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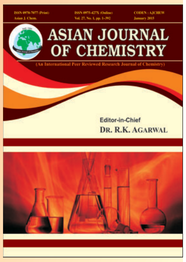

Voltammetric Studies and Micro Level Determination of Arsenic in Aqueous Matrices

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A differential pulse polarographic method for the trace determination of arsenic is presented. The preliminary investigations have indicated the suitability of a complexing media of 0.01 M citric acid in 0.01 M sodium acetate, where As(III) showed a sharp DP reduction peak at -0.93V *vs* SCE. Linearity of the calibration curve was achieved upto 8.5 ppm with a detection limit of 0.009 μg/mL. The coexisting metal ions such as Cu(II), Pb(II), Cd(II) and Zn(II) did not interfere. The differential pulse polarogram method has been applied successfully for the determination of arsenic contents in industrial wastes analysis.

Keywords: Arsenic, Differential pulse polarogram, Industrial wastes analysis.

INTRODUCTION

The measurement of inorganic arsenic in the environment has received considerable attention over the past 40+ years due to its toxicity and prevalence in drinking water[1]. Groundwater contamination of arsenic can occur from various anthropogenic sources such as pesticides, wood preservatives, glass manufacture and miscellaneous arsenic uses. These sources can be monitored and controlled. The relative toxicity of arsenic depends mainly on its chemical form and is dictated in part by the valence state[2]. As(III) is considered more toxic than As(V) as inorganic arsenicals(III) are associated with several acute and chronic adverse effects[3]. Arsenic is reported to cause acute and chronic metabolic disorders in humans[4]. Due to its carcinogenic and other delirious effects on human health and aquatic environment, it is imperative to develop precise and accurate method for the determination of arsenic at very low concentrations.

Among the instrumental techniques used in the trace determination of arsenic such as atomic absorption spectrometry[5-9], ICP-AES[10] and HPLC-ICP MS[11], the polarographic method is more suitable due to simple sample preparation, no interference from major interferants and low cost of instrumentation.

Anodic stripping voltammetry has been widely reported in the determination of arsenic in diverse matrices using gold microelectrode[12], gold coated diamond thin film electrode[13,14], modified glassy carbon electrode[15], gold nanoparticle modified carbon nanotubes[16], glassy carbon electrode modified with cobalt oxide nanoparticles[17], lateral gold electrode[18]. Somer and Almas have used catalytic hydrogen wave in differential pulse polarogram determination of trace quantities of arsenic[19]. Elenkova and Tsoneva[20] and Buldini *et al.*[21] have described diffe-rential pulse polarogram determination of arsenic in ferrotungsten and semiconductor silicon, respectively. Brussciotti and Duby[22] have shown applicability of cyclic voltammetry in study and determination of arsenic. Sharma *et al.* [23-25] have reported differential pulse polarogram trace determination of arsenic in effluent samples. Differential pulse polarogram trace level determination of selenium[26,27] and thorium[28] has been reported earlier.

In the present work a detailed study of As(III) was made in complexing and non-complexing media which has resulted in optimization of differential pulse polarogram conditions for determination of total arsenic as As(III) in waste waters from metal alloy industries at sub-μg levels.

EXPERIMENTAL

All of the chemicals used were of analytical grade purity and were prepared in doubly distilled water. Stock solution of arsenic was prepared from arsenic trioxide (Batch no. 047/127/25043; S.D. Fine Chem. Pvt. Ltd., Boisar).

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 polarographic measurements. A dropping mercury electrode was used as the working electrode. The instrumental settings for the differential pulse polarogram were as follows: pulse amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse, 0.5 sec; scan rate, 12 mV/sec; and charging current compensation, 20 %.

Saturated calomel and platinum wire were used as the reference and auxillary electrodes, respectively.

A UV-visible spectrophotometer (Model - 108) of Systronics, India, was used for comparing the results from polarographic studies which had a wavelength range from 190-900 nm. The 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.

Industrial waste water samples were collected from Marudhar and Basni Industrial Areas of Jodhpur consisting metal and alloy industries. These were filtered in order to separate any suspended particulate matter. To obtain detectable quantities of arsenic, the water samples were preconcentrated to 1/10th of their original volumes by boiling. To 100 mL of this aliquot, 1 mL of oxidizing mixture (HNO_3:H_2SO_4; 5 mL:1 mL) was added, the contents were heated until the solution fumed to remove biological and organic matrices. The filtered sample was then reduced with sodium molybdate dihydrate to convert all forms of arsenic present in solution to trivalent arsenic. Thus, the total arsenic content would be determine as As(III).

