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Quantitation of trace amounts of nitrite in water samples using 4-amino-3-hydroxynaphthalene-1-sulfonic acid and central composite design

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ABSTRACT

A simple, selective and very sensitive method for the spectrophotometric determination of nitrite in water has been developed and optimum reaction conditions along with other analytical parameters have been evaluated. Optimum conditions of the factors influencing the reaction were explored by central composite design (CCD). The variables chosen were pH of the acidic solution and volume of 4-amino-3-hydroxynaphthalene-1-sulfonic acid. The method is based on the reaction of nitrite with 4-amino-3-hydroxynaphthalene-1-sulfonic acid. The absorbance of the product at 303 nm obeyed Beer's law in the concentration range of 0.001-0.200 mg L^{-1} of nitrite. A detection limit of 5×10^{-4} mg L^{-1} was obtained for the determination of nitrite by the proposed method. The method was successfully applied to determine nitrite in water sample. The RSD of the method for determination of nitrite in water samples was 6%. The method is capable in determination of trace amounts of nitrite in water samples.

KEYWORDS

Nitrite;
Spectrophotometric;
Central composite design;
4-amino-3-hydroxynaphthalene-1-sulfonic acid;
Water sample.

INTRODUCTION

Nitrite is an important water pollutant and an excess concentration of nitrite in drinking water is hazardous to health, especially to pregnant women.[1] Traces of nitrite and nitrate in drinking water may lead to methemeglobmenia in infants, and with long term exposure is a possible cancer risk. In view of the increasing interest in the quality of natural and sewage water, nitrite levels when correlated with other forms of nitrogen in water, can provide an index of organic pollution in water,[2] making the determination of exact concentration of nitrite in water desirable. Thus, determination of nitrite is of great importance in environment and food analysis and a simple, sensitive and selective determination of nitrite is highly desirable.

In the last two decades, many strategies have been developed to facilitate determination of nitrite.[3] An excellent review on the detection and determination of nitrite has been reported by Moorcroft et al.[3] Methods used to determine trace amounts of nitrite in water are polarography,[4] flow injection analysis,[5-7] voltammetry,[8] spectrofluorimetry,[9,10] chromatography,[11-14] potentiometry,[15-17] capillary electrophoresis,[18-20] membrane sensors,[21,22] elec-

troanalysis[23,24] and amperometry.[25,26] However, most of these methods are expensive, laborious, time consuming and may damage the environment.

Analyses based on spectrophotometric methods are recommended methods in these conditions.[27-38] Nitrites are normally determined by the Griess reaction[39] using various reagents[40,41]. Many of these reaction systems suffer from the inorganic species and have low sensitivity[42-44]. A number of other spectrophotometric methods have also been reported for the determination of nitrite using different reagents, p-nitroaniline (PNA) and o-methoxyphenol[45], 4-nitroaniline and 1-naphthol[46]. p-aminophenylmercaptoacetic acid[47]. 4-aminobenzoic acid[48].

In this paper, we have developed a simple and selective method for nitrite determination. The method is based on the reaction between nitrite and 4-amino-3-hydroxynaphthalene-1-sulfonic acid.

EXPERIMENTAL

Apparatus and software

An Agilent UV-Vis spectrophotometer model 8453 with diode array detector with 1 cm path length quartz cells was used for recording spectra. A JENWAY ion-meter model 3345 was employed for pH measurements.

Design and analysis of the central composite experiments were carried out by MINITAB (Minitab Inc. Release 14.0) statistical package.

Reagents and solutions

All chemicals used were of analytical reagent grade, and doubly distilled water was used in the preparation of all solutions in the experiments. Sodium nitrite, ethanol and hydrochloric acid were supplied by Merck (Darmstadt, Germany). The reagent 4-amino-3-hydroxynaphthalene-1-sulfonic acid (AHNSA) was supplied by BDH Chemicals Ltd Poole England. A 100.0 mg L^{-1} standard solution of nitrite stock was prepared in doubly distilled water. Stock 1.0×10^{-3} mol L^{-1} solution of AHNSA was prepared in doubly distilled water and ethanol (1:1). Working solutions were prepared by diluting the standard stock solution to appropriate volume with doubly distilled water whenever required. Acidic solution (pH = 1.6) was prepared by adjusting the pH of doubly distilled water by adding hydrochloric acid and sodium hydroxide.

