature (250^o), 3-carboxy-4-hydroxybenzenesulphonic acid or 2-(acetyloxy)benzoic acid are decomposed and converted into 2-hydroxybenzoic acid, decreasing the sensitivity for the determination of nitrate at trace level [10].

Similar detection limits for nitrite are not found in all these three systems due to the instability of nitrite at this temperature [11].

The present method may be preferred due to its improved detection limits, low spectral interference, easy availability and low cost of the reagent.

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