The test solutions were deaerated for 20 mins by passing nitrogen, which was purified by bubbling it through a vanadous chloride scrubbing solution[29]. All the experiments were carried out at 25 ± 1 °C.

RESULTS AND DISCUSSION

Polarographic characteristics: The electroreduction of arsenic was investigated initially with media such as nitric acid, hydrochloric acid, sulfuric acid, thioglycolic acid/sodium acetate and tartaric acid/hydrochloric acid, where poorly developed polarographic waves were obtained with these media showing unsuitability of these supporting electrolytes.

Finally a complexing medium of citric acid in presence of 0.01M sodium acetate was found to be most adequate in which As(III) gave a well-defined polarographic wave at a potential of -0.94 V for the reduction of As(III) to its elemental state as shown in Fig. 1. Analysis of the direct current polarographic wave illustrated that the electrode process was diffusion controlled and not fully reversible in nature.

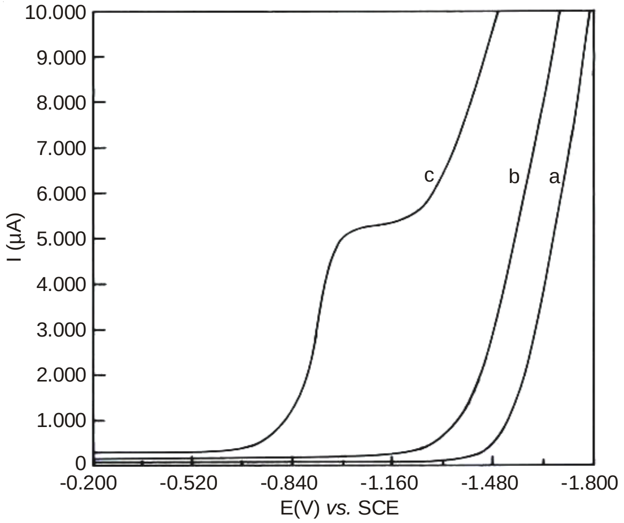

Fig. 1. DC polarogram of arsenic(III); (a) Blank solution of 0.01 M sodium acetate (b) Blank solution of 0.01 M citric acid in 0.01 M sodium acetate (c) 1 × 10^{-4} M As(III) in 0.01 M citric acid/0.01 M sodium acetate

Optimum differential pulse polarogram conditions: Differential pulse polarogram reduction of As(III) in presence of 0.01 M citric acid in 0.01 M sodium acetate gave a sharp peak at -0.94 V. The linearity of peak height *vs.* concentration was noticed in 0.009-8.50 ppm range of arsenic concentration. The characteristics of calibration curve drawn between concentration and current (Fig. 2) were as follows:

Slope = 0.5525; Intercept = 0.0919; Coefficient of correlation (r) = 0.9977; Standard deviation = ± 2.2258.

The differential pulse peak was found suitable for quantitation of arsenic where a limit of determination of 0.009 µg/mL was achieved.

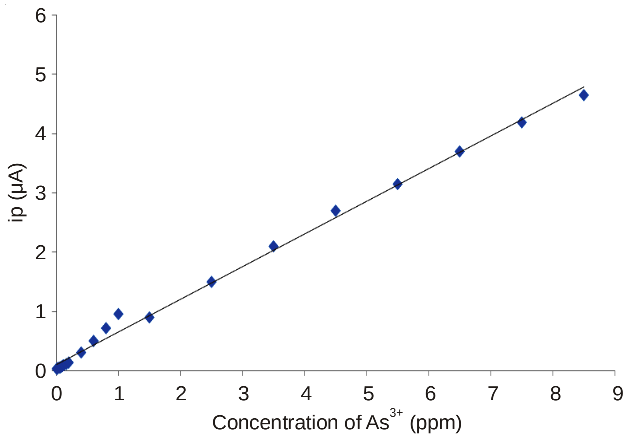

Fig. 2. Plot of calibration curve, concentration in (ppm) *vs.* peak current (µA), Minimum concentration = 0.009 ppm and maximum concentration = 8.50 ppm

Interference study: The coexisting interferants copper and lead which are mostly present with arsenic in ores and minerals were monitored during the differential pulse polarogram determination of As(III). Peak potential of Cu(II) in 0.01M citric acid/0.01 M sodium acetate was found to be more positive (> 0.0V), indicating no interference. Similarly, Pb(II) is reduced at -0.39 V which is well-separated from As(III) at -0.94 V. Other common metal ions such as cadmium and zinc also gave distinguishable differential pulse peaks and did not interfere as shown in Fig. 3.

