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A simple and sensitive spectrophotometric method for the determination of trace amounts of nitrite in environmental and biological samples using 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid monosodium salt

Padmarajaiah Nagaraja *, Naef Ghllab S. Al-Tayar, Anantharaman Shivakumar, Ashwine K. Shrestha, Avinash K. Gowda

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570006, India

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ABSTRACT

A very simple, sensitive, fairly selective and rapid spectrophotometric method for the determination of trace amounts of nitrite has been described. This method is based on the diazotized intramolecular coupling of electrophilic diazonium cation with the phenolic group of 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid monosodium salt (AHNDMS) in a phosphate buffer solution of pH 7.5. The cyclic product has a purple color with maximum absorbance at 560 nm and is stable for 6 h. Optimum reaction conditions and other important analytical parameters for the maximum color development were established. Beer's law was found to obey for nitrite in the concentration range of 0.1–1.6 $\mu g\,ml^{-1}$ with molar absorptivity of $2.6 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ and Sandell's sensitivity of 0.0075 $\mu g\,ml^{-1}$. The effect of interfering ions on the determination is described. The recommended method was applied for the determination of nitrite in different water, soil and human saliva samples. The performance of the recommended method was evaluated in terms of Student's *t*-test and variance ratio *F*-test, which indicated the significance of proposed method over the reference method.

1. Introduction

Nitrite is one of the important water pollutants. Excess concentration of nitrite in drinking water is hazardous to health, especially for infants and pregnant women. Nitrite reacts readily with secondary and tertiary amines and amides in human body producing toxic and carcinogenic nitrosamines compounds [1,2]. They also oxidize iron in hemoglobin of the red blood cells to form methemoglobin, which is unable to carry oxygen causing blue baby syndrome [3,4].

The use of nitrites in many applications such as food preservation, fertilizers, detergent, wood pulp, dye and synthetic fiber industries has caused serious pollution problems [5–7]. Nitrites may also be produced in distribution system through the activities of microorganisms on ammonia.

The necessity of nitrite monitoring has been recognized by most health authorities world wide, with legislation often levied on permissible levels in drinking water. At present the US EPA considered the maximum contaminant level (MCL) that is allowed for nitrite in drinking water is 1.0 $\mu g\,ml^{-1}$ [8]. As a consequence of widely recognized problem, there is a need to develop methods for monitoring the nitrite ion levels in environmental matrices, which is desirable from the stand point of environmental analytical chemistry.

Nowadays, in the development of new analytical methods, the amount and toxicity of the reagents used and of wastes produced are as important as any other analytical feature. Some of analytical methods use reagents or generate chemical wastes which are more toxic than the species being monitored [9]. Hence, there is a great need to develop methods which are less harmful to human health and are environment friendly.

There are numerous methods developed so far for the determination of nitrite in environmental samples, which include spectrofluorometry [10–12], chromatography [13–16], potentiometry [17–19], capillary electrophoresis [20–22], membrance sensors [23,24], flow injection analysis [25–29], electroanalytical [30,31], and amperometric [32,33]. Most of these methods are not suitable for routine determination of nitrite in environmental samples because some of them are costly or need skilled person to handle. Also, some of them are time consuming or require separation procedures.

Still, the most frequently employed methodology for the determination of nitrite is spectrophotometric method [34–46]. Most of these methods have the disadvantage of toxicity of the reagents

* Corresponding author at: Analytical Chemistry, DOS in Chemistry, University of Mysore, Manasagangothri, Mysore 570006, Karnataka, India. Tel.: +91 821 2412557; fax: +91 821 2421263.
E-mail address: profpn58@yahoo.com (P. Nagaraja).

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used and insufficient sensitivity or use expensive reagents. The APHA and AOAC official method of analysis involves the reaction of N-(1-naphthyl) ethylenediamine dihydrochloride with sulphanilamide [5,47]. This method requires careful control of acidity at each step of the process and has a carcinogenic effect [48].

In this paper, a very simple and selective method for nitrite determination based on the reaction between nitrite and 4-amino-5-hydroxynaphthaline-2,7-disulphonic acid monosodium salt only as a single reagent in phosphate buffer solution has been developed. The method is sensitive, requires no control of temperature and does not suffer from most of the potential interferences. The proposed method was successfully applied for the determination of nitrite in environmental and biological samples.