Calibration curve

Volume equivalent to 1.5 mL of stock solution of AHNSA was transferred to 5.0 mL volumetric flask. The solution was diluted to volume of 5.0 mL by addition of acidic solution with optimized pH (pH = 1.6). To this mixture, 0.05–10 μL of stock 100.0 mg L^{-1} standard nitrite solution was added. The mixture was maintained at room temperature for 40 min for completion of the reaction. After 40 min, while the solution has been maintained at room temperature, its spectrum was recorded in a 1 cm path-length quartz cell against reagent blank which is prepared in the same manner but in the absence of nitrite. It must be mentioned that the maximum absorption was reached at 40 min after mixing.

Sample preparation for determination of nitrite in water sample

Water samples (Drinking water) were analyzed within same conditions of acquiring calibration data. Firstly, pH of the water sample was adjusted to 1.6. A volume equivalent to 3.5 mL of the resulting sample without dilution was transferred to a 5 mL volumetric flask containing 1.5 mL AHNSA. After shaking well and standing for 40 min, the spectrum of the sample was recorded in a 1 cm path-length quarts cell against the reagent blank.

RESULTS AND DISCUSSION

Central composite experimental design and optimization of the factors

The optimization of parameters (volume of reagent and pH of the acidic solution) requires many experiments. The total number of experiments required for optimization can be reduced by using experimental design techniques. The purpose of the experimental design is extraction of the maximum amount of information of the system in an economical way[49]. Experimental design methodology involves changing all variables from one experiment

to the next, simultaneously. The reason for this is that variables can influence each other, and the optimum value for one of them might be related to the values of the others[50]. Central composite design (CCD), an experimental strategy for seeking the optimum conditions for a multivariable system, is an efficient technique for optimization. A full factorial requires many experiments at multilevel mode. CCD provides almost the same information that multilevel full factorial design gives, but with fewer experiments[51,52]. In CCD, it is assumed that the central point for each factor is 0 and the design is symmetrical around it. Factors and their considered levels of design are shown in TABLE 1. For a system with two factors (n = 2), CCD consists of 12 experiments. Values of the factors in these 12 experiments and obtained responses are shown in TABLE 2.

Analysis of variance (ANOVA) of the experiments performed (TABLE 2) has been given in TABLE 3 and TABLE 4. As can be inferred from data in TABLE 3 and TABLE 4, effect of none of the factors and terms (linear, squared and interaction) are statistically significant at 95% confidence level ($p < 0.05$). The sign of the coefficient of the factors give information about the negative or positive effect of the factors on the response. Therefore, increasing both pH and the volume of the reagent can decrease the response. However, since the interaction between two factors is positive and is relatively high, the pure effect of two factors on the response should be calculated.

In Figure 1, the variation of the absorbance of the reaction product with pH and volume of the reagent (AHNSA) is shown. As can be seen from Figure 1, in the intermediate values of the factors studied, the response increases.

Optimized values of the factors for determination of nitrite based on the reaction with AHNSA were obtained by analysis of the results of experiments collected in TABLE 2. The optimized values of the factors were volume of AHNSA (mL) = 1.5 and pH = 1.6.

Absorption spectra

The reaction between nitrite and AHNSA has been shown in Scheme 1. In Figure 2, spectra of the calibration samples after 40 min are shown. No significant changes were observed in the absorbance values within the temperature range 10-35 °C. The product was stable for about 2 hours in the solution.