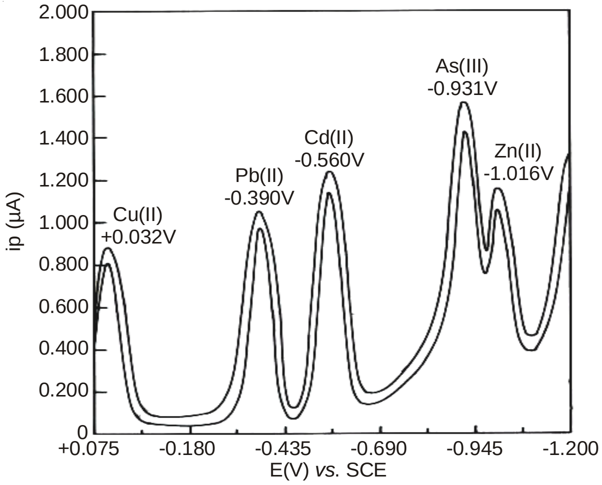

Fig. 3. Differential pulse polarogram of As(III) in presence of Cu(II), Pb(II), Cd(II) and Zn(II) in 0.01 M citric acid/0.01 M sodium acetate; Cu(II) = 8 ppm; Pb(II) = 18 ppm; Cd(II) = 15 ppm; As(III) = 3 ppm and Zn(II) = 5 ppm

TABLE- 1
RESULTS OF ARSENIC DETERMINATION IN INDUSTRIAL WASTE WATER SAMPLES

S. No.	Sample	Arsenic conc. (µg/mL)		S.D. (±)	R.S.D. (%)	Recovery (%)
		Added	Determined*			
1	Jupiter alloys	1.5	1.43	0.050	3.49	95.33
2	Suncity alloys	1.6	1.53	0.048	3.13	95.42
3	Navkar metals	2.5	2.44	0.036	1.47	97.60
4	Mehnot metals	2.0	1.98	0.020	1.01	98.83
5	Ronk industries	1.8	1.73	0.015	0.87	96.30

*Average of three determinations

Precision and accuracy: A test solution of known concentration of As(III) was analyzed under the optimized experimental concentrations to evaluate the reproducibility of differential pulse polarogram measurements. The results obtained were in a good agreement with a relative error of 5.2 %, inferring that the differential pulse polarogram determination of arsenic is precise and accurate.

Analytical applications: The differential pulse polarogram reduction of As(III) in 0.01 M citric acid in 0.01 M sodium acetate medium was made the basis for arsenic determination in industrial waste water samples. The prepared samples were taken into the polarographic cell and differential pulse polarograms were recorded in the potential range of -0.2 to -1.1 V and peak current was noted at -0.93 V after making the blank correction. It was done by recording the current of the supporting electrolyte alone without any salt and subtracted it from the peak current obtained for the test solutions. Concentrations were determined from the difference of these two currents using the standard addition method. The results of determination of total arsenic as As(III) in different industrial waste water samples are summarized in Table-1.

The validity of differential pulse polarogram determinations of arsenic in waste water samples was demonstrated by comparing the results with UV-visible spectrophotometric method based on the reaction of As(III) with citric acid in aqueous medium. The comparative data are given in Table-2.

TABLE-2
COMAPRISION OF RESULTS OF As(III) DETERMINATION BY DP POLAROGRAM AND UV-VISIBLE SPECTROPHOTOMETRY

S. No.	Sample	Arsenic (µg/mL)		
		Added	DPP	UV-visible
1	Jupiter alloys	1.5	1.43	1.45
2	Suncity alloys	1.6	1.53	1.51
3	Navkar metals	2.5	2.44	2.49
4	Mehnot metals	2.0	1.98	1.97
5	Ronk industries	1.8	1.73	1.80

n = number of determinations = 3

Conclusion

The described differential pulse polarogram method for the determination of arsenic in industrial waste water samples is specific, sensitive and rapid with a simple approach comprising low cost instrumentation as compared to the widely used mass spectrometry and absorption spectrophotometry.

Furthermore, this method enables sequential determination of µg levels of arsenic in presence of copper and lead which are mostly present with arsenic in ores and minerals. The results of arsenic determined by the present method are quantitative in terms of measurement (concentration limit: 0.009 µg/mL).

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