2. Experimental

2.1. Apparatus

Systronics spectrophotometer model 106 with 1 cm matched glass cell was used for measuring the absorbance. A pH-meter, EQUIP-TRONICS Model EQ-614 was employed for measuring pH.

2.2. Reagents

All the chemicals used, were of analytical reagent grade or of the highest purity available. Double distilled water was used throughout the experiments for dilution of the reagents and samples. Glass vessels were cleaned by soaking in acidified solution of $K_2Cr_2O_7$, followed by washing with concentrated HNO_3 and rinsing several times with distilled water.

2.2.1. Standard sodium nitrite solution (1000 $\mu g\,ml^{-1}$)

A 0.150 g of sodium nitrite (Merck, Germany) was dried at 110 °C for 4 h and dissolved in distilled water in a 100 ml volumetric flask. A small amount of sodium hydroxide was added to prevent the decomposition of nitrite to nitrous acid. Few drops of chloroform were added to inhibit the bacterial growth and thus make the nitrite solution stable [49]. Working solution was prepared by diluting standard solution of sodium nitrite to appropriate volume with distilled water whenever required.

2.2.2. 4-amino-5-hydroxynaphthalene- 2,7-disulphonic acid monosodium salt (AHNDMS) (0.5%, w/v)

A 0.5 g of AHNDMS (Sigma, USA) was dissolved in 0.4 M HCl in 100 ml volumetric flask. The solution was stable for 1 week under refrigeration (0–10 °C).

2.2.3. Phosphate buffer solution (0.5 M, pH 7.5)

This solution was prepared by mixing of 0.5 M solutions of KH_2PO_4 and K_2HPO_4 in 25:75 (v/v) ratio.

2.2.4. Solutions of foreign ions

Solutions containing suitable concentrations of potentially interfering ions were prepared in distilled water or appropriate solvent, to be used whenever required.

2.3. Recommended procedure

To a series of 10 ml standard flasks, 0.1–1.6 ml of 10 $\mu g\,ml^{-1}$ of standard sodium nitrite solution and 0.5 ml of 0.5% of AHNDMS solution were added, followed by 1 ml of phosphate buffer solution of pH 7.5. The contents of each flask were shaken thoroughly and kept aside for 2 min, which was then made up to the mark with distilled water. Absorbance was measured at 570 nm against reagent blank, which was prepared in the same manner except the addition of nitrite. Beer's law graph was constructed by plotting absorbance against nitrite concentration.

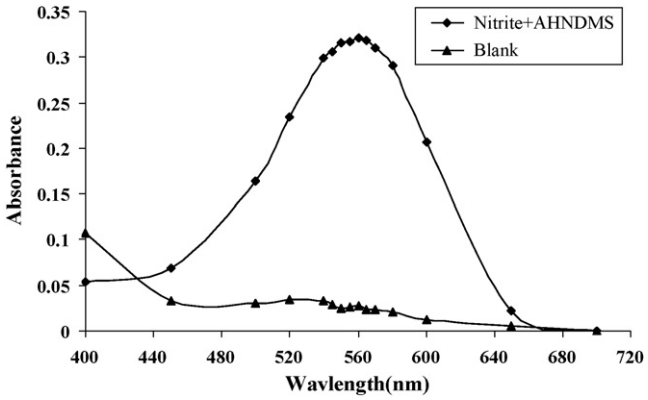

Fig. 1. Absorption spectra of nitrite with AHNDMS.

2.4. Determination of nitrite in water samples

Water samples (tap, lake, river, sea and rain) were collected without adding any preservative in polyethylene bottles and analyzed within 6 h. Sea water samples were frozen at 0 °C within 1 h of sampling. Water samples were filtered through a Whatman No. 41 filter paper, and then an aliquot of the filtrate was taken for analysis by the recommended method and reference method [5,47].

