Original Paper

Adsorptive Voltammetric Studies on the Cerium(III)–Alizarin Complexon Complex at a Carbon Paste Electrode

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Abstract. A novel procedure was developed for the determination of trace cerium on the basis of anodic adsorption voltammetry of the Ce(III)–alizarin complexon (ALC) complex at a carbon paste electrode (CPE). The procedure is convenient to determine cerium individually in the presence of other rare earths because there is a 100 mV difference between the peak potentials of Ce(III)–ALC and other rare earth(III)–ALC complexes in a supporting electrolyte of 0.08 M HAc–NaAc and 0.012 M potassium biphthalate (pH 4.7) when performing linear-scanning from -0.2 to 0.8 V (*vs.* SCE) at 100 mV/s. The second-order derivative peak currents are directly proportional to the Ce(III) concentration over a range of 6.0×10^{-9}–3.0×10^{-7} M. The detection limit is as low as 2.0×10^{-9} M ($S/N = 3$) for a 120 s preconcentration. An RSD of 3.5% was obtained for 15 determinations of Ce(III) at a concentration of 4.0×10^{-8} M on the same CPE surface. The method was applied successfully to the determination of cerium in samples of rare earth nodular graphite cast iron.

Key words: Cerium; alizarin complexon; carbon paste electrode; anodic adsorptive voltammetry.

Like most rare earth metal ions, cerium yields only an ill-defined reduction wave at an extremely negative potential at a mercury electrode in aqueous solution. Fortunately, oxidation of Ce(III) to Ce(VI) at an electrode is possible, and by formation and deposition of insoluble Ce(VI) compounds at the surface, stripping voltammetric determination of cerium becomes feasible. For the cathodic stripping voltammetric determination of cerium at a graphite electrode a detection limit of 6.0×10^{-8} M was reported [2]. The determination of cerium by potentiometric stripping [3] was also reported. Apart from that, many indirect polarographic procedures for the determination of light rare earths or total rare earths (including cerium) were described [4–9], but the sensitivity of the above methods was not quite satisfactory. Adsorption stripping voltammetry became a sensitive and effective means for trace measurement of many analytes. Joseph Wang [10] presented the procedure for the determination of lanthanum, cerium and praseodymium by adsorptive stripping voltammetry onto a static mercury drop electrode. The procedure yielded a detection limit of 1×10^{-10} M for 20 min accumulation. Yet these methods had little specific selectivity for cerium, and the toxicity of mercury restricts their practical application. Recently a sensitive differential pulse anodic stripping voltammetry for the determination of Ce(III) on a glassy carbon electrode modified with poly(catechol) was developed [11]. In recent years, CPE attracted increasing interest in voltammetry due to

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its non-toxicity, easy preparation, wide operational potential window, renewable surface and stability in various solvents [12]. It was exploited for the determination of zirconium [13, 14], scandium [15, 16] and middle and heavy rare earths [17], but the determination of cerium alone by adsorption voltammetry at a CPE was not reported.

An adsorptive voltammetric method for measuring only cerium is described for the first time based on the adsorption accumulation of the Ce(III)–ALC complex at a CPE. The peak potential of the Ce(III)–ALC complex is about 100 mV more positive than that of other rare earth–ALC complexes under the same experimental conditions. It is possible to determine cerium independently in the presence of other rare earths. Because the contents of cerium are generally much higher than those of other rare earths in mineral, metallurgical samples, this approach serves to conveniently determine cerium in samples without separating other rare earths.

Experimental

Apparatus and Reagents

All electrochemical experiments were performed on a JP-303 polarographic analyzer (Chendu Instrument Factory, China) with a three-electrode system consisting of a CPE working electrode, a calomel (saturated KCl) reference electrode, and a platinum wire auxiliary electrode. A pHS-3C model pH meter was used to measure pH values.

Stock standard solutions of 1.00×10^{-2} M Ce(III) and Ce(IV) were prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (Beijing Chemical Factory, China) in dilute HNO_3 and by dissolving $Ce(SO_4)_2 \cdot 4H_2O$. An appropriate amount of ALC (Merck) was dissolved in 0.1 M NaOH and adjusted to a reddish color with several drops of 0.1 M HCl before diluting to give a 1.0×10^{-3} M stock solution. A mixed buffer containing 1.0 M acetate (HAc–NaAc) and 0.15 M potassium biphthalate (KHP) was adjusted to pH 4.7 with sodium hydroxide solution. Spectrally pure carbon powder and chromatographically pure ethyl-benzene-silicon oil were used to prepare the CPE. All solutions were prepared from quartz doubly distilled water, and all reagents were of suprapure or analytical grade.

