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Voltammetric Studies and Determination of Antimony(III)

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A detailed voltammetric study of Sb(III) has resulted in optimization of analytical conditions for determination of antimony at low concentration of submicrogram level by using differential pulse polarographic method. Among different supporting electrolytes investigated for the study of Sb(III), 0.8 M glycolic acid-ammonia was found most adequate where a well-defined wave was obtained at -0.30 V for the electroreduction of Sb(III) to Sb(0). It was observed that on increasing the concentration of Sb(III) the peak current increased linearly up to a concentration of 30 ppm. Limit of determination was observed to be 0.01 µg/mL. Cu(II), Pb(II), Cd(II), As(III) and Zn(II) did not interfere. The differential pulse polarography determination of antimony(III) was evaluated for its accuracy and precision in terms of standard deviation and percentage error. The method has been successfully applied for analysis of antimony in industrial waste samples and atomic absorption spectrophotometer method was used to compare the results obtained by differential pulse polarography.

Keywords: Differential pulse polarography, Antimony, Industrial waste samples.

INTRODUCTION

The determination of toxic trace metals in industrial waste samples has gained wide attention as seepage of effluents cause metal pollution of the aqueous environment [1]. Antimony is known to be a genotoxic element *in vitro* and *in vivo*. It is now recognized as a global contaminant and has aroused the global concerns recently [2]; however, the biogeochemical behaviour of antimony is still largely unknown [3]. In view of wide applications of antimony in industries and its detrimental effects, it is important to determine antimony concentrations in different aqueous systems. Thus, it is appropriate to develop an analytical method of simple approach for the determination of antimony in industrial waste samples.

The principal oxidation states of antimony in its compounds are -3, +3 and +5. Voltammetric methods such as anodic stripping voltammetry and differential pulse polarography can identify and determine different ionic forms of an element due to the certain selectivity of the redox potentials [4]. These methods are thus more suitable for the studies and determination of antimony. In stripping analysis, intermetallic compound formation on the electrode surface causes significant interference during the deposition [5], therefore, we have envisaged the suitability of differential pulse polarography in present work. The observations have enabled in developing optimal conditions for the determination of antimony at low concentration.

The lector-reduction of Sb(III) in sulfuric acid-thiocyanate solution was investigated by polarography and cyclic voltammetry by Jacobsen and Rojahn [6]. Huiliang and coworkers [7] have determined Sb(III) and Sb(V) in natural waters by flow constant current stripping analysis with gold fibre working electrode. Capodaglio *et al*. [8] proposed a method to determine subnanomolar levels of antimony in fresh water and seawater by cathodic stripping voltammetry. The use of differential pulse adsorptive stripping voltammetry for the determination of Sb(III) and Sb(V) using pyrogallol as a complexing agent was described by González *et al*. [9]. A very sensitive electrochemical procedure for the trace determination of antimony was described by Zhang *et al*. [10]. In recent years a lot of work has been reported by scientists all around the world on voltammetric studies for sensitive determination of antimony [11-16]. Differential pulse polarographic determination of arsenic [17], cadmium [18], selenium [19] and mercury [20] on similar lines were described earlier.

EXPERIMENTAL

A microprocessor based pulse polarographic analyzer (Model CL-362) in combination with a drop-timer assembly, all of Elico Limited, Hyderabad, India, was used for voltammetric measurements. A dropping mercury electrode was used as the working electrode. The instrumental settings for the differential pulse polarography were as follows: pulse

amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse, 0.5 s; scan rate, 12 mV/s; and charging current compensation, 20 %. Saturated calomel electrode and platinum wire were used as the reference and auxiliary electrodes, respectively.

An atomic absorption spectrophotometer (Model AA-2380) of Perkin Elmer, USA, was also used for sample analysis. The instrument had a wave length range from 1900-9000 Å and a Czerny tuner grating monochromator which separates adjacent lines, thus widening the linear range of calibration curve. Slit-width was selectable in 3 steps of 1.9, 3.8 and 9.5 Å. Point-Focus burner optics permitted a high sensitivity analysis by passing a light beam of very small size through the flame. Lamp current control was adjustable in 20 steps at 2 mA intervals. Sample aspiration flow control was adjustable by variable 3-line flow system.

