

# Sensitive Polarographic Determination of Cerium(IV) in Environmental Samples by using Catalytic Hydrogen Currents at DME

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**Abstract:** A simple, sensitive and specific polarographic method is proposed, based on the catalytic hydrogen wave of Ce(IV)-Piperidine complex in the presence of NH<sub>4</sub>Cl-NH<sub>4</sub>OH at dropping mercury electrode. The Ce(IV)-Piperidine complex produce a catalytic hydrogen wave at -0.41 V Vs SCE in NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium (pH~5.6) and the results are compared with DPP method. The peak height is proportional to metal ion concentration. New method has been successfully applied for the determination of cerium in water, soil and human hair samples.

**Keywords:** Catalytic hydrogen wave, dropping mercury electrode, Polarographic method, Cerium(IV), piper dine.

## I. INTRODUCTION

Rare earth elements (REE) are widely used in industry, agriculture, forestry and animal husbandry and much attention is now being paid to the study of REE in environment [1]. Cerium is a silvery metallic element, resembles iron in colour and luster, but it is soft and both malleable and ductile. It is a second highly reactive element among rare earth elements. It is the most abundant of the rare earth elements, making up about 0.0046% of the earth's crust by weight.

Cerium is industrially important and is used in nuclear reactor, in alloy with nickel and chromium and in microwave devices, lasers, masers and in television sets, besides agriculture, forestry, animal husbandry and in environment. Optimum concentration of some light rare earth elements including Ce are useful in agronomy as well as for environmental pollution assessment studies of biochemical processes [2,3]. Ce salts have been used to remedy from vomiting during pregnancy, depressant of central nervous system, astringents and antiseptics [4]. Increasing industrial use and reports on Ce toxicity make it essential to have analytical procedures suitable for monitoring Ce in environmental and related fields [5].

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-AES [6-8] or electro thermal vaporization ICP-AES after HPLC separations [9,10], spectrofluorometric [11,12], stripping voltammetry [13,14] reported for the determination of cerium are of high cost and may not be available at most laboratories. Spectrophotometric determination of cerium [15] is based

on the catalytic effect of cerium and many kinetic spectrophotometry methods for the determination of cerium have been established [16-20].

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 piper dine that gives catalytic currents with the metal at dropping mercury electrode (DME). The results are compared with differential pulse polarography.

## II. MATERIALS AND METHODS

### 2.1. Instrumentation

#### 2.1.1. DC Polarography

The current-voltage curves are recorded using a DC polarographic analyzer, model CL-358 coupled with model LR-101 strip chart recorder manufactured by Elico Private Limited (Hyderabad, India). Effects of mercury height on polarographic currents are studied using DC recording polarograph model CL-25 of Elico Pvt. Ltd., Hyderabad.

#### 2.1.2. Differential Pulse Polarography

The current-voltage curves are recorded using polarographic analyzer, model CL-362 coupled with optional printer manufactured by Elico Private Limited (Hyderabad, India). The pH measurements are made by using pH meter; model LI-120 (Elico Pvt. Ltd.) with glass electrode of pH range 0-13. The temperature is maintained at 25±0.2 °C and the flow of mercury at 2.5 sec per drop.

### 2.2. Reagents

All chemicals used are of analytical reagent grade unless specified otherwise. The solutions are prepared in double distilled water and diluted to required strength. 5% NH<sub>4</sub>OH and 1% HCl is used for pH adjustments. Gelatin and Triton X-100 are prepared and diluted as per

requirement. Piperidine (S.D. fine-chemicals Ltd.) solutions is used.

Water samples are pre concentrated by evaporation and standard addition method is used for analysis.

**2.3. Applications**

**2.3.1. Water Samples**

One liter of the drinking water samples collected from different areas of Tirupati town is re concentrated by evaporation.

**2.3.2. Soil Samples**

About 2 g of soil collected from agricultural farms, tirupati is dried, digested by wet digestion method<sup>1</sup> and brought in to solution.

**2.3.3. Human Hair Samples**

Hair samples (0.5 g) is heated under reflux with 10 ml of nitric acid and 1ml of per chloric acid at 75<sup>o</sup>C for 2 hours then at 200<sup>o</sup>C for 10 minutes and cooled to room temperature. After addition of 10 ml of hydrochloric acid, the solution is heated at 100<sup>o</sup>C for 5 minutes and diluted to 25 ml with water. Aliquots of this solution is taken for analysis.

