



Polarographic Study of Cerium(IV)-Antipyrine Complexes at DME in Various Water Samples

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(Received: 29 January 2013;

Accepted: 11 November 2013)

AJC-14367

A catalytic polarographic method for the determination of microgram quantities of Ce(IV) is developed based on the catalytic currents of cerium(IV) in the presence of $\text{NH}_4\text{Cl-NH}_4\text{OH}$ at pH 5.8 with antipyrine. Antipyrine produces catalytic current with Ce(IV) at peak potential -0.1 to -0.6 V vs. SCE. The procedure is applied for the estimation of Ce(IV) in various water samples. The method is simple, sensitive and free from interference of many metal ions.

Key Words: Catalytic currents, Cerium(IV), Antipyrine, Ammonium chloride, Differential pulse polarography.

INTRODUCTION

Cerium is an iron-gray lustrous metal. Among rare earths, cerium is the most widely distributed element averaging 22 ppm in the earth's crust. Analytically, Cerium in its tetravalent state differs significantly from all other lanthanides due to its immense oxidizing ability in acidic solutions. It is a popular oxidant in analytical¹ and organic² application, because it is highly reactive, inexpensive and readily available in high purity. Cerium(IV) has also been used as an oxidant in studies of the homogeneously³ and heterogeneously⁴ catalyzed oxidations of H_2O to O_2 and Cl^- to Cl_2 . Cerium is industrially important and is used in nuclear reactor, alloys with nickel and chromium, microwave devices, lasers and masers, and television sets^{5,6}. The oxalate salts of the metal have been used to remedy vomiting during pregnancy, while other salts of the metal have been used depressants of the central nervous system, astringents and antiseptics⁵. The increasing industrial use of cerium as well as reports on cerium toxicity makes it essential to have analytical procedures suitable for monitoring cerium in the environment and related fields. This necessitated the development of convenient and reliable analytical methods for the determination of cerium. Analytical techniques, such as ICP-AES⁷⁻⁹ or electrothermal vaporization ICP-AES after HPLC separations^{10,11}, spectrofluorometry^{12,13}, stripping voltammetry^{14,15} reported for the determination of cerium are of high cost and may not be available at most laboratories. Spectrophotometric determination of cerium¹⁶ is based on the catalytic effect of cerium and many kinetic spectrophotometry methods for the determination of cerium have been established¹⁷⁻²¹.

It is desirable to develop a more facile, sensitive, selective, rapid and economical method for the determination of cerium(IV) in various water samples by using antipyrine that gives catalytic currents with the metal at dropping mercury electrode (DME). The results are compared with differential pulse polarography.

EXPERIMENTAL

D.C. polarograph: The current-voltage curves are recorded using a D.C. polarographic analyzer, model CL-357 coupled with model LR-101 strip chart recorder manufactured by Elico Private Ltd (Hyderabad, India). Effects of mercury height on polarographic currents were studied using D.C. recording polarograph model CL-25 of Elico Pvt Ltd, Hyderabad.

Differential pulse polarograph: The current-voltage curves are recorded using polarographic analyzer, model CL - 362 coupled with optional printer manufactured by Elico Private Limited (Hyderabad, India). All pH measurements are made using pH meter, model LI - 120 (Elico Pvt. Limited, India) with combined electrode of pH range 0-13.

A 99 % pure antipyrine obtained from Aldrich Chemical Laboratory, USA is accurately weighed and dissolved in double distilled water and is used as the stock solution.

Stock solutions of the Ce(IV) are prepared from accurately weighed ammonium ceric sulphate AnalaR samples by dissolving in distilled water and diluted to required strength with double distilled water. The supporting electrolyte, ammonium chloride used in the present study is of AnalaR grade. Triton X-100 is weighed and is made upto 100 mL in a standard flask and is diluted as per requirement.

Procedure: A measured amount of the supporting electrolyte, ligand and maximum suppressor are added to the required aliquots of Ce(IV) solution under study and the solution is made upto 25 mL with triple distilled water. This is then transferred to the polarographic cell and deoxygenated by passing nitrogen and polarographed. A test run of the supporting electrolyte without the electroactive species is also taken in order to record residual current (Fig. 1).

