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Method development for the voltammetric determination of nitrite in diverse matrices

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Catalytic electroreduction of nitrite ion in presence of thioglycolic acid in ammonium acetate buffer medium shows the possibility of devising an analytical method for determination of nitrite at low concentration. A wide linear range of 0.9-9 µg/mL is achieved. The limit of quantification is found to be 0.7 µg/mL using differential pulse polarography method. The method has been successfully applied for the analysis of nitrite content in marine waters and industrial wastes.

Keywords: Nitrite, Voltametric determination, Thioglycolic acid

Nitrite reacts with hemoglobin in blood streams and forms methemoglobin which causes breathing problems. It can also produce carcinogenic nitrosoamines by reaction with amines[1]. Thus, nitrite is a concerned nitrogen species and attracts to have a simple and convenient method of its determination at micro levels.

Voltammetric methods have proved useful in such studies. These can identify and determine ionic forms of a species due to their selectivity of the redox potential[2]. On these lines the determination of chlorate[3], iodate[4], sulfide[5] and bromide[6] has already been reported elsewhere. Herein detailed investigations of nitrite ion in presence of 0.1 M thioglycolic acid (TGA) in ammonium acetate buffer medium reveals the optimum analytical conditions for determination of nitrite. Gao and Zhao[7] have described single sweep polarographic determination of nitrite. Anodic stripping voltammetric analysis of nitrite in food samples is given by Santos et al.[8]. De silva and Mazo[9], and Liu et al.[10] have determined nitrite by using gold disc and graphite electrode, respectively. A cyclic voltammetric method for determination of nitrite is shown by Niaz et al.[11] Amperometric determination of nitrite has also been recently reported by Yu et al.[12] The authors have envisaged the suitability of differential pulse polarography (DPP). It has enabled nitrite determination along with chloride, bromide, sulfide and sulfite without any interference. DPP results of analysis of different samples also compares favourably with the UV-visible spectrophotometric method.

Materials and Methods

Chemicals and reagents

Chemicals used were of analytical grade purity. Stock solution of nitrite was prepared from sodium nitrite of Loba Chemie (Batch No. 21234). Test solutions were deaerated for 20 min. by passing nitrogen prior to measurements. It was purified by bubbling through a vanadous chloride scrubbing solution[13]. All solutions were made in milli-Q water. Experiments were carried out at ±298 K.

Preparation of sample

100 mL aliquot of the water sample was treated with an oxidizing mixture of perchloric acid and nitric acid to destroy biological and other materials[14]. Sulfide was removed as by its reduction with zinc acetate and sodium hydroxide[15].

Instrumentation

A microprocessor based pulse polarographic analyzer (Model CL-362) in combination with drop timer assembly, all of Elico Ltd., Hyderabad, India, was employed for polarographic measurements. Current voltage curves were recorded by an Epson printer (Model LX-300 + II). The instrumental settings for DPP were as follows: pulse amplitude, 25 mV, drop time, 0.25 s, scan rate, 12 mV/s. A dropping mercury electrode (DME) and platinum wire were used as working and auxiliary electrode, respectively.

Potentials were noted against a saturated calomel electrode (SCE). A UV-visible spectrophotometer (Model SL-160) of Elico Ltd. was also used for sample analysis. The light source employed was tungsten-halogen deuterium lamp. A wide range photomultiplier worked as detector. The spectral band width of resolution was 0.5 nm. The pH of solutions was measured by a digital pH meter (Model 5000) of Lab India.

Results and Discussion

Electrochemical characteristics

The standard potential of NO_2^- ion is more positive (E°= + 0.99 V). Therefore, it is rather difficult to study nitrite at mercury electrode. However in presence of complexing medium its reduction potential would be shifted to sufficiently negative direction as to be measurable at DME. In this way, different electrolytes were investigated and 0.1 M TGA in 0.1 M ammonium acetate- acetic acid buffer (pH 4.5) was found most adequate. It was also noticed that polyvalent cations like zirconium(IV)[17] and uranium(VI)[18] catalyse the electroreduction of nitrite. In present work U(VI) of 4×10^{-5} M concentration was used in all measurements.

DPP Studies: Optimization of analytical conditions

U(VI) catalysed electroreduction of NO_2^- in presence of TGA and ammonium acetate buffer medium gave a sharp DP peak at -1.21 V. The variation of reagent concentration revealed that peak current of nirite increases upto 0.1 M as shown in Fig. 1 and DPP data are given in Table 1. The pH variation (Fig. 2) observations indicated the suitability of pH 4.5. Peak current was found linear with concentration of nitrite from 0.9 ppm to 9 ppm. DPP diagrams of standard solution of nitrite are presented in Fig. 3. DPP of the blank solution with U(VI) at a given concentration of 4×10^{-5} M is recorded in Fig. 4. The calibration curve characteristics were noted as slope = 0.408, intercept = 0.030 and coefficient of correlation (r) = 0.996. It has been drawn in Fig. 5.

