Spectrophotometric Flow Injection Determination of Nitrate and Nitrite in Potable Water using 8-Hydroxyquinoline

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Summary: A method based on the principle of flow injection analysis is described for the determination of nitrate and nitrite. A minicolumn of copperized cadmium is used which reduces nitrate to nitrite, which in turn is diazotized with 4-aminobenzoic acid and 8-hydroxyquinoline. The resulting azo compound is quantified at 485 nm. The procedure is applied to potable water samples. The sampling rate for both species was 60 hr^{-1}. The relative standard deviation was 0.8% for nitrite and 1.0% for nitrate.

Introduction

The broad acceptance of flow injection analysis (FIA) is undoubtedly due to its versatility, which allows the methods to be used in conjunction with a wide variety of detectors and analytical techniques. This trend is likely to continue, because FIA systems enhance the performance of various instruments by increasing the sensitivity over 100 times [1-2], by allowing speciation and removing matrix effects.

Several methods are available for the determination of trace amounts of nitrate and nitrite. These include ion selective electrodes [3,4], and direct spectrophotometric methods [5-8]. Indirect spectrophotometric methods involve the reduction of nitrate to nitrite followed by diazotization and coupling. Copperized cadmium [9,10] and titanium (III) chloride [11] have been used for the reduction processes based on flow injection analysis.

In this work a method is described for the determination of nitrate and nitrite based on F.I.A by reduction with copperized cadmium and derivatization by 4-aminobenzoic acid and 8-

hydroxyquinoline. This method has been successfully applied to the determination of nitrate and nitrite in potable waters.

Results and Discussion

Various experimental aspects were optimized on the basis of univariate approach to obtain a manifold (Fig. 1) with significant accuracy using 5.0 ppm nitrate and 2.5 ppm nitrite solutions. The effect of different concentrations of 4-aminobenzoic acid and 8-hydroxyquinoline were tested and the results are shown in Fig. 2. As is evident from the graph maximum signals for azo dye formation were obtained at 25 x 10^{-3}M 4-aminobenzoic acid and 3.0 x 10^{-3}M 8-hydroxy quinoline and were therefore selected for subsequent studies.
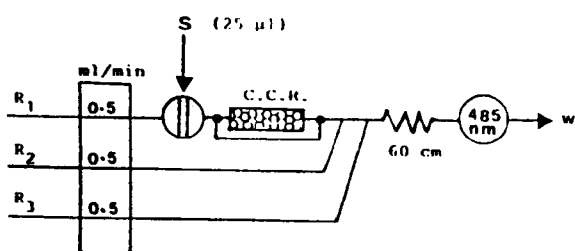

Fig.1: Flow injection manifold for the determination of nitrate and nitrite.
R₁ = Tris buffer 0.01 M, pH 7.0.
R₂ = 4-aminobenzoic acid and
R₃ = 8-hydroxyquinoline
C.C.R. = Copperized cadmium reactor.

In the sample carrier channel the effect of replacement of Tris- HCl buffer with deionised water and ammonium chloride solution of different concentrations were investigated. When water and ammonium chloride were used separately as a sample carrier, small peaks and precipitates were observed on-line which resulted in non-steady baseline. The use of Tris-HCl buffer (0.01 M, pH 7.0) gave a significant peak height with a steady baseline and therefore was selected.

Fig. 3 shows the effect of pHs of 4-aminobenzoic acid and 8- hydroxyquinoline on the diazotization process. The absorbance was increased in the range of pH 1.0 - 2.0 and 11.0 - 12.0 respectively and decreased on further increase. Therefore the pH 2.0 of 4-aminobenzoic acid and pH 12.0 of 8-hydroxyquinoline were selected and used. The effect of copperized cadmium reactor length was also tested. A column of 4.0 cm in length was selected because of the reasonable reduction and good reproducibility.