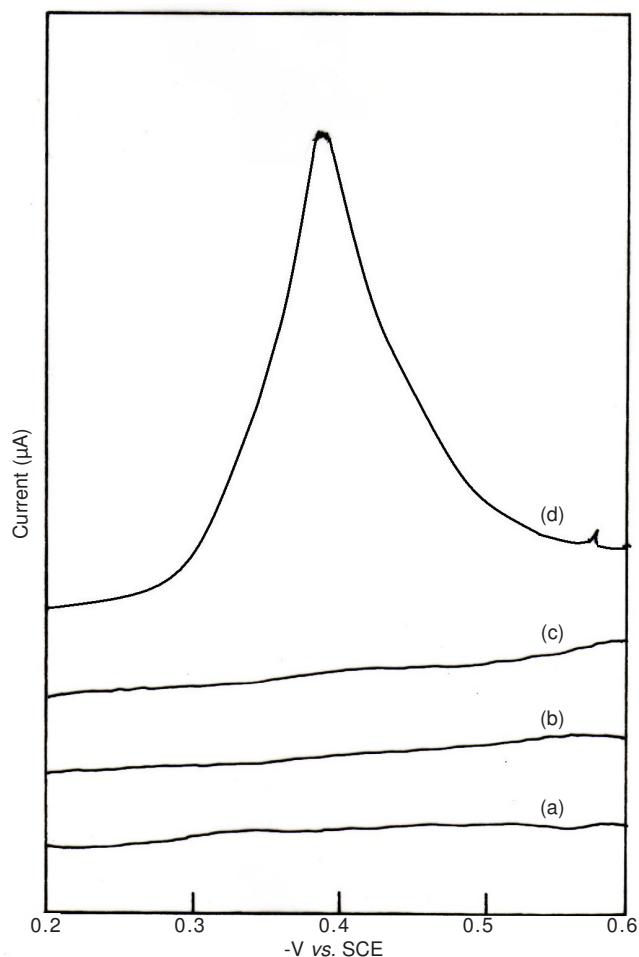


Fig. 1. Polarographic curves of cerium(IV) in NH_4Cl - NH_4OH medium in the presence of antipyrine

- (a) 0.15 M NH_4Cl , pH-5.8 (b) a + 0.5×10^{-6} M Antipyrine
(c) a + 3.0 ppm Ce(IV) (d) b + 3.0 ppm Ce(IV)

RESULTS AND DISCUSSION

Effect of pH: Effect of pH on solutions containing 3 ppm of cerium(IV) ion in 0.2 M ammonium chloride was studied, using 0.1×10^{-6} M of antipyrine as complexing agents, varying the pH from 5 to 9 adjusting with ammonium hydroxide. With increasing pH, the height of the catalytic wave increased and after attaining a maximum peak current at pH 5.8 for antipyrine. The wave height decreased with further increase in pH. The maximum wave height of the polarograms was selected as optimum pH which was maintained in all other studies. The results are graphically presented in Fig. 2.

Effect of supporting electrolyte concentration: Nature of the catalytic hydrogen peak is studied by changing the ammonium chloride concentration in the range of 0.05 to 0.5 M

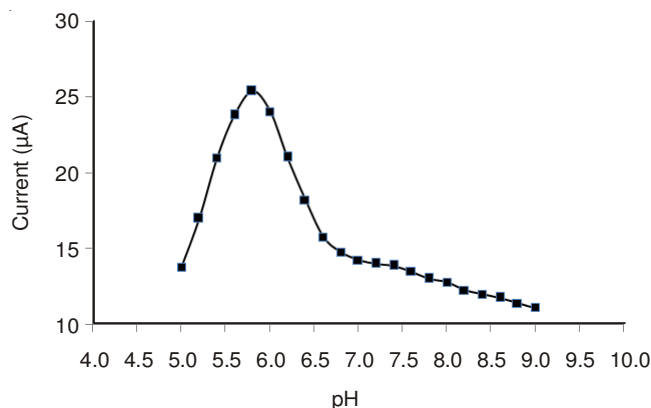


Fig. 2. Effect of pH for the determination of Ce(IV) in various water samples using antipyrine with catalytic current technique at DME

at DME, keeping the cerium(IV) concentration at 3 ppm and ligand concentration at 0.1×10^{-6} M of antipyrine and adjusting the pH to 5.8 for antipyrine.