The pH studies were made by a Systronics digital pH meter (Model-355).

Sample preparation: Glassware and polyethylene containers were soaked in 2 M nitric acid for atleast one week and washed with double distilled water prior to use. Samples of waste waters were collected from different sites of Marudhar and Basni Industrial Areas of Jodhpur. These samples were filtered to separate particulate matter and these were acidified with HCl to pH ~ 2 for storage purposes [21]. A 50 mL aliquot was digested with an oxidizing mixture of nitric acid and sulfuric acid to destroy biological materials. The contents were heated till the solution fumed and then were transferred to a volumetric flask with required volume of double distilled water.

All of the chemicals used were of analytical grade purity and were prepared in doubly distilled water. Stock solution of antimony was prepared from antimony potassium (+) tartarate ($KSbOC_4H_4O_6$); Batch No.-B/707774 (Sisco Research Laboratories Pvt. Ltd., Mumbai).

All of the experiments were carried out in an air-conditioned laboratory, where the temperature was maintained at 25 ± 1 °C. The solutions were deaerated by bubbling purified nitrogen for 20 min prior to voltammetric measurements. The purification of nitrogen was achieved by passing it through vanadous chloride scrubbing solution [22].

RESULTS AND DISCUSSION

Polarographic characteristics: Preliminary observations on electroreduction of Sb(III) indicated the suitability of glycolic acid (0.8 M) in ammonia where a single polarographic wave of Sb(III) to elemental state was obtained at -0.30 V *vs.* standard calomel electrode. $E_{1/2}$ of the wave was found to be pH dependent where it shifted towards more negative potential on higher pH. At a pH of 3.7, the wave appeared to be well-defined in terms of wave current as shown in Fig. 1.

The wave height increased linearly with the concentration of antimony in range of 1.0×10^{-5} M to 1.0×10^{-3} M. The nature of the electrode reaction was evaluated by log-plot analysis (Fig. 2), which illustrated that the electrode process involving three electron reduction, corresponding to Sb(III) → Sb(0) was not fully reversible.

Optimal differential pulse polarography conditions: Sb(III) also showed a sharp differential pulse peak at -0.30 V. A linearity of peak current was observed between 0.01 and

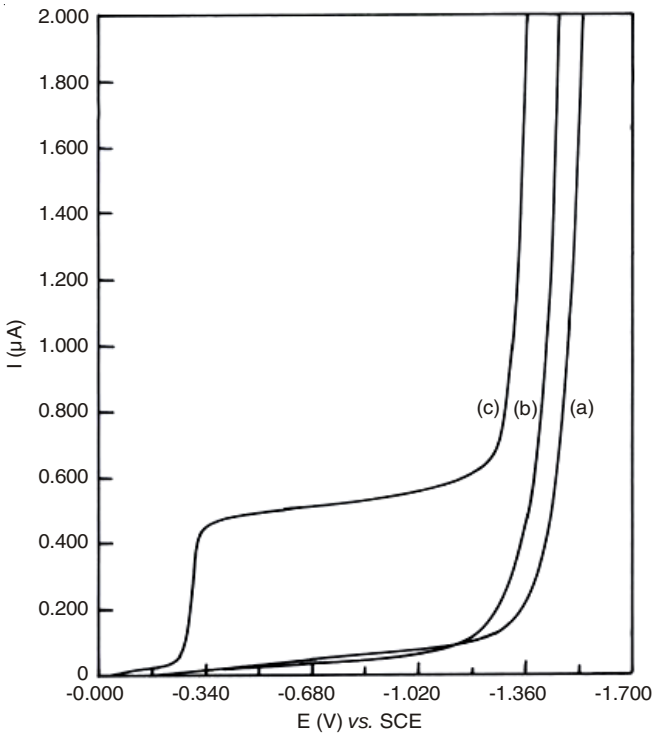

Fig. 1. DC polarogram of antimony(III) (a) Blank solution of NH_3 (pH 3.7); (b) Blank solution of 0.8 M glycolic acid in NH_3 (pH 3.7); (c) 1.5×10^{-4} M antimony(III) in 0.8 M glycolic acid/NH_3 (pH 3.7)