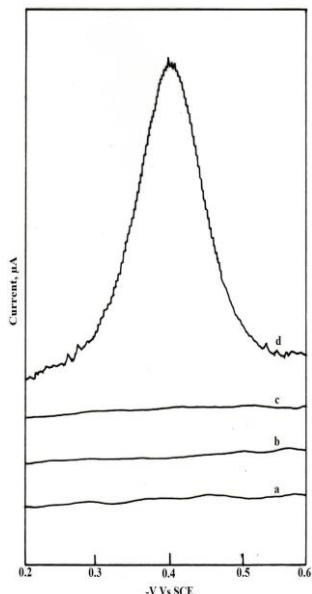


Fig.1 : Polarographic curves of Cerium(IV) in NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium in the presence of Piperidine.

- (a) 0.15 M NH<sub>4</sub>Cl, pH ~5.6
- (b) a + 0.5x10<sup>-6</sup>M Piperidine
- (c) a + 3.0 ppm Ce(IV)
- (d) b + 3.0 ppm Ce(IV)

Table-1: Quantitative Experimental Conditions for Cerium(IV) Determination through Cerium(IV)-Piperidine Catalytic Hydrogen Wave

Conditions	Piperidine
pH	5.6
NH <sub>4</sub> Cl, M	0.15
Piperidine, mM	0.5x10 <sup>-6</sup>
Cerium(IV), ppm	0.1- 5.0

**III. RESULTS AND DISCUSSION**

**3.1. Effect of pH**

Effect of pH on solutions containing 3.0 ppm of Ce(IV) ion in 0.2 M ammonium chloride was studied, using 0.1x10<sup>-6</sup>M of piperidine as complexing agent, varying the pH from 5.0 to 7.0 adjusting with NH<sub>4</sub>OH/HCl. With increasing pH the height of the catalytic wave increased and after attaining a maximum peak current at pH 5.6 for Piperidine. The wave height decreased with further increase in pH. The maximum peak height of the polarograms was selected for optimum pH which was maintained in further studies. The results are graphically presented in Fig.2.

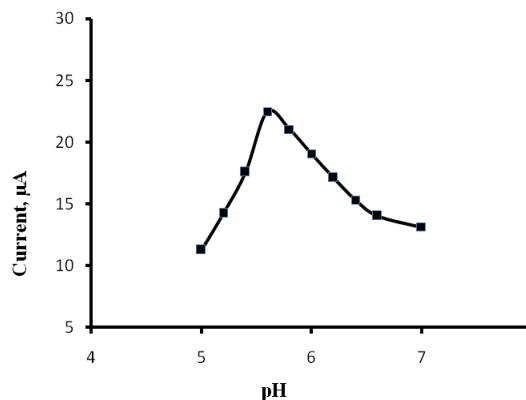


Fig.2: Effect of pH for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME

**3.2. Effect of supporting electrolyte concentration**

Nature of the catalytic hydrogen peak was studied by changing the ammonium chloride concentration in the rang of 0.05 to 0.5 M at DME, keeping the cerium ion concentration at 3.0 ppm and ligand concentration at 0.1x10<sup>-6</sup>M of piperidine and adjusting the pH to 5.6 for piperidine.

The polarograms are well defined in 0.15 M NH<sub>4</sub>Cl 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.

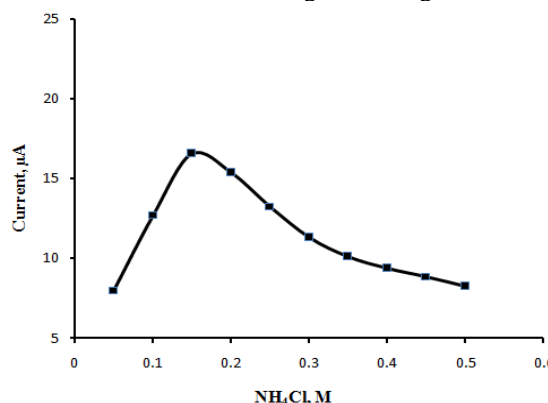


Fig.3: Effect of supporting electrolyte for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME

### 3.3. Effect of reagent concentration

Series of solutions containing 3.0 ppm of cerium ion, 0.15 M ammonium chloride with  $0.1 \times 10^{-6}$  to  $1.0 \times 10^{-6}$  M ligands are polarographed, maintaining the pH of the solution at 5.6 in case of piperidine. The peak current does not vary linearly with all concentrations of ligand which was a typical characteristic nature of catalytic waves and results obtained are represented graphically in Fig. 4.