2.5. Determination of nitrite in soil samples

Soil samples were collected in plastic pouch from different sites (manured garden soil and farmland soil). Samples were dried at 60 °C in an electronic oven for 24 h, cooled to room temperature and ground in a mortar to get fine dust, then sieved through cotton cloth. Each sample (5 g) was mixed with 20 ml of distilled water and shaken well, after 5 min the solution was filtered through a Whatman No. 41 filter paper and the soil was washed with distilled water until about 100 ml of filtrate was collected [50]. The filtrate was made up to the mark with distilled water and aliquots were analyzed by recommended method and reference method [5,47].

2.6. Determination of nitrite in human saliva

Unstimulated human saliva samples were collected directly into glass bottles. Immediately, aliquots were centrifuged at 1000 rpm for 5 min to separate solid materials and then diluted or taken as it is to determine nitrite by the recommended method and reference method [5,47]. When the samples were not analyzed immediately after collection, centrifuged saliva was diluted with 0.1 M sodium hydroxide solution to prevent decomposition of nitrite and to restrain microbial reduction of nitrate to nitrite.

3. Results and discussion

3.1. Absorption spectra

Amino group of AHNDMS undergoes diazotization in presence of nitrite in an acidic medium to form diazonium cation, which gets coupled with hydroxyl group in AHNDMS to form purple color when phosphate buffer (pH 7.5) is added. The wavelength of maximum absorption of the color formed is obtained at 560 nm with negligible absorbance for the corresponding reagent blank (Fig. 1).

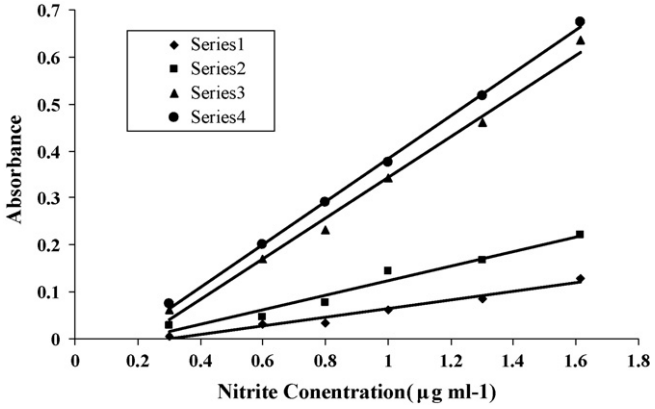

Fig. 2. Effect of different buffer solutions on the color absorbance. Series (1) 1 ml of 1 M of NaOH, Series (2) 2 ml of 0.5 M of the buffer solution ($NaOH + Na_2HPO_4$), Series (3) 2 ml of 0.5 M of the buffer solution ($NaOH + K_2HPO_4$), and Series (4) 1 ml of 0.5 M of the buffer solution ($K_2HPO_4 + KH_2PO_4$). All those buffer solutions were at pH 7.5 and all solutions diluted to 10 ml with distilled water.

3.2. Effect of AHNDMS concentration

The effect of varying concentrations of AHNDMS on the color intensity and stability has been studied by adding AHNDMS solution in the range of 0.1–3 ml (0.5%, w/v) to a series of fixed nitrite concentration in 10 ml volumetric flask. It was found that, the maximum intensity and stability of the color formed was obtained with 0.5 ml of (0.5%, w/v) AHNDMS solution in 10 ml of final volume.

3.3. Effect of hydrochloric acid

Acidic medium was necessary for diazotization. The use of hydrochloric acid medium to form diazonium cation was found to give better results than that of sulphuric acid. Hydrochloric acid concentration in the range of 0.2–1 M was found necessary for complete diazotization. Therefore, 0.4 M hydrochloric acid was used to dissolve AHNDMS to obtain maximum color intensity.