The effect of flow rates and mixing coil length was calibrated (Fig. 4) to obtain the best overall flow rate and mixing coil length in terms of sensitivity, sampling rate and reagent consumption. A maximum response (peak height) was obtained at a flow rate of 0.3 ml min⁻¹ per channel, but due to peak broadening and sample dispersion, the flow rate of 0.5 ml min⁻¹ was used. The mixing coil
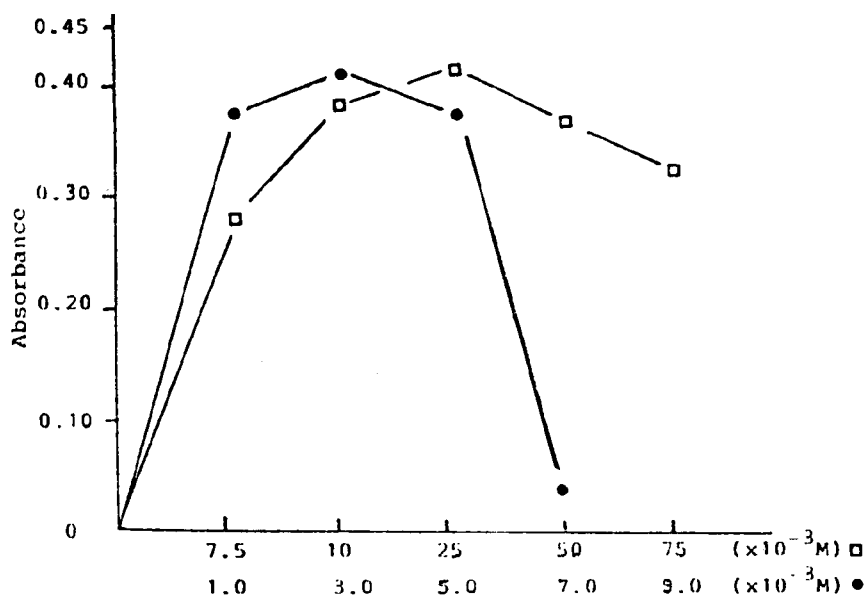

Fig. 2: Effect of 4-aminobenzoic acid (□) and 8-hydroxy- quinoline (●) on the azo compound formation.
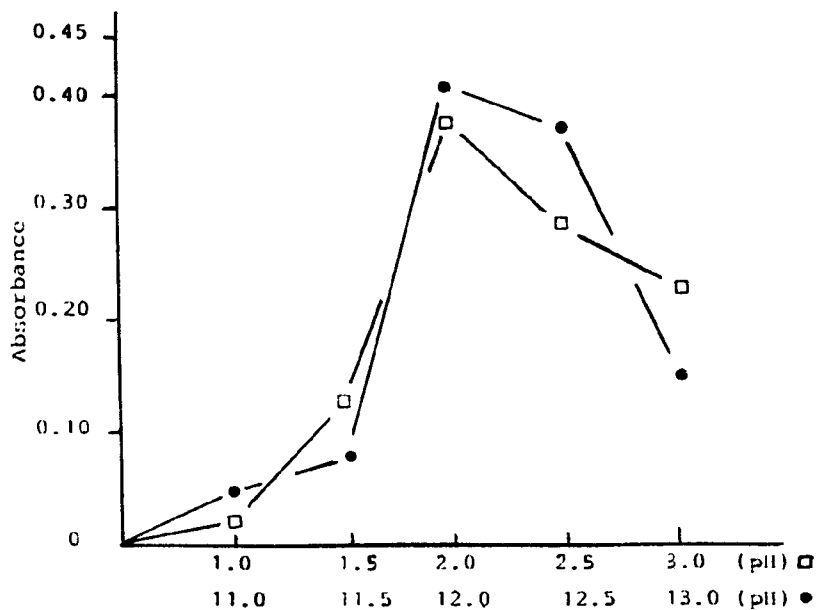
Fig. 3: Effect of pH of 4-aminobenzoic acid (•) and 8- hydroxyquinoline (�‍□) on the derivatization process.
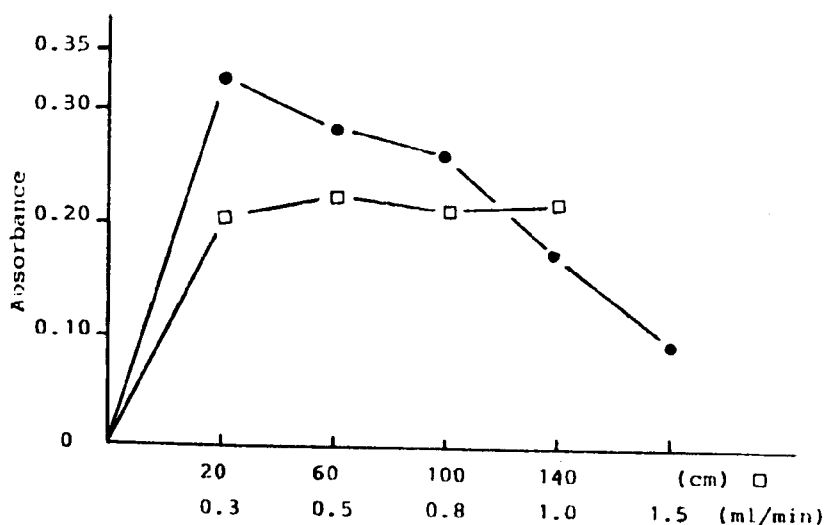

Fig. 4: Effect of flow rate (•) and mixing coil length (□) on the peak height, absorbance.

length of 60 cm was used, as that produced a detectable product.