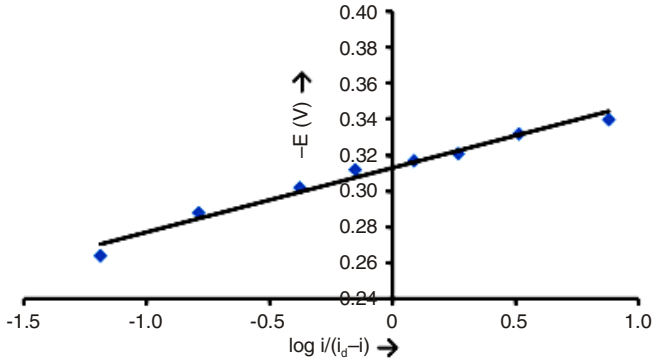

Fig. 2. log-plot analysis of Sb(III) reduction in 0.8 M glycolic acid/NH_3

30 ppm of antimony concentration as shown in Fig. 3. The characteristics of the calibration curve were as follows: Slope, 0.0296; Intercept, 0.0711; Coefficient of correlation (r), 0.9921; Standard deviation, (±) 8.487.

Limit of determination: The differential pulse peak was found suitable for quantitation of antimony where a limit of determination of 0.01 μg/mL was achieved.

Interference: Differential pulse polarograms of antimony were also recorded in the presence of other cations commonly present in industrial waste samples such as Cu^{2+}, Pb^{2+}, Cd^{2+}, As^{3+} and Zn^{2+}. The differential pulse peaks of these metal ions were distinguishable from each other and indicated no interference in determination of antimony as shown in Fig. 4.

Analytical applications: The differential pulse polarography reduction of Sb(III) in glycolic acid (0.8 M) in ammonia medium was made the basis for antimony determination in industrial waste samples. The prepared samples were taken into the polarographic cell and differential pulse polarograms

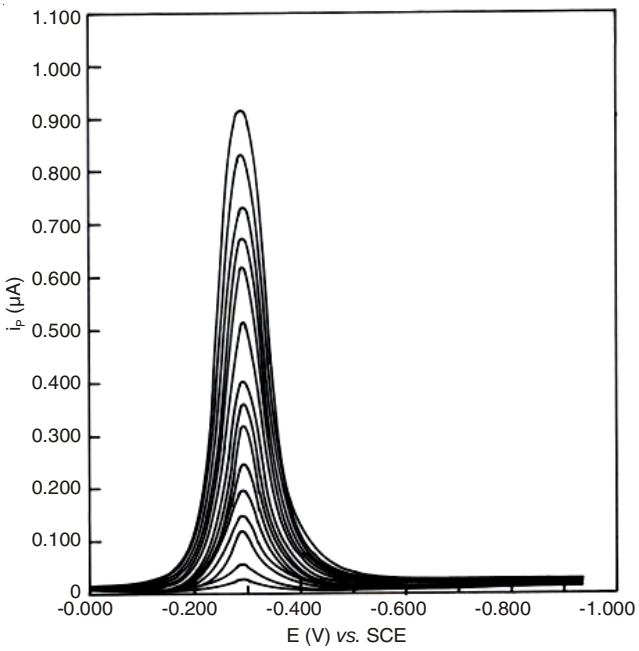

Fig. 3. Differential pulse polarograms of antimony(III) at different concentrations in 0.8 M glycolic acid/NH_3 (pH 3.7)