3.4. Effect of buffer solution

Nitrite reacts with AHNDMS in HCl medium to form diazonium cation, which gets coupled with hydroxyl group in AHNDMS to form purple color in basic medium. Sodium hydroxide was used to form this color but it was not stable. Effect of different buffer solutions at varying concentrations in different pH levels was studied. The results showed that, the use of buffer solutions containing $NaOH + K_2HPO_4$ or $NaOH + Na_2HPO_4$ at optimum concentration and pH with respect to each, gave stable color but the intensity and linearity were not good as shown in Fig. 2. However, the use of 0.5 M

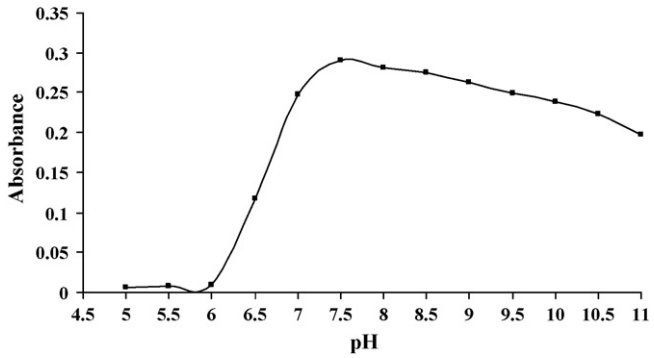

Fig. 3. Effect of different pH levels on the color development at 0.8 µg ml^{-1} of nitrite.

Table 2
Optical parameters for the determination of nitrite with AHNDMS.

Parameters	Characteristic
Color	Purple
λ_{max} (nm)	560
Stability (h)	6
Beer's law range (µg ml^{-1})	0.1–1.6
Molar absorptivity (l mol^{-1} cm^{-1})	2.6×10^4
Sandell's sensitivity (µg cm^{-2})	0.0075
Optimum photometric range (µg ml^{-1})	0.2–1.4
Detection limit (µg ml^{-1})	0.0069
Quantification limit (µg ml^{-1})	0.021
Regression equation[a]	
Correlation coefficient	0.9986
Slope (a)	0.4345
Intercept (b)	0.0537
Standard deviation[b]	0.0014
Relative standard deviation[b] (%)	0.46
Reaction time (min)	2

[a] $Y = ax + b$ where x is the concentration of nitrite in µg ml^{-1} and Y is the absorbance.
[b] Ten replicates measurements.

Table 3
Within-day and between-day precision studies on the determination of nitrite.

Nitrite added (µg ml^{-1})	Within-day		Between-day	
	Nitrite found[a] (µg ml^{-1})	RSD%	Nitrite found[a] (µg ml^{-1})	RSD%
0.5	0.498	0.36	0.497	0.53
1	0.997	0.42	0.995	0.82
1.5	1.495	0.61	1.492	0.74

[a] Mean value of five determinations carried out over five days.

Table 1
Effect of diverse species on the spectrophotometric determination of nitrite (1 µg ml^{-1}).

Diverse species	Tolerance limit (µg ml^{-1})	Diverse species	Tolerance limit (µg ml^{-1})
Br^-	25,000	F^-	350
K^+	12,500	Zn^{2+}, Zr^{4+}	250
Urea, SCN^-, Ni^{2+}, Cl^-	2500	Ba^{2+}	150
NH_4^+	3000	Pb^{2+}, Mg^{2+}, Al^{3+}, HCO_3^-	100
EDTA, Cd^{2+}, Mn^{2+}	2000	Hg^{2+}, Fe^{3+} [a]	50
Na^+, NO_3^-, tartarate, oxalate, hydroxylamine	1000	IO_3^-	9
CH_3COO^-, citrate	750	Ce^{4+}, Cu^{2+}	2.5
Ca^{2+}, SO_4^{2-}, SO_3^{2-}, WO_4^-, perchlorate	500		

[a] Masking by the addition of 0.5 ml of 0.3 M sodium fluoride.

Table 4
Application of recommended method for determination of nitrite in real water, human saliva and soil samples.

