

Volta metric Ultra traces Determination of Beryllium in Real Samples

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Abstract-- A simple and convenient method is described for the determination of low concentration beryllium in industrial wastes. It is based on the differential pulse polarographic reduction of Be^{2+} in complexing medium of dimethyl formamide in acetate buffer. Linearity of the calibration curve was observed in between 0.05 to 10 ppm. The limit of determination was achieved 0.01 $\mu\text{g/ml}$. The measurements were found quantitative in terms of standard deviation ± 0.07 and the comparison of results by UV-Vis spectrophotometric method suggests validity of the DPP method.

Keyword- Beryllium, industrial wastes, DPP.

I. INTRODUCTION

Among the toxic trace metals, beryllium is a deadly poisonous metal. It is also carcinogenic. Inhalation of beryllium dust causes severe and irreparable lung damage. The disease is called berylliosis. The main sources of beryllium in the environment are the industries of metals where it is used in alloys with copper and nickel and imparts excellent electrical and thermal conductivities. The copper alloy is used to make spark-proof tools [1]. Thus it is appropriate to develop an analytical method of simple approach for the determination of beryllium in industrial waste waters.

The stripping voltammetry and differential pulse polarography (DPP) are sensitive voltammetric methods comparable to other instrumental techniques reported for the determination of beryllium such as flameless atomic absorption [2, 3], X-ray fluorescences spectrometry [4], reversed phase high performance liquid chromatography [5] and solid phase spectrometry [6]. Voltammetric methods can characterise and determine different ionic forms of an element such as in case of beryllium standard state, Be^{2+} , is considered stable in solutions. Thus, it is of interest to investigate the suitability of these methods in determination of low concentration beryllium.

The electrochemical data on beryllium revealed that it is rather difficult to obtain a well-defined wave of Be^{2+} due to its more reduction potential (-1.97 E°/V) [7]. However, in presence of a suitable complexing media, the reduction potential would be shifted to a sufficiently negative potential as thus to be measurable at dropping electrode [8]. In this manner Jovanic and Rekalic [9] have reported polarographic reduction of Beryllium (II) in presence of oxamide and rubeanic acid. Ceisiclskc [10] et al have described pulse polarographic studies of the Beryllium-calcone complex at mercury electrode. Trace measurement of beryllium by adsorptive stripping voltammetry and potentiometry using Beryllium-throin complex onto the stationary mercury electrode is given by Wang and Tian [11]. Wang et al [12] have also reported adsorptive stripping voltammetric measurement of trace beryllium at the mercury electrode in ammonium buffer containing arsezano- I. Sun et al [13] have shown adsorptive voltammetric behaviour of Be (II) in $\text{NH}_3\text{-NH}_4\text{Cl}$ medium.

Herein a study of electroreduction behaviour of Be (II) in presence of dimethylformamide at a dropping mercury electrode shows the possibility of developing a voltammetric method for determination of beryllium at low concentrations. Similar studies related to iron [14], nickel and cobalt [15], indium [16], silver [17] and tellurium [18], are reported earlier.

II. EXPERIMENTAL INSTRUMENTATION

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

A UV-Vis spectrophotometer (Model-108) of Sustronics, India was also used in studies. It covers wavelength range of 190-900nm. The tungsten halogen deuterium lamp and wide range photomultiplier were the light source and detector, respectively. The spectral band width of resolution was 0.5nm.

The pH measurement was made by a digital pH meter (Model-335) of Systronic, India. Prior to measurements instruments was calibrated with buffer solutions.

III. CHEMICALS AND REAGENTS

Chemicals used were of analytical purity. Stock solution of beryllium was prepared from beryllium sulphate (Batch No.01Y/0501/31) of s.d fine chemicals. All solutions were made in purified water obtained from Elix (Mill-Cl Advantage A10) of Millipore, SAS, France.

IV. SAMPLE PREPARATION

1ml of an oxidising mixture of nitric acid and sulphuric acid was added to 50ml aliquot of industrial waste water sample. Contents were heated on a hot plate until solution was fumed to remove all organic and biological matters. It was then transferred to a volumetric flask and made upto the requisite volume with distilled water [19]. Test solutions were deaerated for 20 min. by passing purified nitrogen prior to measurements. It was done by bubbling N_2 through a vanadous chloride scrubbing solution [20].

All experiments were carried out at $\pm 298\text{K}$ in an air – conditioned laboratory.

V. RESULTS AND DISCUSSION

A. Preliminary investigations

The electroreduction of Be^{2+} in presence of dimethylformamide was studied in different supporting electrolytes such as acetate buffer, sodium perchlorate and

tetramethylammonium perchlorate. The observations indicated the suitability of 0.01M acetate buffer where a well-defined polarographic wave, representing Be (II) - Be (0), was obtained at -1.84V.

B. Effect of Complexing reagent

The polarographic wave height increased with the concentration of dimethylformamide upto 0.01M. Higher concentration of complexing reagent did not change the limiting current. All measurements were, therefore made in these conditions. The polarographic wave appears to be diffusion controlled, although electrode process of Be (II) - dimethylformamide in acetate buffer was not fully reversible.

C. DPP Studies

Beryllium (II) also gave a sharp DP peak at -1.84V. Peak current increased in proportion to beryllium concentration from 0.01ppm to 10ppm. It is shown in Fig.1. The calibration curve (Fig. 2) characteristics were as followings: slope, 0.3370; intercept, 0.512; coefficient of correlation (π), 0.9992.