The polarograms are well defined in 0.15 M NH_4Cl for ligand and the peak height increased upto 0.15 M. The peak height decreased beyond this concentration and therefore, 0.15 M concentration was maintained for further studies and results obtained are given in Fig. 3.

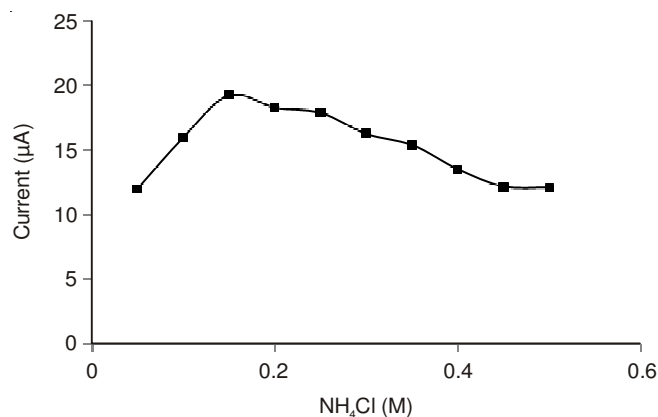


Fig. 3. Effect of supporting electrolyte for the determination of cerium(IV) in various water samples using antipyrine with catalytic current technique at DME

Effect of reagent concentration: Series of solutions containing 3 ppm of cerium(IV), 0.15 M ammonium chloride with 0.1×10^{-6} to 1.0×10^{-6} M ligand are polarographed, maintaining the pH of the solution at 5.8 for antipyrine. The peak current does not vary linearly with all concentrations of ligand which is a typical characteristic nature of catalytic waves and the results obtained are represented graphically in Fig 4. From the results it is seen that the peak height increased linearly with ligand concentration only up to 0.5×10^{-6} M for antipyrine. With further increase in ligand concentration the wave height is independent of concentration and shows that the complex was stable. Therefore, the concentration of the ligands where the maximum wave height obtained is fixed for quantitative studies. The peak potential of the catalytic wave shifted towards more negative potentials on increasing the ligand concentration, up to the maximum concentration reported above and remained constant beyond these concentrations. Plot of $\{[\text{Ligand}] / i_p\}$

vs [ligand] was a straight line (Fig. 5.) and confirms that adsorption phenomenon was involved in the electrode reaction process.

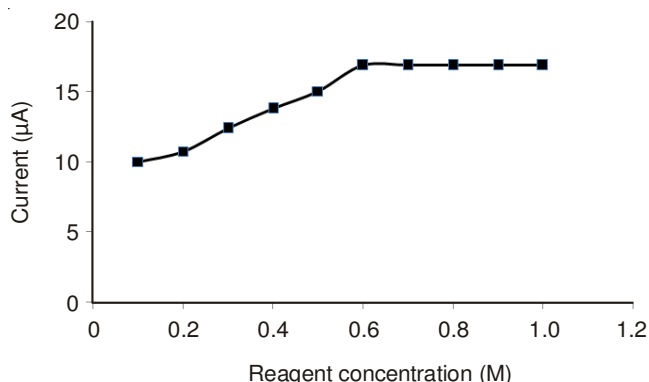


Fig. 4. Effect of reagent concentration for the determination of cerium(IV) in various water samples using antipyrine with catalytic current technique at DME

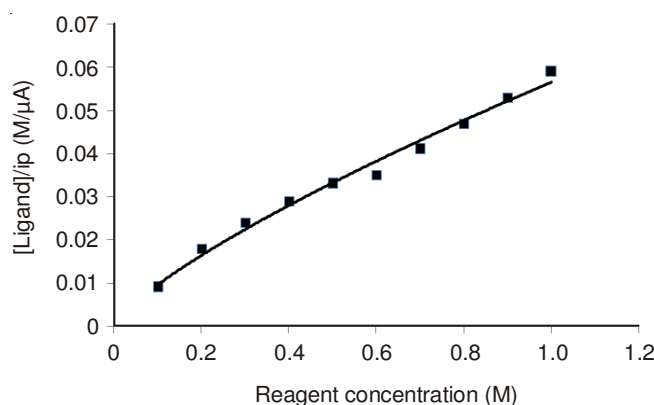


Fig. 5. Longmuir adsorption isotherm plot for the determination of cerium(IV) in various water samples using antipyrine with catalytic current technique at DME

