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Research Article

VOLTAMMETRIC STUDIES AND DETERMINATION OF OXYHALIDES

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Abstract

A simple, rapid and sensitive differential pulse polarographic (DPP) method for the determination of low concentration bromate in samples of industrial waste water is presented. Iodate did not interfered. A linearity between bromate concentration and peal height was obtained with a correlation of coefficient of 0.99. The detection limit was 0.6 µg/ml. The method has successfully been applied for the analysis of bromate in industrial waste waters.

Keywords: Bromate, DPP, real samples, trace determination

Introduction

The aim of the work was to develop suitable voltammetric methods of simple approach for the determination of oxyhalides which are usually present at very low concentration. The determination of chlorate (Sharma P. and Songara S., 2008) and iodate (Sharma P. and Songara S., 2007) has already been reported. In the present work attention was focused on oxybromine species (bromate) which has a definite toxicological importance. Hypobromite (BrO^-) and bromate (BrO_3^-) are the important oxybromine species. These are not typically derived from natural sources and are produced when ozone and chlorine dioxide (as disinfectant) react with the bromide ion generally present in raw water supplies of streams, lakes and reservoirs. Bromate is used as strong oxidant, food additive and analytical reagent (Emsley J., 1998; Pontius F.W., 1990). A longer term exposure of bromate above maximum contaminant limit (MCL) of 0.01 mg/L may increase the risk of cancer (Laws E.A., 1981). It is thus imperative to develop a convenient method for the determination of bromate.

Voltammetric methods are considered more suitable to the conventional methods for oxyhalides estimation (optical and ion selective electrodes) because the measurement of chemical form of the concerned ion is possible due to certain selectivity of the redox potential

(Bard A.J. et al., 1988). These methods can also be used under widely differing experimental conditions which is an important aspect in case of water samples. Differential pulse polarography (DPP) and stripping voltammetry have proved useful in such determinations. However, during stripping voltammetry, very positive potential of halide ions causes problem in obtaining the true polarographic wave for analytical purpose (Copeland T.R., 1974). Therefore, the suitability of DPP is envisaged in present studies.

Lingane and kolthoff (Lingane J.J. and Kolthoff I.M., 1939) have studied bromate ion in acidic and alkaline supporting electrolytes. They concluded that bromate bromated reduced to bromide irreversibly involving $6e^-$ as followings :

$$BrO_3^- + 6H + 6e^- \longrightarrow Br^- + 3H_2O$$

Curti and Locche (Curti R. and Locche L., 1957) have observed polarographic reduction of bromate and chlorite in anhydrous ammonia at -1.228V. Gupta et al. (Gupta B.K. et al., 1974; 1974) have described polarographic behaviour of bromate in aqueous organic solvent mixture. A polarographic method for determination of bromite ion in alkaline media has been

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given by Krivis (Krivis A.F.,1968). Here, the determination of bromate in 0.05M barium chloride medium using DPP method has been evaluated. The results obtained by suggested procedure have also been compared by UV-vis. spectrophotometric method.

Materials and Methods

Instrumentation

A microprocessor based pulse polarographic analyzer (Model CL–362) in combination with a drop–timer assembly, all from Elico Limited, Hyderabad, India, was used for voltammetric measurements. Current voltage curves were recorded by an Epson printer (Epson–LX–300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode; pulse amplitude, 25 mV; drop time, 0.5 s; scan rate, 12mV/sec and charging current compensation, 20%. The saturated calomel electrode (SCE) and platinum wire worked as reference and auxiliary electrodes, respectively. The pH measurements were made by a digital pH meter (Model-5000) of India.

Sample analysis was also carried out by a UV-vis spectrophotometer (Model-108) of Systronics, India. It has a wavelength range of 190-900 nm. The tungsten-halogen deuterium lamp and wide range photomultiplier were also used as the light source and detector, respectively. The spectral band width of resolution was 0.5 nm.

