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Pradeep Sharma^a; Rakesh Sharma^a

^a Electroanalytical Laboratory, Department of Chemistry, J.N.V. University, Jodhpur, India

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SEQUENTIAL TRACE DETERMINATION OF NITRATE AND NITRITE IN NATURAL WATERS BY DIFFERENTIAL PULSE POLAROGRAPHY

PRADEEP SHARMA* and RAKESH SHARMA

*Electroanalytical Laboratory, Department of Chemistry J.N.V. University,
Jodhpur 342003, India*

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Nitrite and nitrate, the two prominent anionic forms of nitrogen have been determined at trace levels in natural waters by differential pulse polarography. Limit of determination of 0.10 µg/ml and 0.003 µg/ml were achieved for nitrate and nitrite, respectively.

Keywords: Chemical speciation; Differential pulse polarography; Nitrate; Nitrite; Trace analysis

INTRODUCTION

The oxidation state specific determination of inorganic anionic species in natural waters is of vital significance in correlation of toxicity with speciation and better understanding of their influence on the environment. Sulfide, nitrite and cyanide are toxic. The concentrations of fluoride and iodide require to be maintained within recommended specified limits. In the present work, attention was focussed on the nitrogen speciation which involves primarily NO_2^- and NO_3^- . Nitrite is considered potentially hazardous to health because of its interaction with haemoglobin in blood to form methemoglobin, having no oxygen carrier ability. Nitrate can also be reduced to nitrite in stomach, and for this reason food and water containing high nitrate contents are dangerous. Nitrite also tends to inhibit the growth of many bacteria after building up to a certain limit. Nitrate is relatively nontoxic and is required for the production of chlorophyll and amino acids^[1].

Nitrate and nitrite concentrations may occur in natural waters as the result of mineral dissolution and industrial discharges. In addition, municipal sewages disposed to water bodies may contribute significant amount of these species^[2]. It is particularly important in the desert and arid region of western Rajasthan where seepage of industrial waste waters raises the risk of affecting the quality of water resources of this area due to percolation of these ions through porous soil of land to the ground waters. It is therefore appropriate to monitor both chemical forms, nitrite and nitrate for a proper evaluation.

*Corresponding author. Fax: +91-291-511191.

Among the instrumental techniques used in trace elemental analysis such as spectrophotometric, spectrofluorimetric, gas chromatographic, isotope dilution mass spectrometric and ion-selective electrodes, voltammetry possesses higher sensitivity particularly for sequential oxidation state-wise determinations^[3] as in case of nitrogen whose aqueous redox chemistry is confined to nitrite and nitrate ions. Differential pulse polarography (DPP) and stripping voltammetry have proved to be useful in such determinations^[4].

The polarographic study of NO_2^- and NO_3^- ions was initially made by Kolthoff *et al.*^[5]. It followed by potentiometric^[6] and cyclic voltammetric^[7] investigations of nitrogen species in alkaline and acid solutions. The role of zirconium in electroreduction of nitrate has been given by many workers. Ogawa *et al.*^[8] have measured the difference between the reduction potentials of NO_3^- in the presence and in the absence of zirconium. Mechelynck and Mechelynck-David^[9] have shown that NO_3^- ions in $1 \times 10^{-5} \text{ M}$ – $5 \times 10^{-3} \text{ M}$ concentration and at pH 2 are polarographically reduced in the presence of 10^{-3} M Zr^{4+} catalyst. Cox and Brajter^[10], and Wharton^[11] have found the Zr(IV) catalysed electrochemical reduction of NO_3^- on mercury electrodes involves the reduction of distinct ZrNO_3^- complexes to give well-defined and completely resolved NO_3^- waves suitable for quantitative analysis. Voltammetric measurement of nitrite and nitrate at platinum^[12], glassy carbon^[13], gold disc^[14], and graphite electrodes^[15] has further been reported. In view of the fact that classical polarography suffers from sensitivity constraints, and during stripping voltammetry, very positive deposition potential of these ions has shown problems, the authors have suggested a DPP method which was successfully applied for the determination of nitrite and nitrate contents in natural waters.

EXPERIMENTAL

Instrumentation

A 174-A polarographic analyzer in conjunction with a Model 174/70 drop timer and a RE0074 X-Y recorder (all from EG&G, USA) was used for polarographic measurements. The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode; modulation amplitude, 50 mV, clock time of pulse, 2 s; and scan rate 5 mV/s. An Ag/AgCl and a platinum wire were used throughout as reference and auxiliary electrodes, respectively. 0.05 M zirconium oxychloride was used as the supporting electrolyte.

A Shimadzu (Model UV-1601) UV-VIS spectrophotometer was also used for sample analysis. It has a wave length range of 190–1100 nm. 50 W halogen lamp and silicon photodiode were used as the light source and detector, respectively. The spectral band width of resolution was 2 nm. Double beam optics was used as a photometric system and the photometric range in terms of absorbance was 0.5–3.99.

Sample preparation

To 100 ml aliquot, 4 mg mercuric chloride was added and the sample was preserved with 0.1 ml chloroform at about 4°C. Prior to analysis, few drops of zinc acetate and sodium hydroxide were added to remove the interference of sulfide which came out in the form of precipitate^[16].