Sample	Amount taken (ml)	Nitrite added ($\mu g\,ml^{-1}$)	Proposed method		Reported method [5,47]		*t*-test[a]	*F*-test[b]
			Nitrite found[c] ($\mu g\,ml^{-1}$)	Recovery (%)	Nitrite found[c] ($\mu g\,ml^{-1}$)	Recovery (%)		
Tap water	1	0	0		0			
	0.5	0.5	0.498 ± 0.46	99.64	0.495 ± 0.44	99.08	1.98	1.08
	1	1.0	0.991 ± 0.32	99.12	0.991 ± 0.27	99.06	0.33	0.99
Lake water[d]	1	0	0		0			
	0.5	0.5	0.489 ± 0.39	97.76	0.492 ± 0.57	98.28	1.71	2.11
	1	1.0	0.993 ± 0.43	99.26	1.005 ± 0.98	100.5	2.57	5.05
River water[e]	1	0	0		0			
	0.5	0.5	0.494 ± 0.37	98.72	0.496 ± 0.53	99.12	1.41	2.06
	1	1.0	0.994 ± 0.27	99.34	0.997 ± 0.17	99.66	2.25	2.61
Sea water[f]	1	0	0		0			
	0.5	0.5	0.489 ± 0.53	97.76	0.488 ± 0.49	97.52	0.76	1.16
	1	1.0	0.986 ± 0.34	98.62	0.987 ± 0.32	98.78	0.77	1.10
Human saliva	1	0	0.117 ± 1.41		0.119 ± 1.52			
	0.5	0.5	0.609 ± 1.49	98.74	0.611 ± 1.01	98.74	0.41	2.19
	1	1.0	1.105 ± 0.89	98.93	1.094 ± 0.48	97.73	2.30	3.55
Soil[g]	1	0	0		0			
	0.5	0.5	0.493 ± 0.58	98.6	0.496 ± 0.89	99.16	1.19	2.05
	1	1.0	0.986 ± 0.44	98.54	0.987 ± 0.30	98.74	0.86	2.08

[a] Tabulated *t*-value for eight degrees of freedom at *P* (0.95) is 2.78.
[b] Tabulated *F*-value for (4,4) degrees of freedom at *P* (0.95) is 6.39.
[c] Mean ± relative standard deviation ($n = 5$).
[d] Kukkaraheli lake, Mysore, India.
[e] Cauvery River, Mysore, India.
[f] Arabean sea, Goa beach, India.
[g] Sericulture Department Field, Mysore University.

phosphate buffer $K_2HPO_4 + KH_2PO_4$ at pH 7.5 was found to give maximum absorbance with good linearity and was used for the determination of nitrite in the recommended procedure. The effect of pH on the color development is shown in Fig. 3.

3.5. Effect of time and temperature on stability of the color

No variation on the absorbance values of color formed was observed in the temperature range of 10–40 °C. Hence the reaction was carried out at room temperature (25 ± 5 °C). The maximum color intensity of the diazotized dye was obtained after 2 min of addition of buffer solution and was stable for 6 h.

3.6. Interferences studies

Validity of the method was assessed by examining the effect of various ions at $\mu g\,ml^{-1}$ levels on the determination of nitrite by the recommended method. The tolerance limit of interfering species was established at the concentrations that do not cause error more than ±3% in absorbance values of nitrite at 1 $\mu g\,ml^{-1}$

Table 5
Comparison of spectrophotometric methods for the determination of nitrite with the recommended method.