TABLE 1 : Experimental factors and their investigated levels

Factors	Levels		
	-1	0	1
pH (X1)	1	2	3
Volume of the AHNSA (mL) (X2)	0.5	1.0	1.5

TABLE 2 : Experiments designed based on central composite design with two factors

# of experiment	pH	Volume of AHNSA (mL)	Response
1	1.0	2.46	0.381
2	3.0	2.46	0.337
3	2.0	1.65	0.998
4	2.0	0.50	0.275
5	3.4	1.65	0.468
6	2.0	1.65	0.301
7	2.0	1.65	0.413
8	1.0	0.84	0.588
9	0.6	1.65	0.295
10	2.0	1.65	0.320
11	3.0	0.84	0.261
12	2.0	2.80	0.223

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TABLE 3 : Analysis of variance for the results of CCD

Source	DF[a]	Adj MS[b]	p[d]
Regression	5	0.021	0.876
Linear	2	0.004	0.945
Square	2	0.04	0.570
Interaction	1	0.02	0.598
Residual Error	6	0.387	
Lake-of-Fit	3	0.06	0.901
Pure Error	3	0.327	

[a]. Degree of freedom; [b]. Adjusted mean of squares error; [c]. Probability value.

TABLE 4 : Analysis of variance (coded units)

Term	Coefficient	P[a]
Constant	0.507	0.007
pH	-0.023	0.861
Volume of AHNSA	-0.036	0.785
pH×pH	-0.0855	0.683
Volume of AHNSA × Volume of AHNSA	-0.217	0.318
pH × Volume of AHNSA	0.138	0.598

[a]. Probability value.

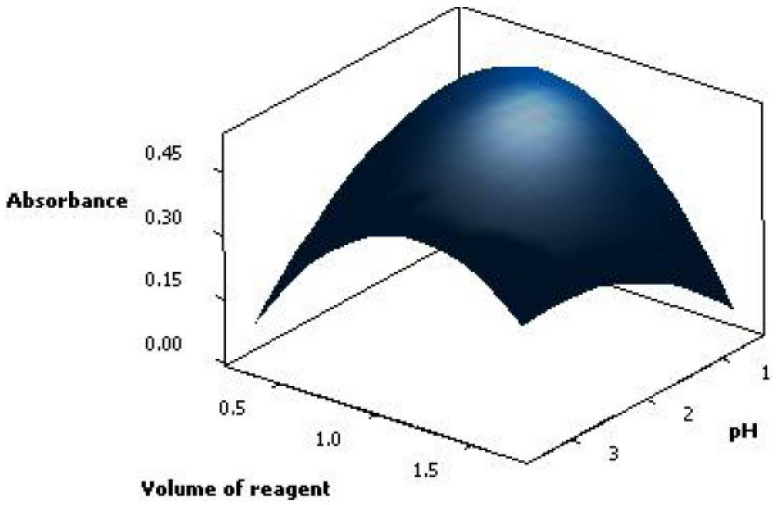
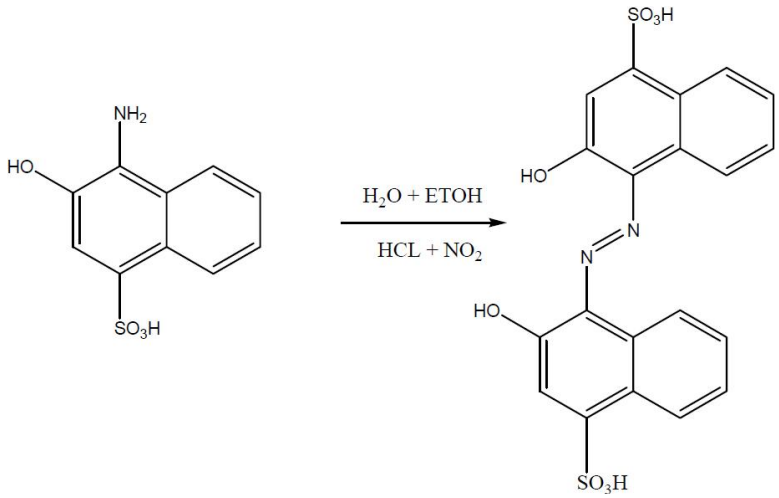