Effect of mercury pressure: The effect of the height of the mercury column on the polarograms of cerium(IV) (3 ppm) in quantitative experimental conditions was investigated and found that the catalytic current as well $i_c \sqrt{h}$ as decreased with the height of the mercury column indicating that the current is catalytic in nature and the experimental observations are recorded in Table-1.

TABLE-1 EFFECT OF MERCURY PRESSURE FOR THE DETERMINATION OF CERIUM(IV) IN VARIOUS WATER SAMPLES USING ANTIPYRINE WITH CATALYTIC CURRENT TECHNIQUE AT DME			
S. No.	Height of the mercury column (cm)	Current (μA)	$i_c \cdot \sqrt{h}$
1	30	13.73	2.51
2	35	13.25	2.24
3	40	12.75	2.02
4	45	12.25	1.83
Conditions: pH 5.8; NH_4Cl 0.15 M; Antipyrine 0.5×10^{-6} M; Ce(IV) 3.0 ppm			

Effect of maximum suppressor: The effect of surface-active substance, Triton X-100 in 0.002 to 0.004 % on the catalytic wave height was studied maintaining the fixed

analytical concentration for ligand (Table-2). It is found that this surface-active agent does not change the nature of the catalytic wave.

TABLE-2 EFFECT OF MAXIMUM SUPPRESSORS FOR THE DETERMINATION OF CERIUM(IV) IN VARIOUS WATER SYSTEMS USING ANTIPYRINE WITH CATALYTIC CURRENT TECHNIQUE AT DME		
S. No	Maximum suppressors	Current (μA)
Triton X-100		
1	0.000	13.76
2	0.002	13.25
3	0.004	12.75
Conditions: pH 5.8; NH_4Cl 0.15 M; Antipyrine 0.5×10^{-6} M; Ce(IV) 3.0 ppm		

Effect of temperature: The current-voltage curves of the systems with ligand are recorded at various temperatures, *i.e.*, 15 to 45 °C. It is found that with increase in temperature the wave height and temperature coefficient values decreased gradually. The current, i_c became completely temperature independent above 30 °C.

Effect of cerium(IV) concentration on peak current: At fixed concentrations of ligand, [0.5×10^{-6} M antipyrine] and 0.15 M ammonium chloride adjusting the pH to 5.6 and 6.2, respectively the metal ion concentration varied between 0.1 to 4.0 ppm and its effect on the current-voltage curves was studied. The peak current increased linearly with cerium(IV) concentration in the range 0.1 to 4.0 ppm with ligand. The calibration plot is shown in Fig. 6. The method suggests that the determination of micro-amounts of cerium(IV) is possible in unknown samples. It was observed that there was no change in the shape of the wave throughout the cerium(IV) concentration range studied.

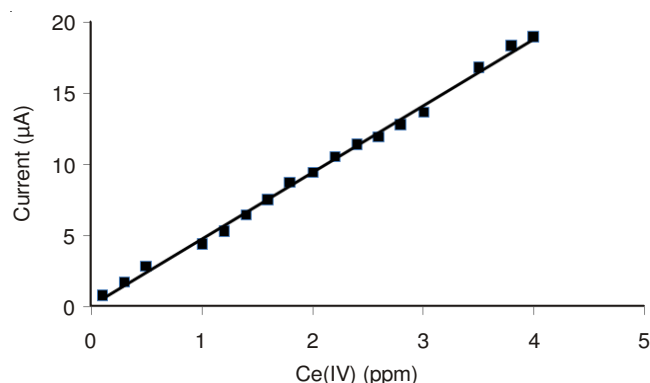


Fig. 6. Effect of cerium(IV) on peak current for the determination of cerium(IV) in various water samples using antipyrine with catalytic current technique at DME