Fabrication and Activation of the CPE

The CPE was prepared as described previously [16]. The smoothed CPE surface was subjected to cyclic scans between 0–1.0 V and 0 to −1.0 V several times in the mixed buffer containing 0.08 M acetate and 0.012 M KHP (pH 4.7) until a reproducible behavior was observed. It was then subjected to preanodization at 1.25 V for 60 s and precathodization at −1.0 V for 60 s. After each run the electrode was placed in 0.2 M HCl and maintained at a cleaning potential of 1.25 V for 60 s to clear the electrode surface of any remaining accumulated analytes and to reactivate the electrode surface.

Procedure

The solution containing aliquots of standard Ce(III), 3.2×10^{-6} M ALC, 0.08 M HAc–NaAc and 0.012 M KHP was pipeted into a 10 mL voltammetric cell. The preconcentration potential of −0.2 V was applied while the solution was stirred. After a 60 s preconcentration period and a subsequent rest period of 10 s, a second-order derivative voltammogram was recorded by applying a positive-going potential scan from −0.2 V to 0.8 V at 100 mV/s. The peak current of the complex was registered at 0.69 V. Oxygen removal from sample solutions is not required since compensation for the reduction current is inherent in second-order derivative voltammetry. All data were obtained at ambient temperature.

Results and Discussion

Voltammetric Behavior of ALC

The (3,4-dihydroxy-2-anthraquinonyl-methyl) imino-diacetic acid is usually called alizarin complexon, which is a complexing agent for metal ions with the main form being H_3L^- at pH 4.7. Apart from the reducible quinone group, the ortho-dihydroxyl groups are attached to the anthraquinonyl. By analogy with the electrochemical character of other catechol derivatives [18, 19], the ALC can undergo a two-electron electrochemical oxidation process to form HL' (see the below reaction scheme).

The cyclic voltammogram of ALC is shown in Fig. 1a. An oxidation peak P_1 occurs at 0.57 V with linear scanning from −0.2 to 0.8 V. There is a small reduction peak at 0.53 V corresponding to P_1 following reverse scanning. The difference between the redox peak potentials is about 40 mV. This implies that the redox processes of the ALC on the CPE are nearly reversible. The second-order derivative peak
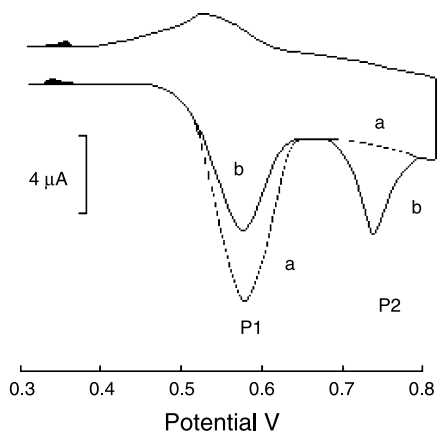
Fig. 1. Cyclic voltammograms. (*a*) 3.2×10^{-6} M ALC, 0.08 M acetate and 0.012 M potassium biphthalate buffer (pH 4.7). (*b*) $a + 2.0 \times 10^{-7}$ M Ce^{3+}. Accumulation time: 60 s, scan rate: 100 mV/s
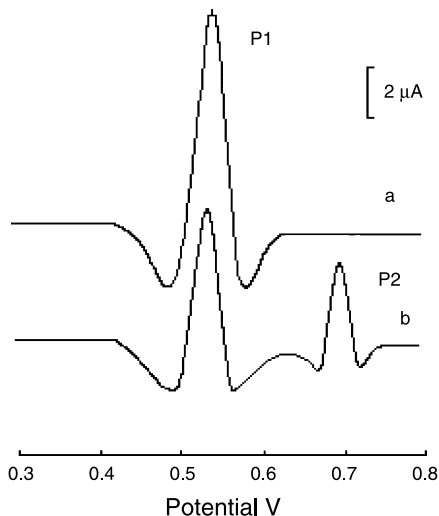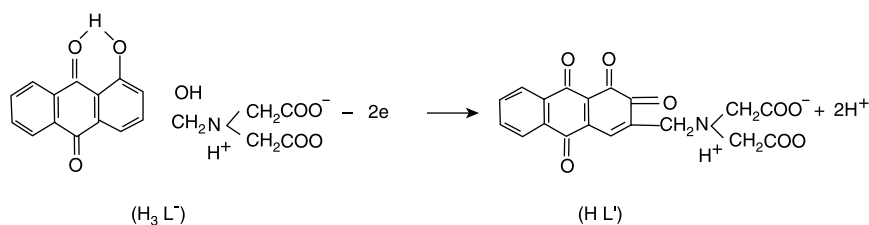
Fig. 2. Second-order derivative voltammograms. (*a*) 3.2×10^{-6} M ALC. (*b*) $a + 4.0 \times 10^{-8}$ M Ce^{3+}. Other conditions as in Fig. 1