From the results it was seen that the peak height increased linearly with Ligand concentration only upto  $0.5 \times 10^{-6}$  M for piperidine. 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 ligand where the wave height was maximum is fixed for quantitative studies. The peak potential of the catalytic wave shifted towards more negative potentials on increasing the ligand concentration, upto the maximum concentration reported above and remained constant beyond these concentrations. Plot of  $\{[Ligand]/i_p\}$  vs  $[Ligand]$  is a straight line (Fig. 5) and confirms that adsorption phenomenon was involved in the electrode reaction process.

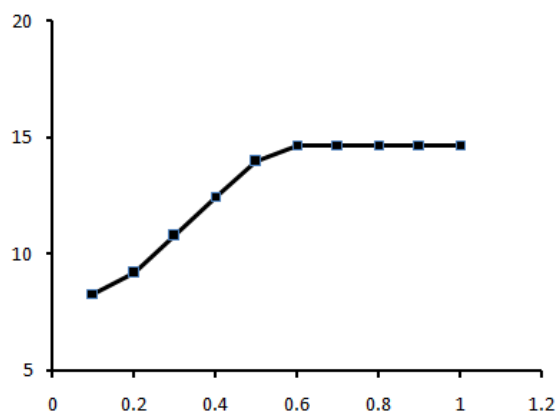


Fig.4: Effect of reagent concentration for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME.

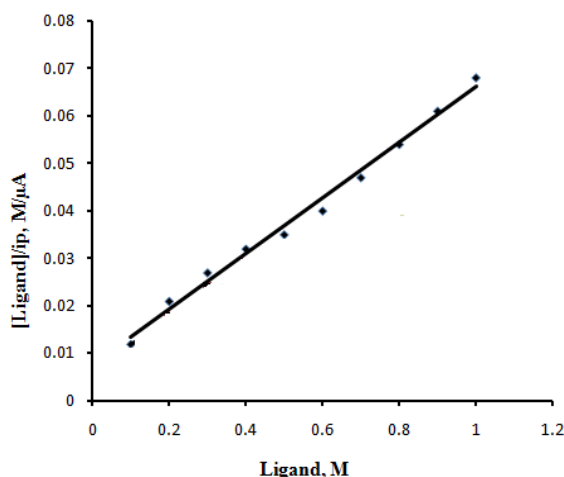


Fig.5: Longmuir adsorption isotherm plot for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME

### 3.4. Effect of Mercury Pressure

The effect of the height of the mercury column on the polarograms of cerium (3.0 ppm) in quantitative experimental conditions was investigated and found that the catalytic current as well as  $i_c / \sqrt{h}$  decreased with the height of the mercury column indicating that the current is catalytic in nature. The experimental observations are recorded in Table 2.

Table-2 : Effect of Mercury Pressure

S.No.	Height of the mercury column, cm	Current $\mu A$	$i_c / \sqrt{h}$
1	30	12.40	2.26
2	35	11.90	2.01
3	40	11.40	1.80
4	45	10.90	1.63

### 3.5. Effect of Maximum Suppressor

The effect of surface active substances, gelatin in the range 0.005 to 0.01% and TX-100 in 0.002 to 0.004 % on the catalytic wave height was studied maintaining the fixed analytical concentrations for piperidine (Table-3). The catalytic wave decreases sharply upto 0.005% gelatin concentration and further increase in concentration of the surface active material suppresses the wave further by only about 2%. The peak potential shifted towards positive potentials and the catalytic peak became round shaped. The suppression of the catalytic wave is found with 0.002 to 0.005 % TX-100 but is small compared to gelatin. The peak potential shifted towards positive potentials in this case also.

Table-3: Effect of Maximum Suppressors

S. No.	Maximum Suppressors	Current, $\mu A$
a) Gelatin		
1	0.000	32.30
2	0.005	21.55
3	0.010	20.80
b) Triton X-100		
1	0.000	32.30
2	0.002	25.25
3	0.004	24.00

### 3.6. 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 beyond 30°C.

### 3.7. Effect of Cerium(IV) concentration on Peak Current

At fixed concentrations of ligand,  $0.5 \times 10^{-6}$  M piperidine and 0.15 M ammonium chloride adjusting the pH to 5.0 to 7.0 respectively the metal ion concentration varied between 0.1 to 5.0 ppm and its effect on the current-voltage curves was studied. The peak current increased linearly with Ce(IV) concentration in the range 0.1 to 5.0

ppm with ligand. The calibration plot is shown in Fig. 6. The method suggests that the determination of micro amounts of Ce(IV) is possible in unknown samples. It was observed that there was no change in the shape of the wave throughout the Ce(IV) concentration range studied.