Cleaning and Conditioning of Labwares

Stringent cleaning of glasswares used for sample preparation and of the cell component is necessary to avoid contamination. It is particularly important when measurements are made at trace levels. For this purpose, these were soaked in 2N nitric acid for atleast one week and washed several times with doubly distilled water. Subsequent conditioning is also of paramount importance to check adsorption.

Sample Preparation

Waste water samples were collected in clean polyethylene containers. These were filtered in order to separate any suspended particulate matter and were acidified with hydrochloric acid to pH 2.0 for storage. A 100 ml aliquot of the sample was treated with 1 ml of oxidizing mixture of nitric acid and sulfuric acid to destroy the biological and organic matters.

Chemicals

Chemicals used were of reagent grade purity. Stock solution of bromate was prepared from potassium

bromate of Loba Chemie, Mumbai (Batch no. 60950). Solutions were prepared in mill-Q-water (Millipore).

The measurements were made in air conditioned laboratory at 25 ± 1^0C. The test solutions were deaerated by bubbling purified nitrogen for 20 mins prior to voltammetric recordings. Nitrogen was purified by passing it through a vanadous chloride scrubbing solution (App. Notes, 1979).

Results and Discussion

Electrochemical characteristics and choice of medium

The reduction of bromate was studied in different supporting electrolytes and 0.05M barium chloride was found most adequate as against the other investigated media. Bromate displayed well defined waves at -1.65V. A typical DC polarogram of bromate in $BaCl_2$ has been shown in figure 1. The limiting current found to increase in proportional to the bromate concentration.

The wave appeared to the diffusion controlled. The plot of E vs log $i/(i_d-i)$ is drawn in figure 2. It gave a straight line with slope of 0.094. Thus electrode reaction was reversible in nature (Kapoor R.C. and Agarwal B.S., 1991).

Optimum DPP conditions : Method Development

DPP reduction of bromate in presence of 0.05M $BaCl_2$ gave a sharp DP peak at -1.65V. Linearity of peak current versus concentration was noticed in range of 0.6 to 14 ppm (figure 3). The calibration curve characteristics were as follows : slope, 0.0791; coefficient of correlation (r), 0.9990; intercept, 0.0368 and standard deviation (±) 0.3561. It has been drawn in figure 4.

Precision and Accuracy

The determination of bromate was evaluated for reproducibility as given in Table 1.

Interference Study

The analysis of industrial wastes by voltammetry has reaveled the presence of lead, cadmium and zinc. Similarly, iodide might be associated with bromate as most iodine exists in nature as iodide I^-. Therefore it is appropriate to study interference of these species. The peak potential of iodide in 0.05M $BaCl_2$ was found to be > 0.0V in positive potential range and thus does not interfere in the determinations. Copper is also reduced at -0.10V. Similarly, DP peaks of lead and cadmium were noticed at different peak potentials and were
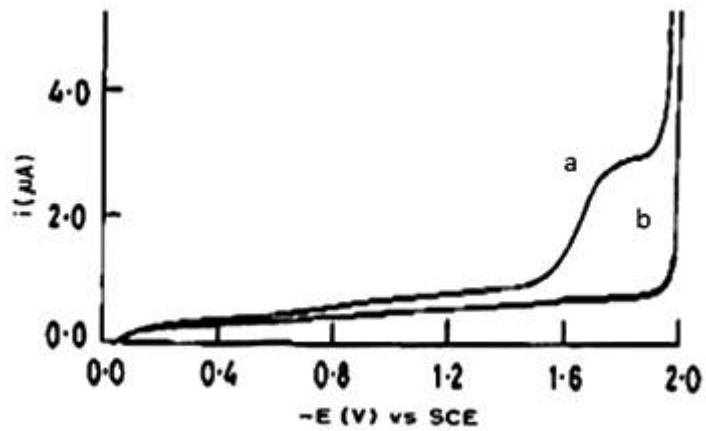
Figure 1: (a) DC polarogram of bromate in 0.05 M BaCl$_2$;
BrO$_3^-$ = 1x10^{-4}
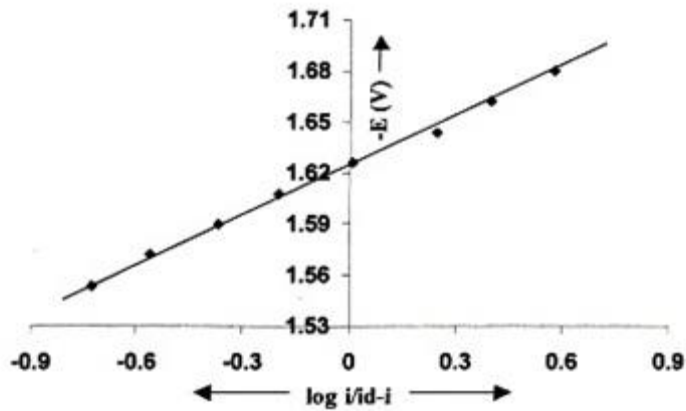(b) DC polarogram of 0.05 M BaCl$_2$