potential of P_1 is at 0.53 V (Fig. 2a). It shifts linearly toward less positive values with increasing pH values over the range of 3.8 to 5.5 with a slope equal to -0.062 V/pH. This indicates that the electrode reaction is involved in the deprotonation process. The number of H^+, m_1, can be calculated according to the following equation:

$$0.0591 \, m_1/n = 0.062 \text{ (at } 25\,°C)$$

where the electron transfer number $n = 2$, $m_1 \approx 2$, i.e. each ALC molecule yields two H^+ during oxidation. The major redox process is assigned as follows:

reported that Ce(III) is combined with ALC at a ratio of 2:2 in HAc–NaAc buffer (pH 4.5–6.5) [19, 20].

Figure 2b shows the second-order derivative voltammogram of the Ce(III)–ALC complex. Here P_2 at 0.69 V is more easily measured, and increases with increasing Ce(III) concentration. It is used for analysis of cerium.

The peak current of P_2 (I_p) increases rapidly with increasing preconcentration period due to the increased surface concentrations of the chelates until a limiting current plateau is reached with the adsorption equilibrium. Such curves are consistent with the curves of a process that is controlled by adsorption. The plot of I_p *vs.* scan rate (ν) in the range of 50–500 mV/s is linear. The above shows that the oxidation current is controlled by adsorption of the complex [21].

Electrode Reaction of Cerium and its Complex

The electrochemical behavior of Ce(III) is very similar to that of other rare earth ions, particularly to the light rare earth ions referred to in previously published polarographic studies [4–9]. The selectivity of the oxidation peak of the Ce(III)–ALC complex in this procedure merits our attention. Because cerium has two oxidation forms – Ce(III) and Ce(IV) – in aqueous solution, we doubt that the formation of the oxidation peak is concerned with the oxidation of

Adsorptive Voltammetric Characteristics of the Ce(III)–ALC Complex

The cyclic voltammogram of ALC in the presence of 2.0×10^{-7} M Ce(III) is shown in Fig. 1b. A new oxidation peak P_2 appears at 0.74 V and P_1 decreases, but no corresponding reduction peak with P_2 in the cathodic branch is observed. This indicates that the new electrode reaction derives from oxidation of the ALC in the Ce(III)–ALC complex at the electrode and that this reaction is irreversible. It was

Ce(III). The following experiments were conducted to clarify this:

(1) In the normal voltammogram, 2.0×10^{-4} M Ce(III) solution yielded a diffusion oxidation peak at 0.91 V when linear scanning was performed from 0 to 1.0 V at 100 mV/s (Fig. 3a). It was clear that the peak resulted from the electrode reaction of Ce(III)$-e \rightarrow$Ce(IV).

(2) No apparent oxidation peak was found when the Ce(III) concentrations were lower than
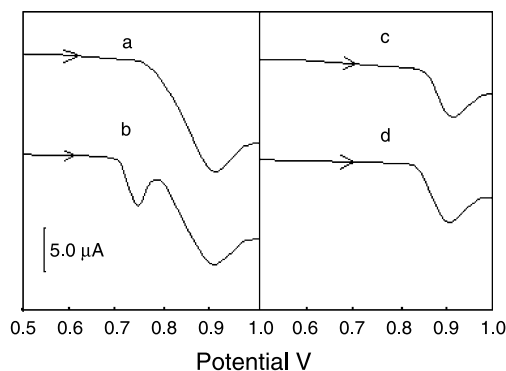
Fig. 3. Normal voltammograms. (*a*) 2.0×10^{-4} M Ce³⁺; (*b*) $a + 5.0 \times 10^{-7}$ M ALC (accumulation time: 60 s). (*c*) 2.0×10^{-4} M Ce⁴⁺; (*d*) $c + 5.0 \times 10^{-7}$ M ALC (accumulation time: 60 s). Other conditions as in Fig. 2

1.0×10^{-6} M. When a small amount of ALC is added to the above solution, a new oxidation peak appears at 0.74 V after 60 s accumulation (Fig. 3b). The peak potential is consistent with that of the above P_2.