Effect of foreign ions: The effect of transition metal ions like Ni(II), Cu(II), Mn(II), Fe(II) and Cr(VI) which are commonly associated with Ce(IV), on the nature and height of the catalytic wave of cerium is studied using 3 ppm cerium(IV) in the quantitative experimental conditions developed. These metal ions do not interfere with Ce(IV) due to its specific conditions. Nickel(II) gets precipitated below pH 9 and Fe(II) at pH 8 and above which can be filtered off. Chromium(VI) does not interfere even when present up to 100-fold excess as its

peak potential was negative to that of cerium(IV). The other metal ions such as Cd(II), Hg(II), V(V), Mg(II), Pb(II), Al(III), Ag(I), U(VI), Se(IV), Te(IV), Sn(IV), do not interfere with Ce(IV) even at 100 fold excess and Zn(II) up to 20 ppm. The only metal ion, Mo(VI) interferes seriously by increasing the wave height and shifting the peak potential of the cerium(IV) catalytic wave. Anions such as fluoride, bromide, iodide, ttrate, sulphate, thiosulphate, perchlorate, carbonate, thiocyanate and phosphate do not interfere with cerium(IV) catalytic wave. Oxalate, citrate and EDTA interfere by completely suppressing the cerium catalytic wave, whereas nitrite and nitrate interfere by increasing the catalytic wave height.

Effect of indifferent cations: The effect of neutral salt and replacement of monovalent cation with divalent cation leads to changes both in the height and the potential location of the catalytic wave. The concentration of NH_4Cl in the solution was kept constant and several amounts of different chlorides were added to the polarographed solutions of 3 ppm Ce(IV) in fixed concentrations of ligand at corresponding pH values. Three alkali chlorides *i.e.*, potassium, sodium and lithium and bivalent cation, calcium were used. With increase in concentration of chlorides the wave height decreased continuously and the decrease of wave height in sodium chloride is slightly less to that of potassium chloride. The decrease is more for lithium chloride and much more for calcium chloride as shown in Fig. 7.

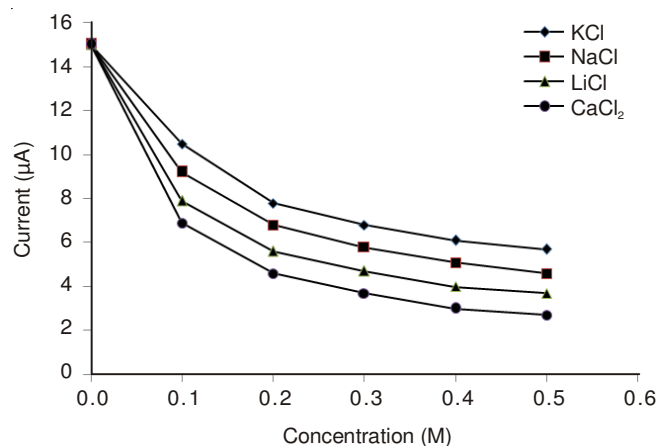


Fig 7. Effect of different ions on antipyrine-cerium(IV) complex at DME for the determination of cerium(IV) in various drinking water samples using catalytic current technique

The catalytic polarographic method was extended for the analysis of trace amount of cerium(IV) in water samples.

Determination of cerium(IV) in water samples: One liter of the water samples collected from Kalyani dam and bore well, Kapillatheertham waterfalls (Tirupati town, Chittoor Dt.) are preconcentrated and analyzed. The results are given in Table-3.

Condition: pH 5.8, NH_4Cl 0.15 M, Antipyrine 0.5×10^{-6} M, I- Kalyani dam, II- bore well, III- Kapillatheertham waterfalls.

The water samples contain slightly high concentration levels of cerium(IV). The results of cerium(IV) compare with differential pulse polarography. The typical differential pulse polarographic curves are shown in Fig. 8.

