**RESEARCH ARTICLE****ELECTROCHEMICAL STUDIES ON METHOD DEVELOPMENT FOR DETERMINATION OF
CERIUM IN AQUEOUS MATRICES****P. SHARMA, RAJNI BAIS AND SONAL BARMERA**Electroanalytical Laboratory, Department of Chemistry, J.N.V.University,
Jodhpur-342 001, India

Corresponding Author: rajni.c31@gmail.com

Abstract

A sensitive and convenient method for the determination of cerium(IV) at sub-microgram level has been developed with good precision and accuracy using differential pulse polarography. It is based on the complexation of Ce(IV) with alizarine in presence of 1M hexamethylene tetramine. The peak height was found linear to the concentration of cerium upto 5 ppm. The limit of determination was achieved 0.10 µg/ml. The proposed method has been successfully employed for the determination of cerium in industrial waste water samples.

Keywords: Cerium, method development, trace determination, waste water samples.

Introduction

It is rather difficult to study cerium metal ion at dropping electrode due to its more negative standard potential i.e. $E^0 > 1.7$ V (Bard et al 1985). Therefore, a supporting electrolyte that forms a sufficient stable complex ion with cerium was used. The half wave potential of the complexed ion would thus be shifted to a sufficiently negative potential range so as to be measured at dropping electrode (Kapoor and Agarwal 1991).

At early state, the redox behavior of Ce^{4+}/Ce^{3+} couple was reported (Wadsworth 1957 and Desideri 1961). The redox couple studies of cerium in sulfuric acid medium were later on studied (Fang et al 2002). Cerium and lanthanum were determined by using adsorptive stripping voltammetry (Wang et al. 1985). The complexation studies of Ce (IV) with EDTA and DTPA by cyclic voltammetry have also been reported (Modiba and Crouch 2008). The author has utilized the complexing ability of alizarine in presence of 1M hexamethylene tetramine to obtain a polarographic wave whose half wave

potential ($E_{1/2}$) is characteristics of Ce^{4+}/Ce^{3+} system. It has enabled the development of optimum conditions for the determination of cerium in real samples of industrial waste water. We have described DPP determination of uranium, thorium and germanium on the same lines (Sharma and Vyas 1999, Dubey and Kherwa 2013 and Gehlot and Sharma 2001).

Materials and Methods**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 auxiliary 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.

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 cerium, 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 (HNO₃ : H₂SO₄; 5 ml : 1 ml) was added, the contents were heated until the solution fumed to remove biological and organic matrices.

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 cerium sulphate (Batch No. 87657, s.d. fine chem.. Ltd., 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°C.

Results and Discussion

Electrochemical Characteristics

Ce⁴⁺ in presence of alizarin in hexamethylene tetramine displayed well defined single wave at a potential of -0.52 V vs SCE (Fig. 1). The wave height increased with the concentration of alizarine upto 4 × 10⁻⁵ M. Higher concentration of ligand did not change the limiting current. Therefore, all measurements were made at this concentration.

The plot of E vs log i/(i_d-i) revealed that electroreduction of cerium(IV) in alizarin hexamethylene tetramine medium was irreversible, although wave appeared to be diffusion controlled.

Differential Pulse Polarographic Studies

Cerium (IV) showed a sharp DP peak in presence of alizarin hexamethylene tetramine at a potential of -0.52 V. It was observed that on increasing the concentration of cerium the peak current increased linearly upto 5 ppm (Fig. 2). The calibration characteristics were as follows: slope, 1.1792; intercept, 0.0499; coefficient of correlation (r), 0.9989 and standard deviation (±) 2.13.

Interference Observations

The possibly associated lanthanides such as La(III) and Gd(III) were monitored during cerium determination where it was noticed that these metal ions did not gave DP peaks in presence of hexamethylene. Similarly, commonly present metal ions in industrial waste waters like copper, lead and zinc did not interfered.

Limit of Determination

The limit of determination of cerium in these conditions achieved was 0.10µg/ml.

Accuracy and Precision

The reproducibility of the method was evaluated by determining cerium in a test solution of known concentration of cerium in the optimized experimental conditions. The data obtained were found quantitative with standard deviation of ± 0.012, and relative error of 3.7% interfering that method is precise and accurate. Data are shown in table 1.

Analytical Applications

DP polarographic reduction of cerium (IV) in alizarin hexamethylene tetramine was successfully applied for the determination of trace level cerium in industrial waste water samples as followings:

Voltammetric Measurements

The prepared samples were taken into the polarographic cell with alizarin hexamethylene supporting electrolyte. DP polarograms were recorded between -0.3 to -1.1 V. Peak currents were measured at -0.52V, after making blank correction. Concentrations were quantified by applying the standard addition method (Willard et al 1974). Results are summarized in table 2.