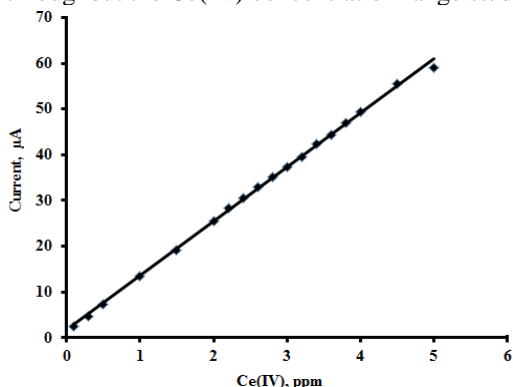


Fig.6: Effect of Ce(IV) on peak current for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME

### 3.8. Effect of Foreign Ions

The effect of various metal ions like Cu(II), Ni(II), Mn(II), Fe(II), Co(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 3.0 ppm cerium(IV) in the quantitative experimental conditions developed. These metal ions do not interfere with Ce(IV) due to its specific conditions. Ni(II) gets precipitated below pH 8 and Fe(II) at pH 9 and above which can be filtered off. Cr(VI) does not interfere even when present up to 100-fold excess as its peak potential was negative to that of Ce(IV). The other metal ions such as Cd(II), Hg(II), Mg(II), Pb(II), Al(III), Ag(I), U(VI), Se(IV), Te(IV), Ce(IV), Sn(IV) and Mo(VI) do not interfere with Ce(IV) even at 100-fold excess and Zn(II) up to 20 ppm. The only metal ion, Mo(VI) interfere seriously by increasing the wave height and shifting the peak potential of the Ce(IV) catalytic wave.

Anions such as fluoride, bromide, iodide, tatrte, thiosulphate, carbonate, sulphate, perchlorate, thiocyanate and phosphate do not interfere with Ce(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.

### 3.9. 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<sub>4</sub>Cl in the solution is kept constant and several amounts of different chlorides are added to the polarographed solutions of 3.0 ppm Ce(IV) in fixed concentrations of ligand at corresponding pH values.

Three alkali chlorides potassium, sodium and lithium and bivalent cation, calcium are 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.

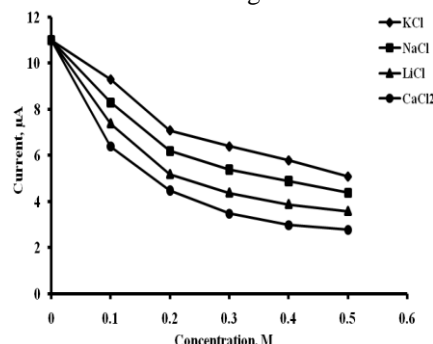


Fig.7: Effect of different ions on Ce(IV)-piperidine complex at DME for the determination of Ce(IV) in various water samples using piperidine with catalytic current technique at DME

### 3.10. Determination of Cerium(IV) in various water samples

One liter of the water samples collected from borewells, kalyani dam, Kapilatheertham water falls, Amara raja batteries, tirupati Chittoor district and industrial waste water samples are pre concentrated and analyzed. The results are given in Table-4. This method was applied for the analysis of cerium in soil samples is dried and digested by wet digestion and the results are shown in Table-5. This procedure was applied for the Hair samples (0.5 g) is heated under reflux with 10 ml of nitric acid and 1ml of perchloric acid at 75°C for 2 hours then at 200°C for 10 minutes and cooled to room temperature. After addition of 10 ml of hydrochloric acid, the solution is heated at 100°C for 5 minutes and diluted to 25 ml with water. The results are shown in Table-6. 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 Figure.8.

Table-4: Determination of Cerium(IV) with piperidine in water samples collected around Tirupati Town, Chittoor District, Andhra Pradesh, India using catalytic hydrogen current (CHC) technique

I Kalyani Dam ; II Bore well ;  
III Kapilatheertham water falls ; IV Amara raja Batteries  
NH<sub>4</sub>Cl, M : 0.15  
Piperidine, M : 0.5x10<sup>-6</sup>  
pH : 5.6