Reagents/reference	λ_{max}	Determination range ($\mu g\,ml^{-1}$)	Molar absorptivity ($l\,mol^{-1}\,cm^{-1}$)	Reaction time (min)	Remarks
(1) 4-(1-Metyl-1-mesitylcyclo butan-3-yl)-2-aminothiazole + N,N-dimethyl aniline [42]	482	0.05–2.00	2.03×10^4	15	Time consuming and extractive
(2) Sulphanilamide + ethyl Acetoacetate [43]	356	0.20–3.00	1.22×10^4	7	Fe^{3+} interferes and less sensitive
(3) *p*-Nitroaniline + diphenylamine [44]	500	0.05–0.80	1.43×10^4	11	Time consuming and less sensitive, miceler media required, Fe^{3+} interfere
(4) 2-Trifluoromethylphenoxa zine and sulphadoxine [45]	530	0.4–1.6	1.3×10^4	2	Less sensitive, high detection limit interfere with Fe^{3+}, IO_3^-
(5) Sulphanilamide + NEDA[a] [5,47]	540	0.05–4.00	4.0×10^4	40	Time consuming, the product can be carcinogenic
(6) Phosphomolybdenum blue complex [48]	814	0.2–3.6	1.1×10^4	30	Less sensitive, time consuming
(7) Peroxovanadate complex [52]	470	6.67–66.7	0.276×10^3	–	Very less sensitive
(8) Sulphanilic acid + 1-naphthol [53]	418	0.02–0.87	1.70×10^4	20	Time consuming and less sensitive
(9) *p*-nitroaniline + ethoxyethylene maleic Acid [54]	439	0.5–16	1.21×10^4	–	Less sensitive, diazotization requires cooling (0–5 °C).
(10) *p*-Nitroaniline + acethylacetone [55]	490	0.50–14.0	3.2×10^4	–	Cu(II), Co(II), and Hg(II) interfere
(11) 5,10,15,20-tetrakis (4-aminophenyl) porphine [56]	434	0.0–0.018	2.63×10^5	–	Time consuming, requires 30 min heating, Fe^{3+} seriously interferes.
(12) *p*-Rosanilinium chloride + NEDA[a] [57]	560	0.04–0.4	8.33×10^3	30	Less sensitive, time consuming, metal ions are interfered seriously
(13) AHNDMS [recommended method]	560	0.1–1.6	2.6×10^4	2	Simple, non extractive, no need of heating, common ions do not interfere

[a] N-(1-naphthyl)ethylinediamine hydrochloride.

level. The precipitate observed in the presence of some metal ions was removed by centrifugation of the solution and measuring the absorbance of the eluent. Fe^{3+} was strongly interfering but was eliminated by the addition of 0.5 ml of 0.3 M sodium fluoride. The tolerance limits of various foreign ions that are likely to interfere during the analysis of nitrite in environmental samples are listed in Table 1.

3.7. Analytical data

In order to test the applicability of the recommended method, the absorbance of a series of solutions, containing varying amounts of nitrite, was recorded against the corresponding reagent blank at 560 nm. The system obeyed Beer's law in the range of 0.1–1.6 $\mu g\,ml^{-1}$ of nitrite and the calibration graph exhibited a straight line. The slope, intercept, correlation coefficient, molar absorptivity and Sandell's sensitivity and other optical parameters are summarized in Table 2.

3.8. Within-day and between-day precision study

To ascertain the ruggedness of the method, five replicate determinations at different concentration levels of nitrite were carried out. The results showed that, the within-day relative standard deviation values were 0.3–0.6%. The between-day relative standard deviation for different concentrations of nitrite obtained from the average of five determinations carried out over a period of five days were 0.5–0.8%. These results indicated that, the recommended method has an advantage of excellent reproducibility in both within-day and between-day precision as shown in Table 3.

3.9. Application of the method

In order to assess the suitability of the recommended method, it was applied for the determination of nitrite in real water, soil and human saliva samples. Fresh water samples collected from various sources were filtered through Whatman No. 41 filter paper, stored at 5 °C to retard bacterial growth, and analyzed within 24 h by the recommended method. Parallel determination was carried out to validate the recommended method with the standard method involving sulphanilamide and N-(1-naphthyl) ethylendiamine dihydrochloride (NEDA) [5,47]. Further, the quantification analysis of nitrite in all soil and saliva samples was performed by the recommended method with good recovery, and there were no significant differences between the results obtained from the recommended method and reference method [5,47].

The results were statistically evaluated in terms of Student's *t*-test and variance ratio *F*-test and the values calculated were found to be less than tabulated values at 95% confidence level indicating no significant differences in the accuracy and precision of the recommended method and the reference method (Table 4).

4. Conclusion

The new suggested procedure offers a simple, rapid, sensitive, selective and economic spectrophotometric method for the determination of nitrite which can be applied to environmental and biological samples with no need for pretreatment or extraction. The suggested method has significant advantages over other existing methods [27,39,48,51,52] due to simplicity of the procedure where only AHNDMS as a single reagent is used. It has less interference by other substances. These advantages make the suggested method superior compared to some of the reported methods as shown in Table 5. The recommended method is non-toxic and safer than other methods where organic solvents are used. Statistical analysis of the results revealed that, the recommended method is on par with the standard methods currently being used for the determination of nitrite.

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