(3) When Ce(III) is replaced by Ce(IV) and the test (1) is repeated, a much smaller oxidation peak appears at 0.91 V (Fig. 3c). It is postulated that a fraction of Ce(IV) is reduced to Ce(III) at less positive potentials.

(4) When several drops of ALC are added to the Ce(IV) solution, the red color of ALC disappears at once, and no new peak appears at 0.74 V after 60 s accumulation, but the peak at 0.91 V increases slightly (Fig. 3d). With increasing ALC concentration, the peak at 0.74 V also appears.

As indicated above, Ce(IV) is reduced to Ce(III) and produces the Ce(III)–ALC complex in the presence of excess ALC. Thus, P_2 is attributed to the electrochemical oxidation of ALC in the Ce(III)–ALC complex.
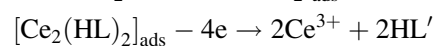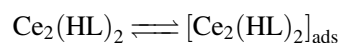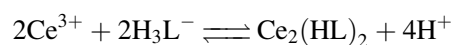
The experiments show that the peak potential of P_2 (E_{P_2}) varies positively with increasing scan rate. There is a linear relation between E_{P_2} and $\lg \nu$ in the range of 50–500 mV/s. The linear regression equation is $E_{P_2} = 0.772 + 0.030 \lg \nu$ ($r = 0.998$), according to:

$$0.0591/\alpha n = 0.030 \text{ (at } 25\,^\circ\text{C)}$$

where $\alpha = 0.5$, $n = 3.94 \approx 4$. Since the complex ratio is 2:2, 4 electrons for oxidation of two ALC are justly lost. This further shows that the peak current of P_2 derives from the complexed ALC and that Ce(III) does not contribute to the measured current.

The peak potential of P_2 hardly changes with changing pH values, indicating that H⁺ is not involved in the redox reaction.

On the basis of the above investigations the overall electrochemical processes can be represented as follows:

$$2Ce^{3+} + 2H_3L^- \rightleftharpoons Ce_2(HL)_2 + 4H^+$$
$$Ce_2(HL)_2 \rightleftharpoons [Ce_2(HL)_2]_{ads}$$
$$[Ce_2(HL)_2]_{ads} - 4e \rightarrow 2Ce^{3+} + 2HL'$$

Optimum Conditions for the Determination of Cerium

Effect of Medium

The Ce(III)–ALC complex yielded the oxidation peak in various electrolytes including HAc–NaAc, HCOOH–HCOONa, KHP, NH₄Ac–HAc, but the peak potential and shape differ slighly. The mixed buffer of HAc–NaAc–KHP was found to be the best for high sensitivity and a good blank baseline. The optimum concentration ranges of HAc–NaAc and KHP are 0.06–0.20 M and 0.01–0.02 M, respectively.
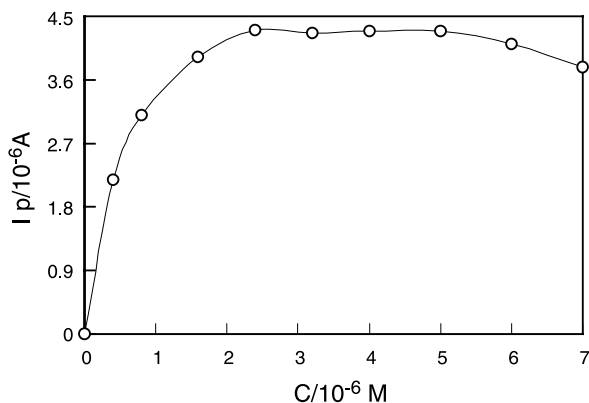
Effect of pH

Figure 4 shows the influence of pH on I_p. It was found that the optimum pH range for the solution is from 4.5 to 4.9.

Effect of ALC Concentrations

Figure 5 shows the effect of ALC concentrations on I_p. I_p increases linearly with increasing ALC levels before it levels off at 1.0×10^{-6} M. The measurements are performed in solutions containing 3.2×10^{-6} M ALC.
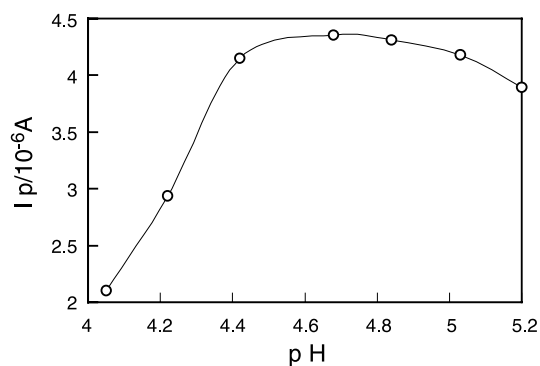
Fig. 4. Effect of pH values on the peak current. Other conditions as in Fig. 2

Fig. 5. Effect of ALC concentrations on the peak current. Other conditions as in Fig. 2

Effect of Preconcentration Potential

A fine blank baseline is obtained at the negative preconcentration potential. The preconcentration potential of $-0.2\,V$ is chosen for further studies.

