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Voltammetric Trace Determination of Europium

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A simple and convenient method is described for the determination of europium based on differential pulse polarographic reduction of Eu(III) in ammonium chloride medium. Linearity of calibration curve was achieved up to 10 ppm with a limit of determination of 0.10 µg/ml. The possible interference of common metal ions was examined and ruled out. The method has been successfully applied for the analysis of europium in industrial waste samples.

Keyword: Lanthanides, europium, differential pulse polarography, industrial waste water analysis.

1. Introduction

Europium is one of the rarest of the so called rare earth group (more correctly termed as lanthanides). It is the most reactive of these metals, reacting with oxygen and water. It is of little use, but is employed in thin film superconductor alloys ^[1]. Therefore, it is appropriate to develop a simple analytical method for the determination of europium.

Several methods such as spectrofluorometry ^[2], spectrophotometry ^[3], and flow injection method ^[4] are reported in the determination of microgram level europium. The procedures require preliminary treatment of the sample (in addition to any concentration step) to bring Eu to the proper state for measurement by preoxidation or reduction.

The voltammetric methods are more suitable, as these can identify and determine different forms of an element as in case of europium which exists in three oxidation states of +3, +2 and 0. Differential pulse polarography (DPP) and anodic stripping voltammetry have proved useful in such determinations. Thus, it is of interest to investigate the suitability of these methods in the determination of europium, which is usually present at ultra-trace concentration.

The electrochemical data on europium has indicated that reduction of Eu(III) to Eu(II) is a change in the 4f

shell. The reduction therefore is expected to be reversible. Further, studies of voltammetric behavior of europium (III) in aqueous solution have been restricted to polarographic studies with DME. Most of the work was done with unbuffered solution where a single wave corresponding to Eu(III) to Eu(II) was noticed by Noddack and Brukl ^[5]. Muishi and Masuda ^[6] have studied nature and determination of europium ion in carbonate solution. Gour and Zutishi ^[7] have investigated Eu³⁺ in formamide media with DME. Polarographic reduction of Eu(III) to Eu(II) has also been demonstrated by Cokal and Wise ^[8] in a medium of acetonitrile.

Jaikishan ^[9] has described a polarographic complex study of Eu(III) with bicine and tricine in the presence of sodium perchlorate. Mlakar ^[10] has reported square-wave voltammetric measurements of Eu(III)-salicylate complex. Other complexing agents such as derivatives of schiff base ^[11] and triethylene tetra amine hexa acetic acid ^[12] have also been used in the polarographic determination of Eu(III).

Kuznetsov and Escard ^[13] have studied electrokinetics of Eu³⁺/Eu²⁺ redox couple by cyclic voltammetry. Abollina ^[14] et al has determined trace europium by adsorptive cathodic stripping voltammetry after complexation with cupferron. Differential pulse polarographic determination of europium in the

presence of humic substances has been given by Janos and Synek ^[15].

In stripping analysis intermetallic compound formation on the electrode surface causes significant interference during the deposition. Moreover, the experimental parameters must be carefully controlled in reproducible measurements. The authors have made a detailed investigation of europium in alkaline medium using classical polarography and differential pulse polarography. The observation have enabled in developing of optimal conditions for determinations of europium at low concentrations. The DPP determinations of rhenium, germanium, osmium, uranium and tellurium were reported earlier ^[16-20].

2. Methods and Materials

2.1 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 with an Epson printer (Epson-LX-300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode 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 were used as reference 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 190-900 nm. The tungsten-halogen deuterium lamp and wide range photomultiplier were also used as the light source and detector, respectively. The spectral bandwidth of the resolution was 0.5 nm.

2.2 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

at least one week and washed several times with doubly distilled water ^[21]. Subsequent conditioning is also of paramount importance to check adsorption ^[22].

2.3 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 an oxidizing mixture of nitric acid and sulfuric acid to destroy the biological and organic matters ^[23].

2.4 Chemicals

Chemicals used were of reagent grade purity. Stock solution of europium was prepared from Eu₂O₃ of Loba Chemie, Mumbai (Batch no. 87657). Solutions were prepared in mill-Q-water (Millipore).

The measurements were made in an air conditioned laboratory at 25±1 °C. 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 ^[24].

3. Results and Discussion

The electroreduction of europium (III) was observed in different supporting electrolytes (Table 1). Among these media, ammonium chloride was found most adequate where Eu (III) gave a sharp differential (DP) peak at -0.70 V corresponding to Eu(III) to Eu(II) reduction as shown in (Fig. 1).