Figure 2: Log plot analysis [plot of E vs log I/(id-i)] of DC polarogram of bromate in 0.05 M BaCl$_2$
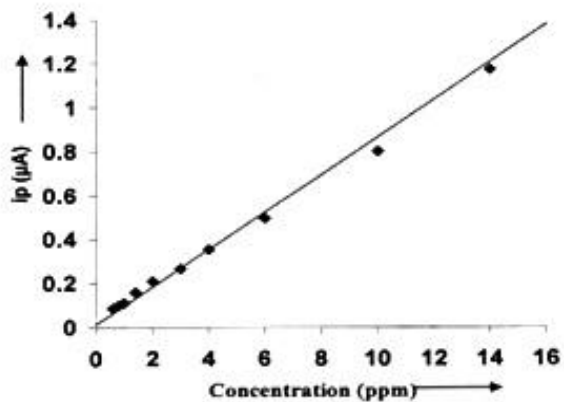

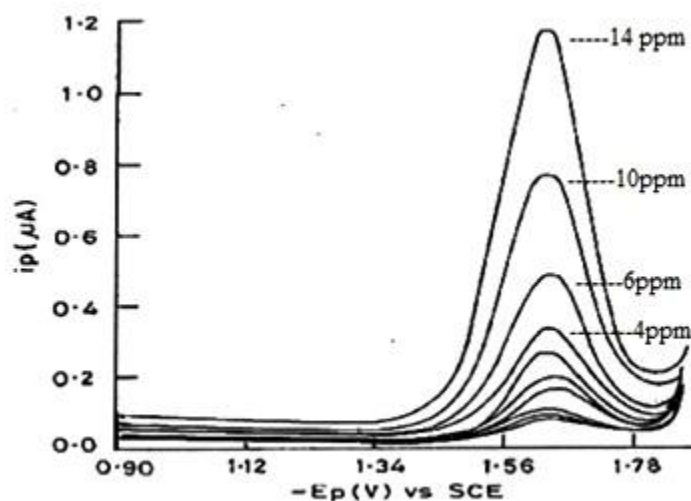**Figure 3**: Linearity of peak current vs concentration of bromate in 0.05 M BaCl$_2$