Sample	Ce(IV) added ppm	CHC method (D.C. Polarography)		DPP method	
		Ce(IV) found ppm	% Recovery=R.S.D <sup>a</sup>	Ce(IV) found ppm	% Recovery=R.S.D <sup>a</sup>
I	0.2	0.198	99.00±2.31	0.194	97.00±2.46
	0.4	0.386	97.25±2.43	0.385	96.25±2.58
	0.6	0.593	98.83±2.57	0.589	98.16±2.61
	0.8	0.798	99.75±2.83	0.793	99.12±2.73
	1.0	0.999	99.90±2.98	0.997	99.70±2.93
	0.2	0.194	93.50±2.28	0.188	94.50±2.35
II	0.4	0.377	94.25±2.33	0.373	93.25±2.42
	0.6	0.579	96.50±2.45	0.581	96.83±2.49
	0.8	0.788	98.50±2.52	0.791	99.12±2.59
	1.0	0.993	99.30±2.75	0.995	99.80±2.83
	0.2	0.195	97.50±2.35	0.192	96.00±2.41
	III	0.4	0.389	97.25±2.47	0.385
0.6		0.583	97.16±2.68	0.577	96.16±2.79
0.8		0.787	98.37±2.82	0.782	97.75±2.86
1.0		0.991	99.10±2.91	0.995	99.50±2.97
0.2		0.197	98.50±2.42	0.194	97.00±2.48
IV		0.4	0.390	97.50±2.53	0.386
	0.6	0.587	97.83±2.67	0.583	97.16±2.73
	0.8	0.792	99.00±2.84	0.789	98.62±2.89
	1.0	0.995	99.50±2.93	0.998	99.80±2.96

<sup>a</sup> 5 ml of the concentrated sample is used.

<sup>b</sup> Relative standard deviation (n=6)



Table-5: Determination of Cerium(IV) with piperidine in soil samples collected in agricultural farms around Tirupati Town, Chittoor District, Andhra Pradesh, India using catalytic hydrogen current (CHC) technique

NH<sub>4</sub>Cl, M : 0.15  
 Piperidine, M : 0.5x10<sup>-6</sup>  
 pH : 5.6

Ce(IV) added ppm	CHC method (D.C. Polarography)		DPP method	
	Ce(IV) found ppm	% Recovery± R.S.D <sup>b</sup>	Ce(IV) found, ppm	% Recovery± R.S.D <sup>b</sup>
2.0	1.970	98.50±2.68	1.967	98.35±2.56
2.2	2.171	98.68±2.47	2.168	98.54±2.59
2.6	2.568	98.76±2.69	2.560	98.46±2.78
2.8	2.788	99.57±2.83	2.783	99.39±2.89
3.0	2.998	99.93±2.93	2.995	99.83±2.98

<sup>a</sup> Relative standard deviation (n=6)

Table-6: Determination of Cerium(IV) with piperidine in human hair samples using catalytic hydrogen current (CHC) technique

NH<sub>4</sub>Cl, M : 0.15  
 Piperidine, M : 0.5x10<sup>-6</sup>  
 pH : 5.6

Ce(IV) added ppm	CHC method (D.C. Polarography)		DPP method	
	Ce(IV) found ppm	% Recovery± R.S.D <sup>b</sup>	Ce(IV) found, ppm	% Recovery± R.S.D <sup>b</sup>
5.0	4.893	97.86±2.21	4.846	96.92±2.32
10.0	9.689	93.78±2.45	9.728	94.56±2.54
15.0	14.84	96.90±2.68	14.89	97.96±2.79
20.0	19.948	98.96±2.81	19.967	99.34±2.87

<sup>a</sup> 5 ml of the concentrated sample is used.

<sup>b</sup> Relative standard deviation (n=6)

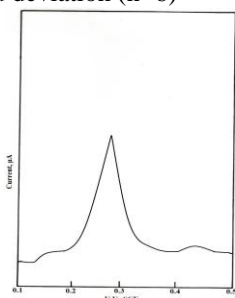


Fig.8.: Differential Pulse Polarographic curve of Ce(IV) in NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium in the presence of piperidine (Current Range : 100 μA, Scanrate : 6 mV/S, Pulse Amplitude : 50 mV, Droptime : 1 Sec, Cerium(IV) : 0.001 ppm)

#### IV. CONCLUSIONS

The analysis of Ce(IV) with piperidine NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium gives catalytic hydrogen wave and its pH effect and NH<sub>4</sub>Cl concentration clear indicates the characteristic property of catalytic surface reaction. The nonlinear portion has the shape of a curve resembling a langmuir adsorption isotherm and therefore the plot of {[Ligand]/i<sub>p</sub>} vs [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 advantage. It is facile, sensity and reproducible for determination of Ce(IV) in various water, soil and human hair samples. The ligand is fairly soluble in water, this indicate the eco-friendly nature of the ligand. The developed method is successfully applied for the determination of Ce(IV) in various water, soil and human hair samples and the results are compared with DPP method.

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