TABLE-3
DETERMINATION OF CERIUM(IV) IN VARIOUS WATER SAMPLES

Sample*	S. No	Ce(IV) added, ppm	Ce(IV) found, ppm	Recovery %
I	1	0.5	0.49	98.00
	2	1.0	1.00	100.00
	3	1.5	1.49	99.33
	4	2.0	1.97	98.50
	5	2.5	2.50	100.00
Average				99.16
II	1	0.5	0.50	100.00
	2	1.0	1.00	100.00
	3	1.5	1.48	98.66
	4	2.0	1.99	99.50
	5	2.5	2.50	100.00
Average				99.63
III	1	0.5	0.49	98.00
	2	1.0	0.99	99.00
	3	1.5	1.50	100.00
	4	2.0	2.00	100.00
	5	2.5	2.49	99.60
Average				99.32

*5 mL of the concentrated sample is used

I- Kalyani Dam, II- Bore well, III- Kapillatheertham waterfalls

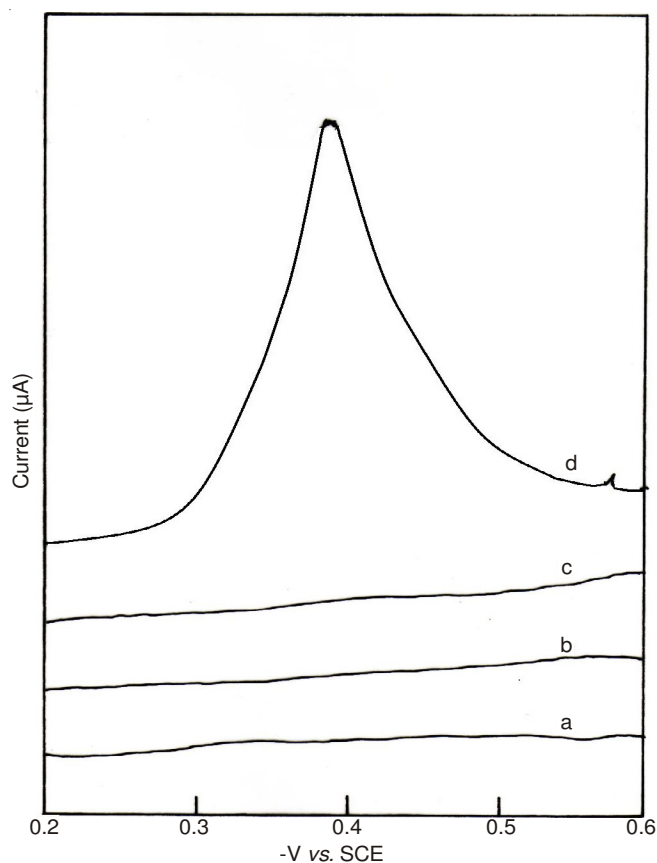


Fig. 8. Polarographic curves of cerium(IV) in NH_4Cl - NH_4OH medium in the presence of antipyrine
(a) 0.15 M NH_4Cl , pH-5.8 (b) a + 0.5×10^{-6} M antipyrine
(c) a + 3.0 ppm Ce(IV) (d) b + 3.0 ppm Ce(IV)

Conclusion

The analysis of Ce(IV) with antipyrine and NH_4OH - NH_4Cl buffer gives catalytic hydrogen wave and its pH effect and NH_4Cl concentration clear indicates the characteristic

property of catalytic surface reaction. The non linear portion has the shape of a curve resembling a Langmuir adsorption isotherm and therefore the plot of $\{[\text{Ligand}] / i_p\}$ vs. $[\text{Ligand}]$ is a straight line. This dependence is due to the adsorption of the catalytically active compound at the electrode surface. All the observations clearly indicate that the catalytic current is of Bridicka type. When current is less than 20 % of its limiting value, it is entirely kinetic in nature (pH effects) and at maximum or limiting current or saturation value it is diffusion controlled [RSH and Co(II) effects]. Between 20 and 100 % Bridicka currents exhibit mixed kinetic diffusion character. In total it is adsorption-kinetic-diffusion controlled combination that plays in determining the nature of the catalytic hydrogen waves.

The present method has the following advantages:

(1) It is facile, sensitive and reproducible for determination of Ce(IV) in various water system.

(2) The ligand is fairly soluble in water. This indicate the eco-friendly nature of the ligand.

(3) The developed method is successfully applied for the determination of Ce(IV) in various water systems and results obtained were in good agreement with differential pulse polarography method.

ACKNOWLEDGEMENTS

The authors are highly thankful to The Head, Department of Chemistry Sri Venkateswara University, Tirupati, India for providing the necessary facilities.

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