Electroanalysis Of Certain Inorganic Anionic Species In Aquatic Environment

P. Sharma*, R. Bais and S. Barmera
Electroanalytical Lab, Department of Chemistry, J.N.V. University, Jodhpur, India
Email:sharma_pk00@yahoo.com

Abstract:

A voltammetric study on sulfide, nitrite and chlorate has concluded in developing of simple and convenient methods of their determination by differential pulse polarography at low concentrations. The methods have been successfully applied for the analysis of these anionic species in diverse matrices.

Keywords: sulfide,nitrite,chlorate,DPP

1. Introduction

The oxidation state specific determination of inorganic anionic species in aqueous systems is of vital significance in correlation of toxicity with speciation and better understanding of their influence on environment. Sulfide, nitrite and chlorate are more concerned species due to their detrimental effects.

Sulfur and its compounds are widely used in industries of paper, pulp, tanneries and textile. These subsequently produce large quantity of sulfide alongwith sulfite, sulphate and thiosulphate. Nitrite inhibits the growth of many bacteria and causes detrimental effects. The municipal sewages disposed to water bodies may contribute significant amount of nitrogen species. The disinfection of water by chlorine and its compounds gives out chlorate alongwith other oxyhalides. Chlorate is further reduced to harmful intermediate product chlorite or possibly hypochlorite in aqueous system. In addition, it is a potent oxidizing agent and may convert haemoglobin to methemoglobin resulting in haemolysis and renal insufficiency [1-2].

Voltammetric methods have proved more useful in such studies as these can identify and determine ionic forms of a species because of certain selectivity of redox potential. In stripping analysis intermetallic compound formation on electrode surface causes significant interferences, therefore authors have made detailed investigations of S^{-2}, NO_2^- and ClO_3^- using differential pulse polarography [3]. The validity of the measurements has further been established by comparing the results of DPP with UV-Vis spectrophotometric method.

2. Experimental

A microprocessor based pulse polarographic analyzer (Model CL-362) in combimation with a drop timer assembly, all of ElicoLimited, Hyderabad, India was used for voltammetric measurements. Voltammograms were recorded by an Epson printer (Model LX-300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode; pulse amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse, 1s and scan rate 12 mV/s. Potentials were measured against a saturated calomel electrode (SCE) and a platinum wire acted as an auxiliary electrode throughout.

A UV-Vis spectrophotometer (Model SL-160) of Elico was also used for sample analysis. It has a wavelength range from 190-1100 nm. A tungsten halogen deuterium lamp and wide range photomultiplier were used as the light source and detector, respectively. The spectral band width of resolution was 0.5 nm.

Test solutions were deaerated for 20 min by passing nitrogen. It was purified by bubbling

through a vanadous chloride scrubbing solution . Chemicals used were of analytical grade. Stock solution of sulfide was prepared from sodium sulfide, nitrite from sodium nitrite and chlorate from potassium chlorate. All experiments were carried out at ±298 K.

3. Results and Discussion

3.1 Electrochemical behaviour of sulfide, nitrite and chlorate: Choice of medium

In preliminary investigations different supporting electrolytes such as sodium chloride, nitric acid, hydrochloric acid, acetic acid, ascorbic acid, oxalic acid and zirconium oxychloride were studied to observe electrochemical characteristics of S^{-2}, NO_2^- and ClO_3^- at thedropping electrode. The media found most adequate for study and determination of sulfide, nitrite and chlorate are given in Table 1.

3.2 Optimum analytical conditions

The optimum analytical conditions for the low concentration determination of sulfide, nitrite and chlorate were found in terms of linearity calibration curve characteristics, interference and limit of determination by DPP method. These are described in Table 2.