All the experiments were carried out at $25 \pm 1^\circ\text{C}$. The solutions were deaerated by bubbling purified nitrogen for 20 min before the polarographic measurements. Nitrogen was purified by passing it through a vanadous chloride solution. All chemicals used were of reagent grade purity. Stock solutions of nitrate and nitrite were prepared from potassium nitrate and sodium nitrite, respectively. Other reagents employed in different steps, as described in text, include: zirconium oxychloride, lead nitrate, cadmium nitrate, copper nitrate, sodium chloride and potassium bromide. Solutions were prepared in doubly distilled water.

RESULTS AND DISCUSSION

NO_3^- showed a sharp DP peak in 0.05 M zirconium oxychloride at -0.95 V . A linearity between peak height and nitrate concentration was observed between 0.10 and 18.0 ppm as shown in Fig. 1. The characteristics of the calibration curve were as follows: slope = $0.4690 \pm 1.59 \times 10^{-3}$; coefficient of correlation (r) = 0.999 and standard deviation, $SD = 3.698 \times 10^{-2}$ ($n = 4$).

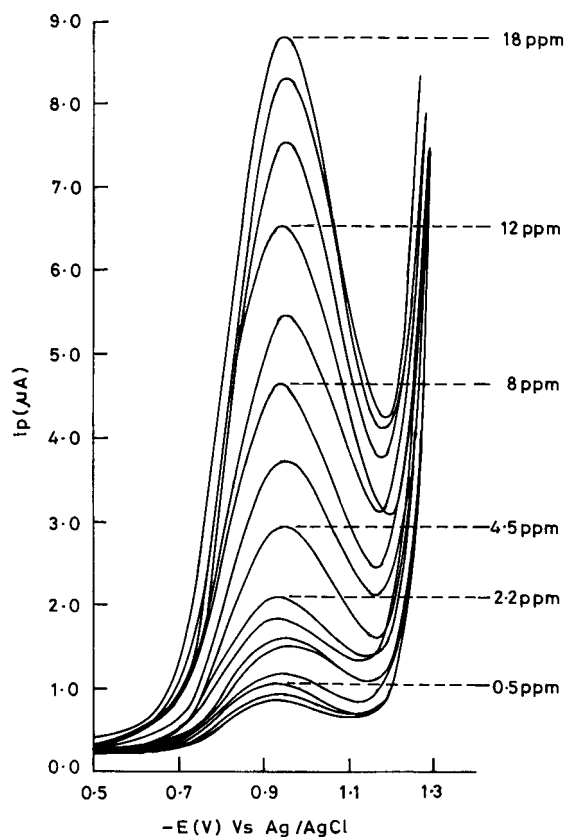


FIGURE 1 Differential pulse polarograms of nitrate at different concentrations in 0.05 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, modulation amplitude, 50 mV, pulse duration 57 ms, clock time of pulse, 2 s, scan rate 5 mV/s W.E., DME.

Interferences

DP polarograms of nitrate were also recorded in presence of other common cations and anions such as copper, lead, cadmium, chloride and bromide. The DP peaks of these ions were distinguishable from each other and had different peak potentials as listed in Table I, thus showed no interference.

Sequential determination of NO_3^- and NO_2^-

The measured volume of the prepared sample was taken into the polarographic cell with a 0.05 M zirconium oxychloride supporting electrolyte for the determination of nitrate and nitrite as follows:

A DP polarogram was recorded over the potential range of -0.5 to -1.4 V and the current was measured at a potential of -0.95 after making blank correction. It was done by recording the current of the supporting electrolyte alone without any salt, and subtracting it from the peak current obtained for test solution of sample analysis. Quantitation provided the total nitrate and nitrite contents. Sample was then treated with 0.2 ml of 0.1 M sulfamic acid for the destruction of nitrite so as to obtain the nitrate concentration in solution by DPP. The concentration of nitrite in a sample was obtained based on the difference in the above two measurements.

The concentrations in all observations were determined by the standard addition method^[17]. Generally two standard additions were made for the quantitation. The results of an oxidation state-wise determination of nitrate and nitrite in natural water samples are summarized in Table II.

TABLE I Peak potentials of metal ions and anions in 0.05 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$

Cation/Anion	E_p vs. Ag/AgCl (V)
Copper(II)	-0.05
Lead(II)	-0.31
Cadmium(II)	-0.50
Nitrate	-0.95
Chloride	+0.26
Bromide	+0.11

TABLE II Natural water analysis for nitrate and nitrite by DPP

Water sample*	Concn. ($\mu\text{g}/\text{ml}$)	
	NO_3^-	NO_2^-
1.	16.37	8.38
2.	16.25	8.33
3.	16.28	7.71
4.	16.29	7.31
Average	16.30	7.93
S.D. (\pm)	0.05	0.51
R.S.D. (%)	0.31	6.43

*underground water of Jhalra situated in old city. $n=3$, no. of replicate.

TABLE III Comparison of results between DPP and UV-VIS spectrophotometry

Nitrogen species	Concn. ($\mu\text{g/ml}$) ^b		SD (\pm)	C.V (%)
	DPP ^a	UV-VIS ^a		
NO ₃ ⁻	16.30	15.29	0.22	0.69
NO ₂ ⁻	7.93	7.88	0.46	0.17

^aAverage of four determinations.

^bunderground waters of Jhalra.

The limit up to which a measurable DP peak of NO₃⁻/NO₂⁻ was observed was taken as its limit of determination. The minimum amount which thus could be determined was found to be 0.10 $\mu\text{g/ml}$ and 0.003 $\mu\text{g/ml}$ for nitrate and nitrite, respectively.

The UV-VIS spectrophotometric method was used to compare the results obtained by DPP. The observations are included in Table III.

Acknowledgements

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