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VOLTAMMETRIC TRACE DETERMINATION OF LANTHANUM

Pradeep Sharma[1], Rajni Bais[2], Mukesh Tiwari[3]

[1,2,3] *Electroanalytical Laboratory, Department of Chemistry, J.N.N.University, Jodhpur (India)*

ABSTRACT

Optimum conditions for the determination of lanthanum at sub µg level have been developed employing differential pulse polarography. A detection limit of 0.5µg/ml has been achieved. The method successfully been applied for analysis of lanthanum in industrial wastes.

Keywords: Differential Pulse Polarography, Industrial Waste Samples, Lanthanum, Trace Determination.

I. INTRODUCTION

Lanthanum is an important lanthanide with great importance and utility. It is used in optical glasses, especially in cameras and television eye piece. Lanthanum (III) salts are used as biological tracers for calcium. Lanthanum added to steel improves its malleability and resistance to impact and ductility. Its another important use in flint of cigarettes. However, lanthanum is mildly toxic by ingestion can causes liver injury. It is thus imperative to develop a convenient method of simple approach for the determination of lanthanum.

Pulse polarography and stripping voltammetry are sensitive electroanalytical techniques comparable with atomic absorption spectroscopy (AAS), neutron activation analysis and spectrophotometry, for the analysis of trace metals [1]. The different ionic forms of an element can also be characterized and determined by voltammetric methods due to selectivity of the redox potential as in case of lanthanum (III) which is most stable in solution [2]. In stripping analysis intermetallic compound formation on the electrode surface causes significant interference during the deposition [3]. Therefore the suitability of differential pulse polarography (DPP) is envisaged in present studies.

Kolthoff and Coetzee [4] have initiated the electrochemical investigations on La(III) in methyl cyanide and acetonitrile media, and concluded one electron polarographic reduction. Treindl [5] has carried out classical, pulse and oscillographic polarography of lanthanum alongwith cerium has been reported by Wang et al [6]. Mukherji [7] utilized the reduction of nitrate ions in the presence of thorium, and lanthanum is utilized for the amperometric determination of these two metal ions.

The reported voltammetric work has indicated that choice of supporting electrolyte in case of lanthanum (III) investigations is limited due to its very negative reduction potential [3]. Therefore detailed comprehensive electrochemical study was carried out in various alkaline and acidic media. It has resulted in development of optimum voltammetric conditions for the determination of trace level lanthanum (III) using DPP. The results obtained have been compared with UV- VIS spectrophotometric method. Similar studies related to iron [8], indium [9] and silver [10] have been reported earlier.

II. METHOD AND MATERIALS

2.1 Instrumentation

A polarographic analyzer (Model 174-A) in combination with an X-Y recorder (Model RE 0074), and drop timer (Model 174/70), (EG&G, U.S.A.) were used for polarographic recordings. The instrumental settings for DPP were as follows: A dropping mercury electrode (DME) was used as working electrode, pulse amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse, 0.5 sec; scan rate, 5mV/sec. The Ag/AgCl and platinum wire were used as reference and auxillary electrodes, respectively.

A UV-VIS 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.

2.2 Sample Preparation

Industrial waste water samples were collected from 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 lanthanum, the water samples were preconcentrated to $1/10^{th}$ 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.

2.3 Chemicals

All of the chemicals used were of analytical grade purity and were prepared in doubly distilled water. Stock solution of cerium was prepared from lanthanum nitrate (Batch No. 57807, Loba Chemie, Mumbai).

The test solutions were deaerated for 20 mins by passing nitrogen, which was purified by bubbling it through a vanadous chloride scrubbing solution.

All the experiments were carried out at 25 ± 1^0C.

III. RESULTS AND DISCUSSION

Preliminary investigations of electro reduction of lanthanum (III) have revealed suitability of 0.1M KCl against the other studied media such as sodium hydroxide, lithium chloride, acetate buffer, potassium nitrate, ammonia-ammonium chloride buffer and tarta rate buffer. La(III) gave a sharp DP peak at -1.87 V for its reduction to La(0), as shown in Fig. 1.