Figure 1 : Variation of the absorbance of the product at 303 nm with volume of the reagent and pH in optimum conditions

The reagent (AHNSA) has two major absorption bands located at 282 and 337 nm, with shoulders at 271, 291 and 324 nm. After addition of nitrite to the solution of AHNSA in optimum conditions, absorption at bands in wavelengths 271 and 291 decrease and in the rest of the ranges increase. Two relatively intense bands at 303 and 347 nm appear which can be used in the analysis.

Analytical data

Under the optimized experimental conditions, one calibration curve was constructed which was linear in the concentration range of 0.001-0.200 mg L^{-1} at the wavelength 303 nm. Adherence to Beer's law was studied by measuring the absorbance of product in nitrite solution. The statistical data of the calibration curve have been reported in TABLE 5. The limit of detection (LOD) and quantitation (LOQ) were calculated according to ICH guide lines using the formulae LOD = 3.3 ×S/b and LOQ =10 × S/b,



Scheme 1 : The reaction between the reagent AHNSA and nitrite

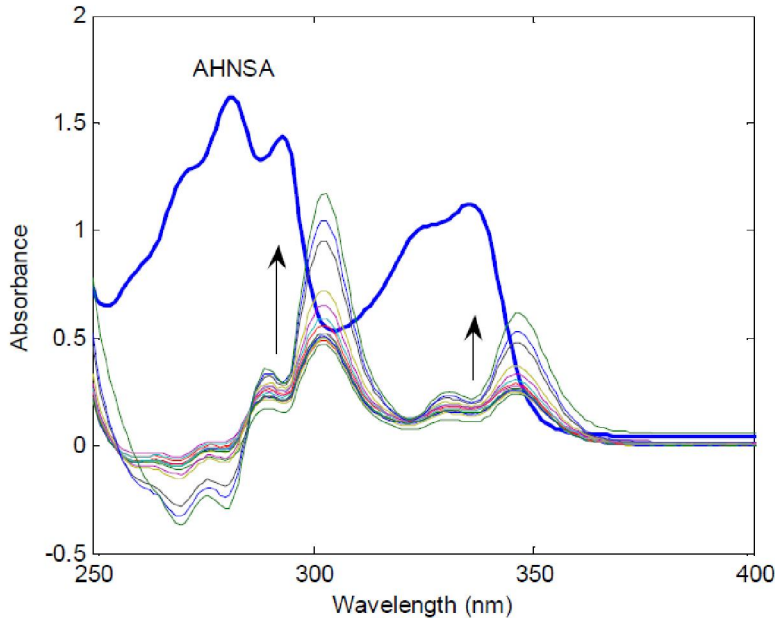


Figure 2 : Spectra of the calibration samples containing 0.001-0.200 mg L^{-1} of nitrite in pH = 1.6 and AHNSA with concentration of 3.0×10^{-3} mol L^{-1} after 40 min. The arrows show the direction of absorbance changes with concentration of nitrite

TABLE 5 : Analytical data of the constructed calibration curve

Parameters	Results
Linear range (mg L^{-1})	0.001-0.200
λmax (nm)	303
Molar absorptivity (L mol^{-1} cm^{-1})	3.6×105^{5}
Limit of detection (mg L^{-1})	5×10^{-4}
Limit of quantification (mg L^{-1})	0.002
Slope (b)	2.8503
Correlation of coefficient (r)	0.994
Standard deviation of slope (Sa)	0.0283
Standard deviation of intercept (Sb)	0.4354
Standard deviation of the regression	0.0872

TABLE 6 : Tolerance limit of different ions in determination of nitrite with concentration of 1.000 mg L^{-1}

Foreign ion	Tolerance limit (mg L^{-1})
SO_4^{2-}	9.01
NO_3^-	8.20
K^+	5.20
Ca^{2+}	2.73
Mg^{2+}	2.74
Fe^{3+}	1.37

TABLE 7 : Determination of nitrite in water samples based on the proposed method

Real sample	Spiked (mg L^{-1})	Found [a] (mg L^{-1})	RE %	RSD %
Drinking water	0.070	0.072	2.86	6.0
Soil1	0.000	0.120	-	3.7
Soil2	0.070	0.193	4.28	1.8

[a]. Mean of three determinations.