Table 1: Precision and accuracy in determination of Ce(IV) by DPP

S. No.	Ce(IV) taken ($\mu\text{g/ml}$)	Ce(IV) found ($\mu\text{g/ml}$)	S.D. (\pm)	R.S.D. (%)	Relative error (%)
1.	0.5	0.475	0.012	0.025	3.7
2.	0.5	0.491			
3.	0.5	0.465			
4.	0.5	0.482			
5.	0.5	0.495			

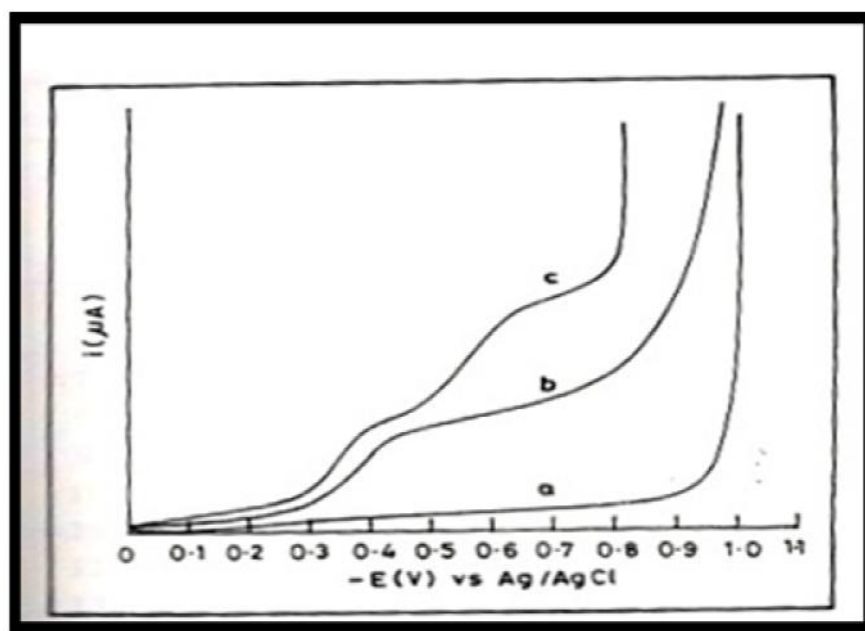
Table 2: Determination of Ce(IV) in industrial waste water

S. No.	Ce(IV) concn. added ($\mu\text{g/ml}$)	Ce(IV) concn. determined ($\mu\text{g/ml}$)	S.D. (\pm)	R.S.D. (%)	Relative error (%)
1.	0.2	0.192	0.015	0.078	96.0
2.	0.6	0.591	0.011	0.019	98.5
3.	1.2	1.189	0.021	0.0182	99.0
4.	1.8	1.754	0.065	0.037	97.4
5.	2.4	2.385	0.080	0.033	99.3

Table 3: Comparison of results of cerium determined by DPP and UV-VIS method

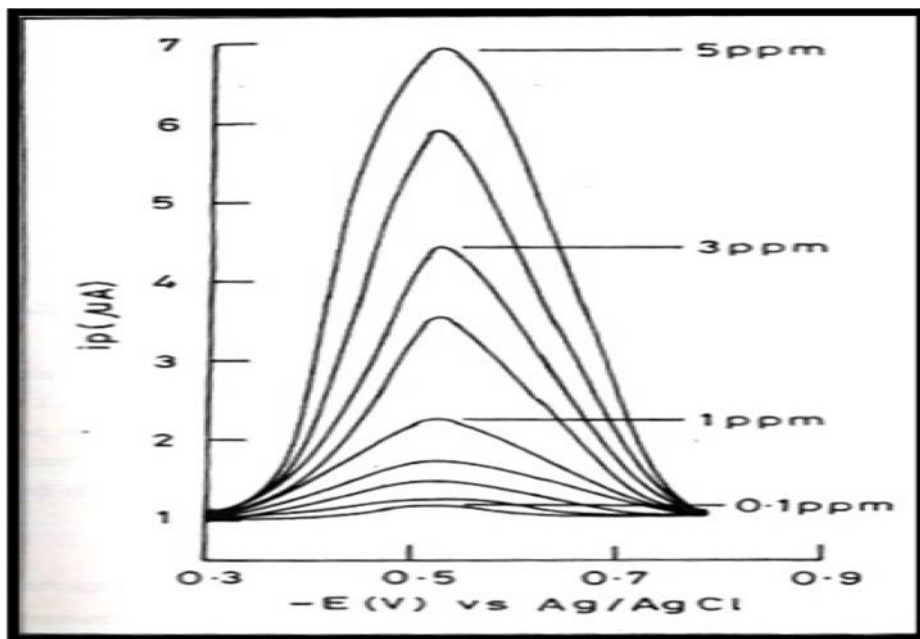
S. No.	Sample	Ce(IV) concn. present ($\mu\text{g/ml}$)	Ce(IV) concn. determined ($\mu\text{g/ml}$)	
			DPP	UV-VIS
1.	A	0.5	0.49	0.48
2.	B	1.0	0.99	0.97
3.	C	2.0	1.97	1.93
4.	D	5.0	4.90	4.86

Fig. 1: DC polarogram of Ce(IV)-alizarine complexone in 1M hexamethylene tetramine
 Ce(IV) = $1 \times 10^{-4}\text{M}$
 Alizarine complexone = $4 \times 10^{-5}\text{M}$



- (a) Blank solution of hexamethylene tetramine
- (b) Alizarine complexone in hexamethylene tetramine
- (c) Ce(IV)-alizarine complexone in hexamethylene tetramine

Fig. 2: DP polarograms of Ce(IV)-alizarine complexone in hexamethylene tetramine at different concentrations



Validation

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

Conclusion

The proposed DPP method is convenient, suitable and simple approach with a concentration limit of 0.10 $\mu\text{g/ml}$ and recovery (98%). Further, compared to non-electrochemical methods such as X-ray diffraction (Balakrishnan 2013), absorption spectroscopy (Reisfeld 1998), X-ray fluorescence spectrometry (Alluyn 1983) and ICP-AES (Rathi 1991), DPP method is more useful in terms of sample preparation; no interference of major ions, and low cost of instrumentation.

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