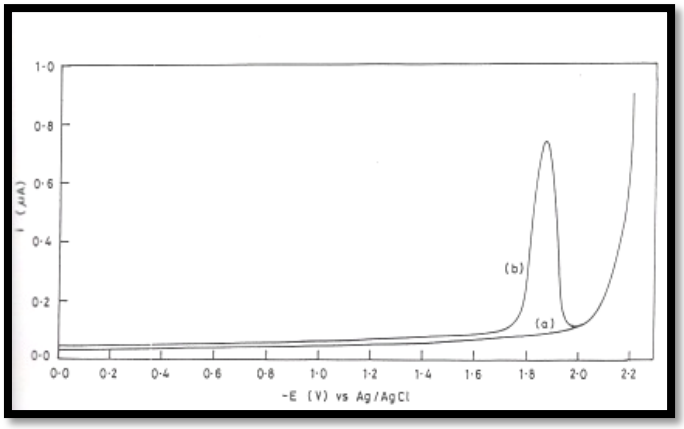

Fig. 1: DP polarogram of La(III) in 0.1 M KCl

(a) blank solution of 0.1 M KCl

(b) 10 ppm La(III) in 0.1 M KCl

3.1 Optimum Conditions

DPP studies showed that peak current increased linearly upto 5.0 ppm concentrations of La(III). DP polarograms at different concentrations of La(III) are shown in Fig. 2.

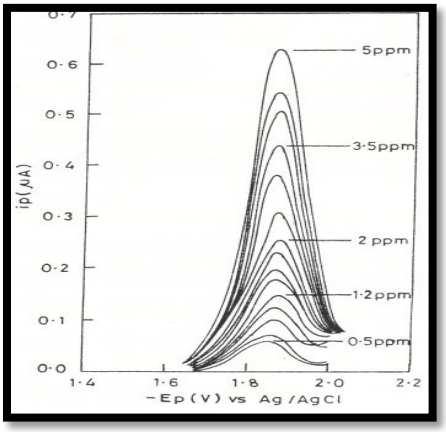

Fig. 2: DP Polarograms of La(III) in 0.1 M KCl at Different Concentrations

The characteristics of calibration curve (Fig. 3) were as followings:

Slope, 0.1269; Intercept, 0.0016; coefficient of correlation (r), 0.999 and standard deviation; ± 0.1852.

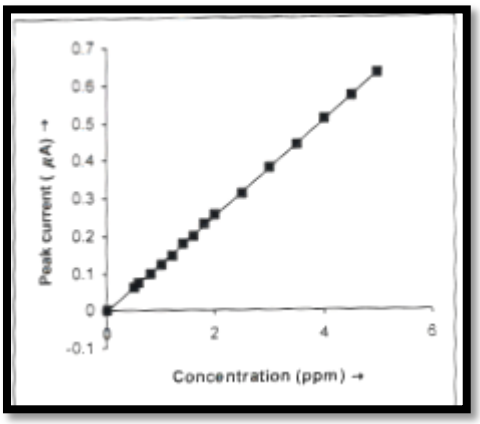

Fig. 3: Peak Current vs Concentration Curve of La(III) in 0.1 M KCl

3.2 Interference Study

The analysis of industrial wastes by voltammetry has revealed the presence of copper, lead, cadmium and zinc [11, 12]. Similarly, zirconium might be associated with lanthanum as it is also used in alloys to improve mechanibility [13]. Therefore it is appropriate to study interference of these metal ions during the voltammetric determinations of lanthanum. The DP peak of Cu(II) in 0.1 M KCl was noticed at -0.22 V, illustrating no interference. Peak potential of Zn(II) was noted at -1.00V, which is well separated from that of La(II) at -1.87 V. Lead and cadmium also gave distinguishable DP peaks (EPS: Pb(II),-0.44V; Cd(II), -0.53V) It has been clarified in Fig. 4. Peak potentials are given in Table 1.