TABLE 8 : Published results for spectrophotometric determination of nitrite

Technique	Matrix	Detection limit (µmol L^{-1})	Linear range (µmol L^{-1})	RSD%	Reference
Visible	Aqueous	0.098	0.11-540	2.2	53
Greiss	Water	0.29	0.29-3.5	4.0	54
Greiss	Water	0.018	0.018-0.43	4.0	54
Visible	Well/Waste water	0.065	0.32-16	3.0	55
Visible	Aqueous	0.2	1-100	2.6	56
Visible	Food/Water	0.02	0.2-54	1.70	57
Greiss	Water	0.11	0.14-2.86	0.42	58
Greiss	Water	0.57	0.71-18.86	0.49	58
Greiss	Water	0.14	0.21-7.21	0.32	58
Visible	Water samples	1.30	1.30-86.9	0.5	59
Greiss	Food/Water/Soil	0.02	0.22-48	2	60
Greiss	Water	0.11	0-3.0	1	61
Visible	Meat/Water	2.2	22-150	3.9	62
Visible	Aqueous	36	71-21400	3	63
Visible	Aqueous	71	71-14300	5	63
Griess	Aqueous	0.011	0.217-36.956	3	64
UV	Drinking water	0.011	0.022-4.350	6	This method

respectively (where S is the standard deviation of the blank signal at 303 nm and b is the slope of the calibration plot). The linearity of the calibration curve is validated by the high value of correlation coefficient (where were close to unity) of the regression equation. The high values of molar absorptivity and low values of LOD indicate the high sensitivity of the proposed method.

Effect of foreign ions

As the system was developed for the analysis of water samples, the interference from foreign ions commonly present in water was studied by adding known amounts of foreign ions to a solution containing 1.000 mg L^{-1} of nitrite. Several species that can occur in the water samples together with nitrite were investigated. The tolerance limit of a potentially interfering ion was taken as its maximum amount causing an error of e" 5% during determination of nitrite in water samples. The tolerance limits for the ions studied are given in TABLE 6. Metal ions such as K^+ , Mg^{2+} , Ca^{2+} and Fe^{3+} were found to inter-

fere, but a large number of these ions were masked with EDTA.

Application

The method was applied to the determination of nitrite in drinking water. As the samples that were available contained no nitrite, synthetic samples were prepared by the addition of known amounts of nitrite, and then analyzed by the proposed method.

Under the optimum experimental conditions, validity of the proposed method was checked by determining nitrite in water sample. The percentage relative standard deviation (RSD %) for determination of nitrite in drinking water was satisfactory. Accuracy was evaluated as percentage relative error (RE %) between the measured mean concentrations and taken concentrations for nitrite. As the value of RE in TABLE 7 shows, the method is accurate.

Comparison of reported methods with proposed method for determination of nitrite

Some of the published methods for determination of nitrite have been collected in TABLE 8. The methods have been compared based on the linear range and detection limit. As can be inferred from data in TABLE 8, the proposed method has the lowest lower limit of linear range. Linear range of the method is also wide. Considering lower limit of the linear range and detection limit, the proposed method is a very sensitive method.

CONCLUSIONS

This paper reports a simple spectrophotometric method for fast determination of nitrite in water samples. Good precision and recovery was obtained when the proposed method was applied to real water samples. The proposed method is very sensitive, as the low detection limit showed. This method offers a simple, cost-effective and rapid alternative to existing methods for nitrite determination. The proposed method is sensitive, requires no control of temperature.

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