3.3 Determination

The DPP method was employed to determine sulfide, nitrite and chlorate in diverse matrices.A typical DP polarogram for determination of chlorate is shown in Fig.1

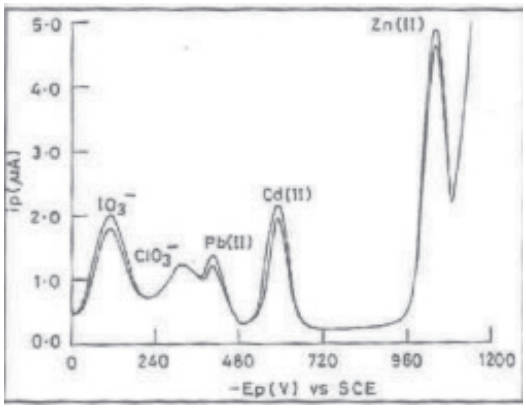


Figure 1: DP polarogram of ClO_3^- -Ti (IV) in presence of lead, cadmium, zinc and iodate in 0.1 M oxalic acid. Ti (IV), 1×10^{-3}M; IO_3^-, 15.90 µg mL^{-1}; ClO_3^-, 2.99 µg mL^{-1}; Pb (II), 18.28 µg mL^{-1}; Cd (II), 18.28 µg mL^{-1} and Zn (II), 36.56 µg mL^{-1}

The validity of the measurements has further been established by comparing the results of DPP with UV-vis spectrophotometric method. The interferences were monitored and ruled out. The concentrations in all observations were

Table 1: Peak potential of anionic forms in different media

Sr. No.	Species	Electrolyte	-Ep (V) vs SCE
1.	Sulfide	0.1 M NaCl in 0.1 M HNO_3 (pH 1.2)	0.18
2.	Nitrite	0.05 M $ZrOCl_2.8H_2O$	0.95
3.	Chlorate	Ti (IV)-0.1M oxalic acid	0.39

Table 2: DPP observations

Sr. No.	Species	Linearity (ppm)	Coefficient of correlation(r)	Limit of determination (µg/ml)
1.	S^{2-}	2.2-8.0	0.99	2.2
2.	NO_2^-	0.10-18.0	0.99	0.03
3.	ClO_3^-	1.0-41.2	0.99	1.0

Table 3: Determination of sulfide, nitrite and chlorate by DPP and UV-Vis spectrophotometry

Species	Sample	DPP±SD (ppm)		UV-Vis (ppm)
		Added	Determined	
S^{2-}	Industrial waste	3.95	3.91±0.03	3.91
NO_2^-	Natural water	-	7.93±0.46	7.88
ClO_3^-	Household water	3.85	3.84±0.10	3.01

determined by the standard addition method [4]. The results are summarized in Table 3.

4. Conclusion

It is concluded that the DPP provides a simple approach for sub-µg level determination of inorganic anionic species. The methods are convenient, specific and rapid in terms of measurements (limit of determination, 1.0 µg ml^{-1}). The developed DPP procedures for sulfide, nitrite and chlorate will be useful in water quality assessment and control laboratories where continuous monitoring of anionic species is mandatory [5-7].

6. Acknowledgement

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7. References

1. R. Sarin, in Trace analysis and technological development (ed. Sankar Das, M). Wiley Eastern Ltd., New Delhi, 1983, pp 135-139.
2. S.E. Manahan, Environmental Chemistry, Inc. Michigan, 1991, pp 128-132.
3. J.R. Pretty, E.A. Blubaugh, J.A. Caruso and T.M. Davidson, Anal.Chem., 1994, 66,1540-1547.
4. H. Willard, L. Merrit and J. Dean, Instrumental Methods of Analysis, 5thedn., D. Van Nostrand, New York, 1974, pp 659-660.
5. P.Sharma, K. Songara and K. Jodha, J. Indian Chem.Soc., 2013,90, 833-836.
6. P. Sharma and R. Sharma, Intl.J.Environ.Anal.Chem., 2002, 82, 7-11.
7. P. Sharma and S. Songara, Indian J.Chem.Tech., 2008, 15, 504-506.