Table 1: Electrochemical characteristics of europium (III)
Eu(III) = 1 x 10⁻⁴M

S. No.	Supporting Electrolyte	-E _{1/2} (V)	i _d (μA)
1.	0.1M KNO ₃	0.67	0.27
2.	0.1 M H ₂ SO ₄	0.76	0.27
3.	0.1M HCl	0.71	0.29
4.	0.1M LiCl	0.68	0.30
5.	0.1M NaClO ₄	0.59	0.21
6.	0.1M NH ₄ Cl	0.70	0.32
7.	0.1M acetate buffer	0.78	0.22

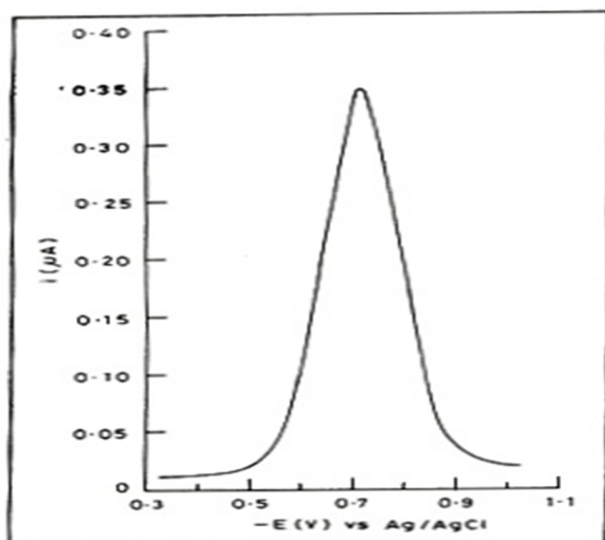


Fig 1: DP polarogram of Eu(III) in 0.1 M NH₄Cl

3.1 Optimum DPP conditions: Method Development

The linearity of peak current versus europium concentration was noticed in the range of 0.5 ppm to 10.0 ppm as shown in (Fig. 2). A calibration curve between the concentration of europium and the peak current is displayed in (Fig. 3). The calibration characteristics were as follows: slope, 0.0316; intercept, 0.0107; coefficient of correlation (r), 0.9919; and standard deviation (\pm), 0.1080.

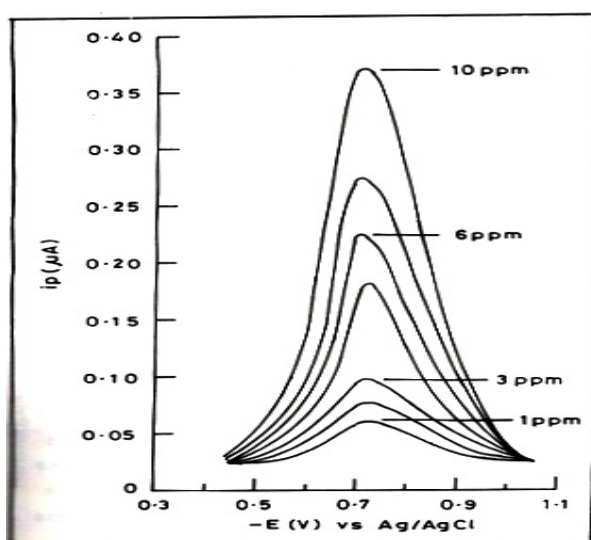


Fig 2: DP polarograms of europium(III) at different concentrations in presence of 0.1M ammonium chloride

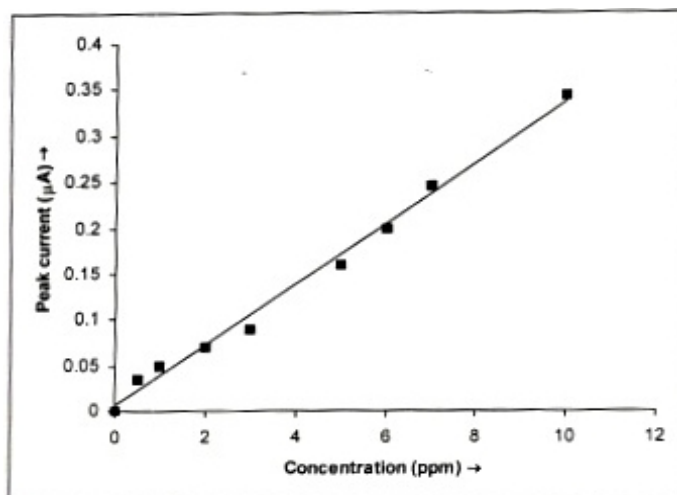


Fig 3: Relationship between Eu (III) concentration and peak current

3.2 Interference Studies

Europium is mostly obtained from bastnae site and monazite ores where lanthanum, cerium and neodymium are likely to be associated with europium. Their interference was examined and it was found that La(III), Ce(IV) and Nd(III) are reduced at very negative potentials and thus did not interfere. Other common metal ions such as Cu(II), Pb(II), Cd(II) and Zn(II) also showed DP peaks at different peak potentials and well separated from Eu(III) in NH₄Cl. It has been clarified in Fig. 4. Peak potentials are listed in Table 2.