Table 1 — DPP data on variation of reagents NO_2^- = 4 ppm, U(VI) = 4×10^{-5}M

Bicine conc. (M)	$-E_p$ (V)	I_p (μA)
0.02	1.18	5.10
0.05	1.20	3.70
0.07	1.20	4.15
0.10	1.21	4.30
0.15	1.19	4.70

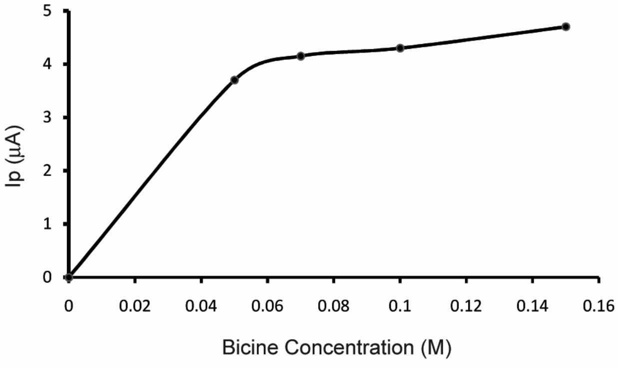

Fig. 1 — Plot of Bicine concentration vs.peak current

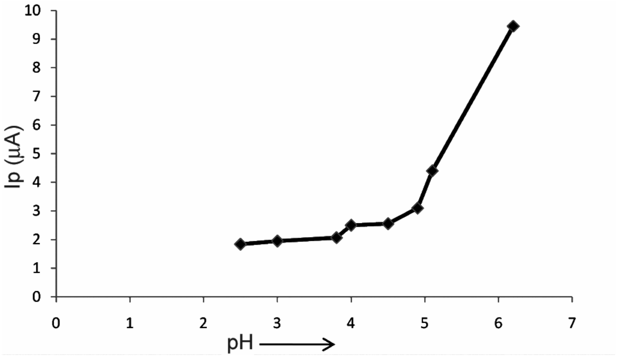

Fig. 2 — Variation of peak current with pH

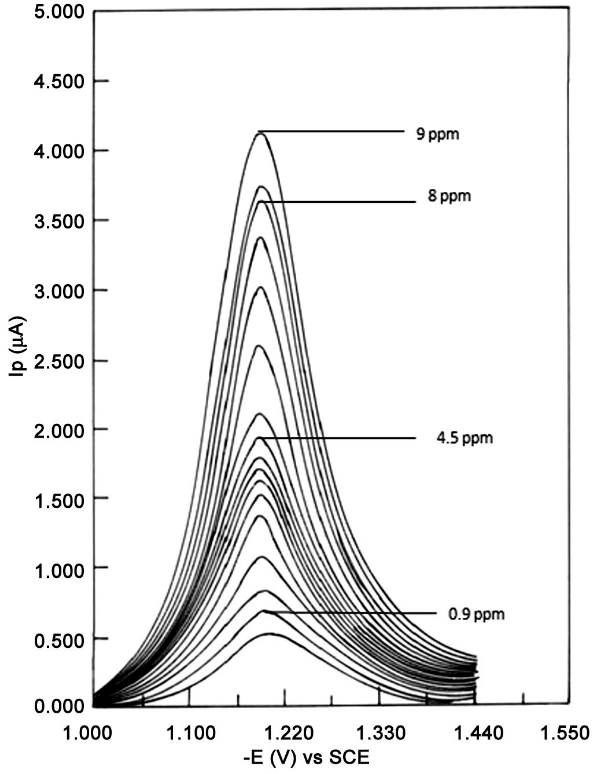

Fig. 3 — DP polarograms of nitrite at different concentrations in 0.1 M ammonium acetate-acetic acid buffer, TGA= 0.1 M, U (VI) = 4×10^{-5} M