VI. OPTIMUM CONDITIONS FOR DETERMINATION OF BERYLLIUM

A. Accuracy and precision

The determination of beryllium by DPP was evaluated for its precision and accuracy. A value of ± 0.07 was obtained for standard deviation at a concentration of 1mg/L (number of replicates; 5), inferring that measurements were reproducible.

B. Interference studies

The analysis of industrial waste waters by voltammetry has shown the presence of lead, cadmium and zinc [21]. These major ions were therefore monitored for interference during the determination of beryllium. DP peaks of Pb(II), Cd(II), and Zn(II) in presence of 0.1M dimethylformamide in 0.01M acetate buffer medium were found distinguishable and well separated from that of Be(II) at -1.84 V.

Further, since berylliums is used in alloys with copper and nickel therefore their interference was also tested. Peak potential of Cu (II) and Ni (II) were -0.07 V and -1.1 V, respectively. Thus, Pb(II), Cd(II), Zn(II), Cu(II) and Ni(II) did not interfered in determination of beryllium. Peak potentials are listed in Table1.

C. Limit of determination

The minimum amount of beryllium which could be determined under the optimal experimental conditions was 0.01 $\mu\text{g/ml}$

VII. ANALYTICAL APPLICATIONS

A. Determination of beryllium in industrial waste waters

a. Sample preparation

1 ml of an oxidizing mixture of nitric acid and sulfuric acid was added to 50 ml aliquot of water sample. Contents were heated on a hot plate until solution was fumed to remove organic and biological matters. It was then transferred to a volumetric flask and made upto the requisite volume with distilled water.

b. Voltammetric measurements

A measured volume of the prepared sample was taken into the polarographic medium of 0.1M dimethylformamide / 0.01M acetate buffer. DP polarograms were recorded from -1.5 to -

2.0 V. The peak current was measured at -1.84 V after making the blank correction. The concentrations were determined by the standard addition method [22]. The results of determination of beryllium in different industrial waste water samples are summarized in Table 2.

The determination of beryllium by the DPP method was found more suitable and convenient. In stripping analysis due to the more negative potential of Be^{2+} (-1.84V), other metal ions present in industrial waste water sample might have been deposited on the surface of electrode and forming intermetallic compound. It subsequently causes significant interference in measurements.

VIII. COMPARISON

UV-Vis spectrophotometric method was used to compare the results obtained by DPP. The comparative data are shown in Table 2. These are quantitative in terms of measurements.

Further, the results of determination of beryllium determined by developed DPP method are in good agreement with other techniques including polarography in view of calibration linearity (0.08 to 1.0 mM) reported by Jovanovic and Rekalic [9] in presence of oxamide and rubeanic acid. Even compared to adsorption voltammetric determination of beryllium in presence of beryllium II (detection limit, $5 \times 10^{-10} \text{M/L}$) [13], our observations are quite reasonable satisfactory.

CONCLUSION

The presence of beryllium in industrial wastes may be due to the set-up of a large number of metal and chemical industries where it is used in alloys with copper and nickel to impart excellent electrical conductivity.

Acknowledgment

Authors acknowledge the University Grants Commission, New Delhi for financial support to carry out the present research work and awarding Research fellowship under RFSMS scheme to V.Kherwa.

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\$ N=5, No.of determination
 # Flowing at outskirts of Industrial Area

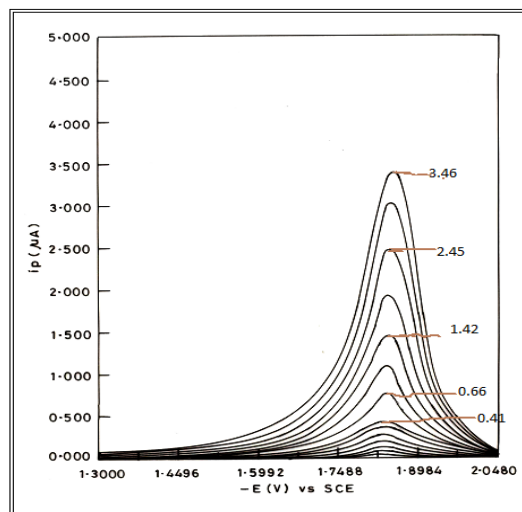


Figure 1:DP polarograms of Be (II) at varied concentration in 0.1M dimethylformamide / 0.01M acetate buffer

Table 1: Peak potential of metal ions in 0.1M dimethylformamide / 0.01M acetate buffer

S.No.	Metal ion	-E _p (V)
1.	Pb(II)	0.34
2.	Cd (II)	0.52
3.	Zn (II)	0.98
4.	Be(II)	1.86

Table 2: Results of determination of beryllium

Sample	DPP ^s ±SD (ppm)	UV-vis (ppm)
1.Basni Industrial Area	0.0734	0.0732
2. Common Nala Effluent#	0.0288	0.0286

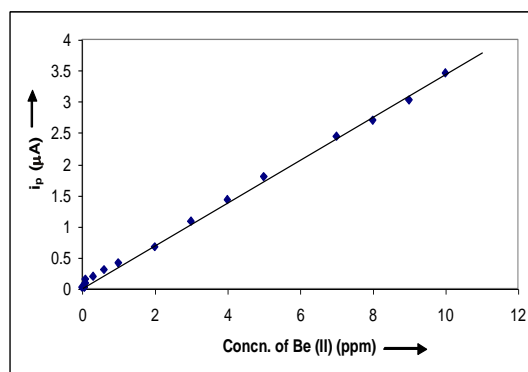


Figure 2: Calibration curve of beryllium concn. vs. peak current