Table 2: Peak potential of metal ions in ammonium chloride

S. No.	Metal Ion	Peak potential -E _p (V) vs AgCl
1.	Copper (II)	0.22
2.	Lead (II)	0.56
3.	Europium (III)	0.71
4.	Cadmium (II)	0.81
5.	Zinc (II)	1.34

3.3 Precision and Accuracy

The DPP determination of europium (III) was evaluated for its precision and accuracy where a standard deviation of ± 0.03 was obtained at a concentration of 2 $\mu\text{g/ml}$. The data revealed that the recoveries were quantitative and determined values agreed with the concentration of europium present in solution.

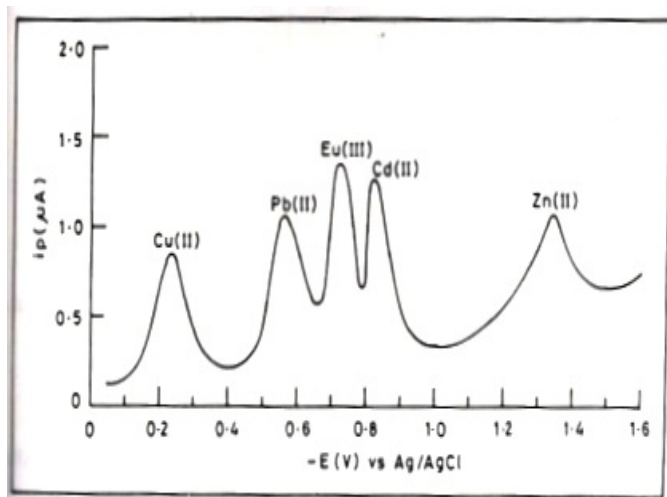


Fig 4: DP polarogram of Eu(III) in presence of Cu(II), Pb(II), Cd(II) and Zn(II) in 0.1M NH₄Cl

3.4 Limit of Determination

The minimum amount of europium (III) which could be determined under the experimental conditions was achieved to be 0.10 μg/ml.

4. Analytical Applications

4.1 Determination of europium in industrial wastes

A 100 ml aliquot of the treated waste water sample was spiked with a known concentration of europium.

4.2 Voltammetric measurements

The prepared sample was taken into a polarographic cell with 0.1 M ammonium chloride. DP polarograms were recorded from -0.3 to -1.1 V and currents were measured at -0.70 V after making blank corrections. The results are summarized in Table 3. The concentrations were determined by standard addition methods [25].

Table 3: Determination of europium (III) in waste water samples

S. No.	Eu (III) added (μg/ml)	Eu (III) determined (μg/ml)	S.D. (±)	R.S.D. (%)	Average recovery (%)
1.	0.5	0.491	0.016	0.033	98.2
2.	1.0	0.979	0.014	0.01	97.9
3.	1.5	1.450	0.07	0.048	96.6
4.	2.0	1.951	0.06	0.030	97.5
5.	2.5	2.459	0.08	0.35	98.3

4.3 Comparison

In order to check the reliability of the applied procedure, the results obtained by DPP were

compared with UV-VIS spectrophotometric method. The comparative data are listed in Table 4.

Table 4: Comparison of results of europium (III) determined by DPP and UV-VIS methods

S. No.	Sample	Eu (III) concentration present (μg/ml)	Eu(III) concentration determined (μg/ml)	
			DPP	UV-VIS
1.	A	0.5	0.495	0.480
2.	B	1.0	0.985	0.970
3.	C	2.0	1.950	1.930
4.	D	5.0	4.900	4.860

5. Conclusion

The results obtained for the determination of europium (III) by proposed DPP method are in good agreement in terms of measurement (concentration limit, 0.10 μg/ml), and recovery (96.5%). This method is more suitable for determination of europium due to its simplicity for sample preparation,

no interference from major ions, and low cost of instrumentation. Further peak potential of the other lanthanides particularly cerium (IV) in ammonium chloride occurred at a more negative potential (> 2.0 V). It was thus more convenient for measurements in the presence of other lanthanides.

6. Acknowledgement

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7. Reference

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