Figures of Merit

Linear Range, Detection Limit and Reproducibility

Under the chosen optimum conditions, a linear calibration curve for cerium is obtained in the concentration range of $6.0 \times 10^{-9}\,M$ to $3.0 \times 10^{-7}\,M$. The detection limit is $2.0 \times 10^{-9}\,M$ ($S/N = 3$) for $120\,s$ preconcentration.

The reproducibility of the results is established with 3.5% RSD for a series of 15 successive determinations of $4.0 \times 10^{-8}\,M$ Ce(III) on the same surface of the CPE.

Interference Study

Under the same conditions as the determination of Ce(III), $4.0 \times 10^{-8}\,M$ of other rare earth ions were tested. No complex peak for La(III), Pr(III), Nd(III) occurs. The complex peaks of Sm(III), Eu(III), Y(III), Gd(III), Tb(III) with ALC almost overlap with the peak of free ALC and no split peak occurs. The other lanthanides produce a complex peak which is about $60\,mV$ more positive than that of free ALC. The Sc(III)–ALC does not produce an obvious complex peak. With increasing La(III) concentration, the peak of the free ALC becomes broad, but a separate complex peak does not invariably appear. When the concentration of Pr(III) and Nd(III) is up to $2.0 \times 10^{-7}\,M$, an oxidation peak of low sensitivity occurs at a potential which is $60\,mV$ more positive than that of

free ALC. With increasing concentration of Sm(III), Eu(III), Gd(III), Tb(III), Y(III), Sc(III), the complex peaks whose potential is about $60\,mV$ more positive than that of free ALC appear.

The above shows that the determination of cerium is possible in the presence of other rare earth elements. However, although the peak potentials of Ce(III)–ALC and other RE(III)–ALC complexes differ by about $100\,mV$, the peak of other RE(III)–ALC complexes can affect the peak shape of the Ce(III)–ALC and interfere with the determination of cerium when the concentration of other RE(III) ions gets significantly higher than that of cerium. A 5-fold excess of La(III), Pr(III), Nd(III), a 3-fold excess of Sm(III), Eu(III), Gd(III), Tb(III), Y(III), a 2-fold excess of Sc(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) do not interfere with the measurement of $4.0 \times 10^{-8}\,M$ cerium, allowing for an error of $\leq 5.0\%$.

The influence of various coexisting metal ions and common anions was tested. Measurements of $4.0 \times 10^{-8}\,M$ Ce(III) are not affected, allowing for an error of $\leq 5.0\%$, by a 1000-fold excess of Ca^{2+}, Mg^{2+}, Ba^{2+}, Cr^{3+}, As(III), Se(IV), B(III), Ge(IV), Mn^{2+}, a 50-fold excess of Cd^{2+}, a 20-fold excess of Pb^{2+}, In^{3+}, Co^{2+}, Zn^{2+}, a 10-fold excess of V(V), Hg^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Sn(IV), Sb^{3+}, a 5-fold excess of Ti(IV), a 2-fold excess of Al^{3+}, Zr(IV), Cu^{2+}, the same quantities of Bi^{3+}, Ga^{3+} and $2.0 \times 10^{-3}\,M$ SO_4^{2-}, PO_4^{3-}, $1.0 \times 10^{-4}\,M$ F^-, $2 \times 10^{-4}\,M$ ascorbic acid. The presence of trace Th(IV) results in positive interference.

Real Sample Analysis

Two standard samples of rare earth nodular graphite cast iron from the Ministry of Chinese Metallurgical Industry were analyzed with the proposed method. Owing to possible interference from Fe, Cu etc. in the samples, a solvent extraction separation (with PMBP in benzene) was used. The samples were treated according to Ref. [22] and measured using the standard addition method. The results are listed in Table 1. It can be seen that the proposed procedure

Table 1. Determination results of cerium in nodular graphite cast iron samples ($n = 5$)

Samples	Found %	Standard value %	RSD %	Standard value of ΣRE %
BH1902-1	0.0098	0.0102	−3.9	0.0205
BH1905-1	0.0118	0.0115	+2.6	0.019

is sufficiently good for practical use without the need to separate cerium from other rare earths.

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