Calibration graph

Six standards of nitrate and nitrite covering the range 1.0 - 9.0 ppm and 0.5 - 4.5 ppm were injected into the optimized system respectively.

Linear calibration graphs were obtained with a correlation coefficient of 0.9990 and a regression equation of y = 0.0096 x - 0.008 for nitrate and a correlation coefficient of 0.9995 and regression equation of y = 0.016 x - 0.001 for nitrite. The detection limit (2 x blank noise) was 0.3 ppm for nitrate and 0.1 ppm for nitrite. The sampling rate for both species was 60 hr^{-1}. The relative standard deviation was 0.8% for nitrate and 1.0% for nitrite.

Effect of diverse ions

The effect of some anions and cations on the determination of nitrate and nitrite was studied by addition method. The results obtained are summarized in Table 1.

Table 1: Effect of various anions and cations (10 fold) on the determination of nitrate (5.0 ppm) and nitrite (2.5 ppm).

Ions	Peak height (mm)	
	Nitrate	Nitrite
None present	77	103
Acetate	75	102
Carbonate	76	100
Chloride	79	101
Ferric	75	105
Potassium	77	100
Sodium	76	102
Sulphate	76	103

*Mean of three readings.

Application of the established method to water samples

The proposed method was applied for the determination of nitrate and nitrite to a sample of Quetta City tap water. The values obtained were 10.0 mg 1^{-1} as nitrate and 0.12 mg 1^{-1} nitrite. The same tap water was analyzed by spectrophotometric procedures based on derivatization with phenoldisulphonic acid and 4-aminosalicyclic acid [12,13] which are almost universal procedures for these two anions. The values 9.3 mg 1^{-1} nitrate and 0.10 mg1^{-1} nitrite were obtained when analyzed by these procedures which are in good agreement with each other.

Experimental

All chemicals were analytical reagent grade. Distilled/deionised water was used in the preparation of all solutions.

4-Aminobenzoic acid solution 0.025 M. pH 2.0

This solution was prepared by dissolving 0.34 g of 4-aminobenzoic acid in 100 ml of 0.1 M hydrochloric acid and pH 2.0 was adjusted with the same concentration of hydrochloric acid.

8-Hydroxyquinoline solution 0.003 M,. pH 12.0

This solution was prepared by dissolving 0.043 g of 8-hydroxyquinoline in 100 ml of 0.15 M sodium hydroxide and pH 12.0 was adjusted by the same concentration of sodium hydroxide.

Nitrate and Nitrite stock solutions

The aqueous 100 ppm nitrate and nitrite solutions were prepared by dissolving 0.14 g of sodium nitrate and 0.15 g of sodium nitrite (over dried) in water, treated with a few drops of chloroform and kept in refrigerator. Working standards were prepared by appropriate dilution with water.

Preparation of copperized cadmium reactors

The cadmium reactor columns were prepared according to the literature [10] by adding 5 g of cadmium powder (100 mesh, 0.15 mm diameter) to 50 ml of a copper sulphate solution (2 g/100 ml) and stirred for 5 min. The resulting copperized cadmium was washed with 2.0 M hydrochloric acid, packed into glass tube (2-6 cm long, 2 mm i.d.), plugged with glass wool and silicone tube pieces. The columns were stored in Tris-HCl buffer (0.01M, pH 7.0).

Apparatus

For the simultaneous determination of nitrate and nitrite, the flow injection manifold used is schematically shown in Fig. 1. The peristaltic pump (Ismatec Reglo 100) was used to propel the carrier and reagents in the system through standard teflon tubing (0.8 mm i.d) at a flow rate of 0.5 ml min⁻¹. Nitrate and nitrite standards were injected into Tris-HCl buffer stream of 0.01 M, pH 7.0 via a rotary valve (Rheodyne 5020) with a 25µl sample volume passed through the reactor column merged with 4-aminobenzoic acid and coupling agent in a 60 cm mixing coil. The absorbance was monitored at 485 nm by a flow through (30 µl) spectrophotometer (LKB Novaspec II) and the output was relayed to a chart recorder (Kipp and Zonen BD 40).

Acknowledgement

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