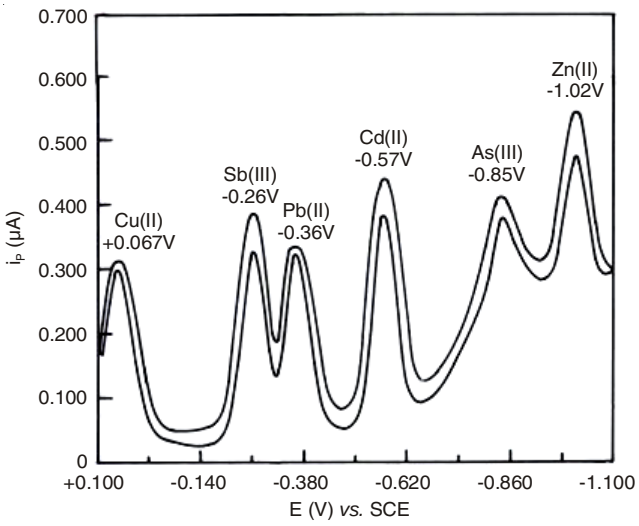

Fig. 4. Differential pulse polarogram of Sb(III) in presence of Cu(II), Pb(II), Cd(II), As(III) and Zn(II) in 0.8 M glycolic acid/NH_3 (pH = 3.7), Cu (II) =5 ppm; Sb(III) = 10 ppm; Pb (II) = 10 ppm; Cd(II) = 15 ppm; As(III) = 4 ppm and Zn(II) = 2 ppm

were recorded in the potential range of 0.00 to -0.70 V. The peak currents were measured at -0.30 V after making blank corrections.

Quantitation in all observations was made by standard addition method [23]. The results of antimony determination in industrial waste samples from Marudhar and Basni Industrial Areas of Jodhpur are summarized in Tables 1 and 2, respectively. An atomic absorption spectrophotometer was used to compare the results obtained by differential pulse polarography (Table-3).

Conclusion

The complexation of glycolic acid with antimony has enabled its trace determination. The suggested differential pulse polarography method is more sensitive, specific and rapid in comparison to the commonly used spectrophotometric methods, *viz*. electrothermal atomic absorption spectrophotometer [24,25], flow-injection electrothermal atomic absorption spectrophotometer [26] and fluorescence quenching method [27], of antimony estimation since it provides a simple approach for trace level determination of antimony in presence of commonly found metal ions such as copper, lead, cadmium, arsenic and zinc. The results obtained by the present procedure are in good agreement in terms of measurement (limit of determination, 0.01 μg/mL) and precision (S.D., (±) 0.049 and percentage error, 1.37 %).

TABLE-1
CONCENTRATION OF ANTIMONY(III) IN INDUSTRIAL WASTE WATER SAMPLES FROM MARUDHAR INDUSTRIAL AREA

Sample No.	Sb(III) concn. (ppm)	Deviation from average
1	0.369	0.016
2	0.418	0.033
3	0.387	0.002
4	0.394	0.009
5	0.360	0.025
	Mean deviation	0.017
	Minimum	0.360 ppm
	Maximum	0.418 ppm
	Average	0.385 ppm
	S.D. (±)	0.022
	R.S.D. (%)	5.71

TABLE-2
CONCENTRATION OF ANTIMONY(III) IN INDUSTRIAL WASTE WATER SAMPLES FROM BASNI II[nd] PHASE INDUSTRIAL AREA

Sample No.	Sb(III) concn. (ppm)	Deviation from average
1	0.189	0.015
2	0.195	0.021
3	0.167	0.007
4	0.172	0.002
5	0.151	0.023
	Mean Deviation	0.013
	Minimum	0.151 ppm
	Maximum	0.195 ppm
	Average	0.174 ppm
	S.D. (±)	0.017
	R.S.D. (%)	9.77

TABLE-3
DETERMINATION OF Sb(III) IN INDUSTRIAL WASTE BY DIFFERENTIAL PULSE POLAROGRAPHY AND ATOMIC ABSORPTION SPECTROPHOTOMETER

S. No.	Sample	Sb(III) concn. (ppm)**	
		Differential pulse polarography	Atomic absorption spectrophotometer
1	Marudhar*	0.385	0.384
2	Basni*	0.174	0.172

*Industrial areas; **Average of five determinations

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