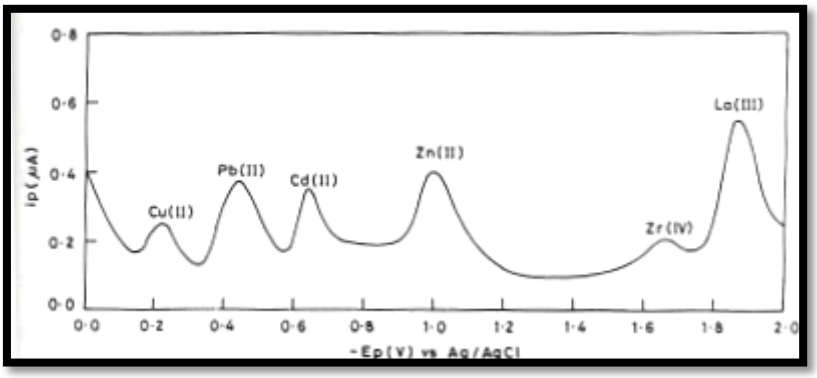

Figure 4: DP Polarogram of La(III) in Presence of Cu(II), Pb(II), Cd(II), Zn(II) and Zr(IV); Cu(II) = 7ppm, Pb(II) = 5 ppm, Cd(II) = 5 ppm, Zn(II) = 9 ppm, Zr(IV) = 13 ppm, La(III) = 3 ppm

Table 1: Peak Potentials of Metal Ions in 0.1 M KCl

S.No.	Metal Ion	Peak Potential –Ep(V) vs Ag/AgCl
1.	Copper(II)	0.22
2.	Lead(II)	0.44
3.	Cadmium(II)	0.64
4.	Zinc(II)	1.00
5.	Zirconium(IV)	1.66
6.	Lanthanum	1.87

3.3 Precision and Accuracy

The reproducibility of the method was evaluated by determining lanthanum in a test solution of known concentration under the optimized experimental conditions. The obtained data were in good agreement in terms of measurement with a relative error of 3.1%, inferring that method is precise and accurate.

3.4 Limit of determination

The limit of quantification lanthanum was found to be 0.5 µg/ml.

3.5 Analytical Applications

The devised optimum voltammetric conditions consisting of medium, calibration, linearity, reproducibility and detection limit were applied to analyse lanthanum in industrial wastes.

3.6 Voltammetric Measurements

The prepared samples were taken into the polarographic medium of 0.1 M KCl and DP polarograms were recorded from -1.4 to 2.0 V. Peak currents were measured at -1.87 v after making the blank correction. The concentrations were determined by standard addition method [14]. The results of determination of lanthanum are presented in Table 2.

Table 2: Determination of La(III) in Industrial Waste Samples

S.No.	La(III) concn. added (µg/ml)	La(III) concn determined (µg/ml)	S.D. (±)	R.S.D. (%)	Recovery (%)
1.	0.5	0.495	0.0229	0.0463	99.00
2.	1.0	0.985	0.0384	0.0390	98.50
3.	2.0	1.960	0.0513	0.0262	98.00
4.	3.0	2.890	0.0862	0.0298	96.33
5.	4.0	3.956	0.1206	0.0305	98.90

3.7 Validation

The results of determination of lanthanum in industrial waste samples were further verified by carrying out comparison studies with UV-Vis spectrophotometric method. The data so obtained are compared in Table 3.

Table 3: Comparison of Results of La(III) Determined by DPP and UV-VIS Method

S.No.	Sample	La(III) concn. present (µg/ml)	La(III) concn. determined (µg/ml)	
			DPP	UV-VIS
1.	A	1.0	0.96	0.91
2.	B	2.0	1.92	1.83
3.	C	3.0	2.81	2.83
4.	D	4.0	3.69	4.00
5.	E	5.0	4.53	4.48

IV. CONCLUSIONS

The suggested method of lanthanum determination is specific, rapid and convenient due to simple sample preparation, no interference from major ions and low cost of instrumentation.

The DPP technique was found more suitable to stripping voltammetry in determination of lanthanum because of higher negative reduction potential of La(III) at – 1.87V. Other metal ions present in waste samples such as copper, lead and zinc would also be thus deposited on the surface of electrode forming intermetallic compound and causing significant interference during the procedure.

V. ACKNOWLEDGEMENT

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