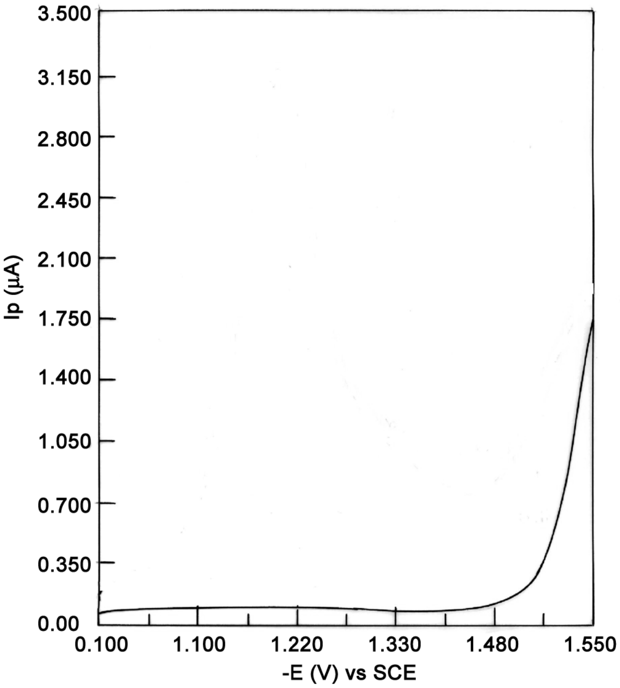

Fig. 4 — DP polarogram of blank solution of 0.1 M ammonium acetate –acetic acid buffer, TGA = 0.1 M, U(VI) = 4 × 10^{-5} M

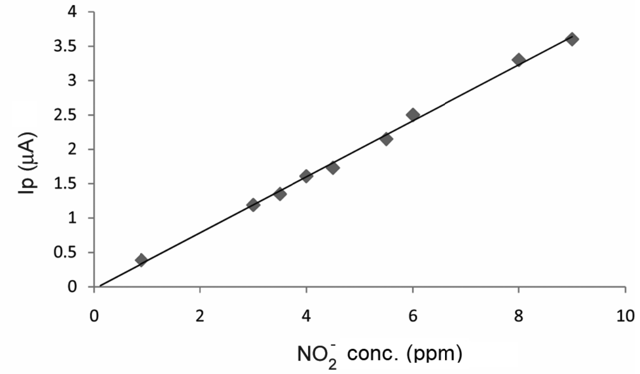

Fig. 5 — Calibration curve of nitrite; concentration vs peak current

Precision and accuracy

The reproducibility of the DPP measurements was evaluated by analyzing the test solution of 1 µg/mL NO_2^-. A relative error of 3% was obtained, inferring that measurements were precise and accurate. The limit of quantification of nitrite in such experimental conditions was found to be 0.7 µg/mL.

Interferences

The interference of major anionic species such as sulfide, sulphite and halides was monitored during the DPP determination of nitrite. The reduction of chloride and bromide occurred at more positive potential (> +0.0 V), thus did not interfered. Similarly, in presence of ammonium acetate buffer medium, sulfite gave a distinguishable DP peak which is well separated from that of nitrite. The likely interference of sulfide was removed during the sample preparation in the form of precipitate. Peak potentials of these species are listed in Table 2. The tolerance level of anionic and cationic species was also checked which was found as followings: S^{2-} , 2.2 µg/mL; SO_3^{2}, 0.7 µg/mL; Cl^- , 0.1 µg/mL and Br^-, 0.3 µg/mL.

Table 2 — Peak potential of anionic species in ammonium acetate buffer

Species	Peak potential vs SCE (v)
Cl^-	+ 0.25
Br^-	+ 0.12
$S_2O_3^-$	+ 0.59
NO_2^-	-1.21

Table 3 — Results of determination of nitrite

Sample	NO_2^- (µg/mL)			
	DPP			UV-visible
	Min.	Max.	A_{ve}±SD	
Rain water	0.99	1.01	0.99±0.09	0.97
Tap water	1.20	1.25	1.22±0.02	1.20
Marine water$^+$	1.29	1.31	1.30±0.01	1.25
Industrial wastes*	1.43	1.47	1.45±0.02	1.44

+ Collected from Arabian Sea, Trombay, Mumbai
*From Basni Industrial Area, Jodhpur

Table 4 — Comparison of DPP results with UV- visible spectrophotometry

Sample	NO_2^- (µg/mL)	
	DPP	UV-vis
Rain water	0.99	0.97
Tap water	1.22	1.20
Marine water	1.30	1.25
Industrial wastes	1.45	1.44

Analytical applications

A measured volume of the prepared sample was taken into the polarographic medium of 0.1 M TGA in ammonium acetate buffer and 4×10^{-5} M U(VI). DP polarograms were recorded in between -1.0 V and -1.5 V. Peak currents were noted at -1.21 V after making blank correction. The concentration of nitrite was determined by standard addition method[19]. The results of determination of nitrite in different samples are summarised in Table 3.

Confirmation

The validity of the present method was demonstrated by comparing the results of DPP with UV-visible spectrophotometric method. It is based on the reaction of sulphanilamide with nitrite and measurement of λ_{max} at 543 nm. The data so obtained were found in good agreement as given in Table 4.

Conclusions

The DPP determination of nitrite is conclusive due to the simple sample preparation and no interferences from major anionic species. It is also more specific to our earlier reported method where nitrite was estimated indirectly from the total content of nitrite and nitrate[20].

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