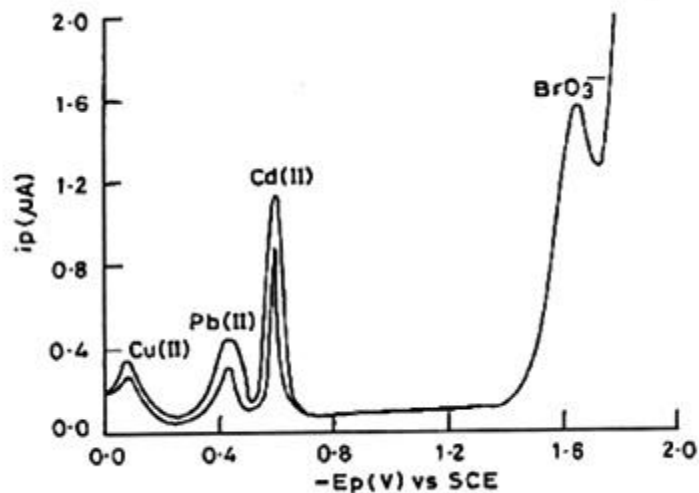**Figure 4:** DP polarogram of bromate at different concentration in 0.05 M BaCl$_2$

Figure 5: DP polarogram of bromate in presence of other ions in 0.05 M BaCl$_2$
Cu(II), 0.93 ppm; Pb(II), 1.87 ppm; Cd(II), 3.74 ppm; BrO$_3^-$, 18.69 ppm

Table – 1 Precision and accuracy of bromate determination in 0.05 M BaCl$_2$

S. No.	BrO$_3^-$ present (ppm)	BrO$_3$ determined (ppm)*	S.D. (±)	RSD (%)
1	1.00	0.9475	0.0227	2.39
2	3.00	2.9543	0.0732	2.47
3	4.00	3.9414	0.0997	2.52

*Average of four determinations

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Table – 2 Bromate determination by DPP and UV-vis spectrophotometry in different sample

S.No.	Sample	BrO$_3^-$ (µg/ml)*			S.D. (±)	C.V. (%)	Recovery (%)
		Added	DPP	UV-VIS			
1	**Waste water**						
	Industrial waste	4.0	3.7123	3.4125	0.1243	3.3505	92.80
	Household waste	4.0	3.8469	3.3210	0.0858	2.2202	96.62
2	**Natural water**						
	Tap water	4.0	3.8828	3.5484	0.0321	0.8284	97.07
	Drinking water	4.0	3.8076	3.0145	0.0433	1.1385	95.19
	Gulab sagar	4.0	3.7483	3.6146	0.0384	1.0269	93.70
	Kaylana lake	4.0	3.7143	3.7271	0.0279	0.7524	92.85
	Tapi bawari	4.0	3.8532	3.7450	0.0427	1.0186	96.33
	Bore well	4.0	3.6378	3.6985	0.0856	2.3545	90.94
3	**Table salt#**						
	Rock salt	4.0	3.5954	3.4859	0.0734	2.0427	89.88
	Common salt	4.0	3.7806	3.6854	0.0463	1.2256	94.51

*Average of four determination
#Concentration in µg/g

distinguished from bromate. It has been clarified in figure 5.

Limit of Determination

The limit of quantification of bromate was found to be 0.6 µg/ml.

Analytical Applications

The devised optimum voltammetric conditions consisting of polarographic medium, calibration linearity, reproducibility and detection limit, were applied to analyse bromate in industrial waste-waters. DPP method was found more suitable to stripping voltammetry in determination of bromate because of higher negative reduction potential of broamate at -1.65V. Other metal ions present in waste water samples such as copper, lead, cadmium and iodate would also be deposited on the surface of electrode forming intermetallic compound and causing significant interference during the stripping process and voltammetric measurements.

Voltammetric measurements

The prepared samples were taken into the polarographic cell with 0.05M BaCl$_2$ and DP polarograms were recorded from -1.3V to -1.8V. Peak currents were noted at -1.65V after making blank corrections. The concentrations were determined by standard addition method (Willard H. et al., 1974). The results of determination of bromate are presented in Table 2.

Validation

The results of DPP determination of bromate in different samples of industrial waste waters were further verified by carrying out comparison studies with UV-vis. spectrophotometric method. The data so obtained are compared in Table 2.

Conclusion

The suggested DPP method for determination of bromate is specific, rapid and convenient due to simple preparation, no interference from major ions and low cost of instruments.

Acknowledgments

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