

Trace Determination of Zirconium(IV) by Anodic Adsorptive Voltammetry at a Carbon Paste Electrode

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Abstract: A new sensitive adsorptive voltammetric method was described for the determination of zirconium at a carbon paste electrode (CPE) in the presence of alizarin complexone (ALC). Optimal analytical conditions are: 1.0×10^{-6} or 5.0×10^{-7} mol/L ALC, 0.20 mol/L HAC-NaAc (pH 4.3), accumulation for 60 s at 0 V (vs. SCE), and linear scanning from 0 V to 1.0 V at 250 mV/s. The peak potential of the complex is at 0.81 V. By using a model JP-303 polarographic analyzer, 2.0×10^{-10} mol/L ($S/N=3$) zirconium can be detected with a 90 s accumulation, when the 2nd-order derivative linear sweep technique is used, and the linear range is 6.0×10^{-10} - 2.0×10^{-8} mol/L (5.0×10^{-7} mol/L ALC) and 2.0×10^{-8} - 2.0×10^{-7} mol/L (1.0×10^{-6} mol/L ALC), respectively. The developed method was applied to the determination of trace zirconium in the ore samples with satisfactory results.

Keywords: Zirconium, alizarin complexone, carbon paste electrode, anodic adsorptive voltammetry.

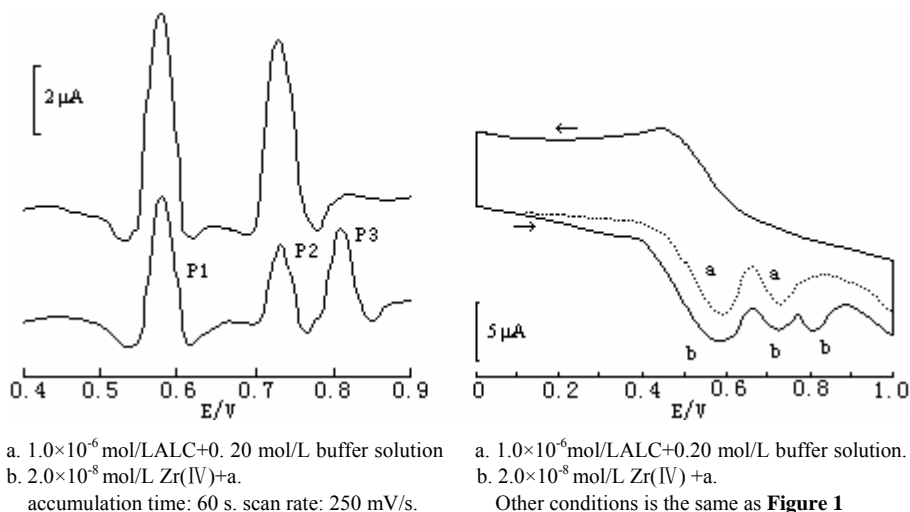
The polarographic complex adsorption wave¹⁻³ and adsorption voltammetry⁴ at a mercury electrode have become sensitive and effective means for trace measurements of zirconium which can not be accumulated electrolytically. The carbon paste electrode (CPE) is used extensively in voltammetry⁵, because of its many advantages, such as easy manufacture, nonpoisonous, cheap price, wide potential window and longer user life. The cathodic adsorptive voltammetry for determination of zirconium at CPE has reported^{6,7}. But anodic adsorptive voltammetry for determination of trace zirconium at CPE has not reported.

A new sensitive anodic adsorptive voltammetric method is described for the determination of zirconium at a CPE in the presence of alizarin complexone (ALC). By using a model JP-303 polarographic analyzer, 2.0×10^{-10} mol/L ($S/N=3$) zirconium can be detected with a 90 s accumulation, when the 2nd-order derivative linear sweep technique is used, and the linear range is $6.0 \times 10^{-10} \sim 2.0 \times 10^{-8}$ mol/L (5.0×10^{-7} mol/L ALC) and $2.0 \times 10^{-8} \sim 2.0 \times 10^{-7}$ mol/L (1.0×10^{-6} mol/L ALC), respectively. The developed method was applied to the determination of trace zirconium in the ore samples with satisfactory results.

In our experiments, the solution containing aliquots of the standard Zr(IV), 1.0×10^{-6} or 5.0×10^{-7} mol/L ALC and 0.20 mol/L HAC-NaAc was transferred to the 25 mL

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Figure 1 The second derivative voltammetric **Figure 2** Cyclic voltammogram



electrochemical cell. The preconcentration potential, 0.0 V, was applied to the working electrode while the solution was stirred. Following a 60 s preconcentration period, the stirring was stopped, and after a rest period of 10 s, the second-order derivative voltammogram was recorded by applying a positive-going potential scan from 0.0 to 1.0 V at 250 mV/s. The peak current of the complex at 0.81 V was registered. All data were obtained at ambient temperature.

The adsorptive stripping voltammograms for the ALC and Zr(IV)-ALC complex are shown in **Figure 1**. As shown in the **Figure**, the peaks potential of the oxidation of adsorbed ALC is at 0.58 V (P_1) and 0.73 V (P_2). When trace Zr(IV) is added into the solution, a new well-defined peak (P_3) appears at 0.81 V. The peak currents of P_1 and P_2 decrease, and the peak current of P_3 increases with increasing Zr(IV) concentration. The appearance of P_3 indicates the formation of the Zr(IV)-ALC complex.

The molar composition of Zr(IV)-ALC was determined by the continuous variations method and the mole ratio method to be $n_{Zr(IV)}:n_{ALC}=1:2$.

When accumulation time was changed from 30 to 180 s, we can observe that, at first, the peak current increases with increasing accumulation time, indicating that before adsorption equilibrium is reached, the longer the accumulation time is, the more Zr(IV)-ALC is adsorbed, and the peak current become larger. However, after a specific accumulation period(150 s), the peak current tends to level off, illustrating that an adsorption equilibrium is achieved. An accumulation time of 60 s was used for further study, because when accumulation time is higher than 60 s, the baseline will turn to be bad.

The peak current of the complex is not affected by a small amount of a cationic surfactant (such as hexadecyltrimethylammonium bromide) and nonionic surfactants (such as TritonX-100), but it is suppressed in the presence of a small amount of anionic (such as sodium dodecylbenzene sulfonic acid).

Figure 2 shows the cyclic voltammograms recorded for 1.0×10^{-6} mol/L ALC at a CPE in the absence(a) and presence(b) of 2.0×10^{-8} mol/L Zr(IV), after stirring at 0.0 V for

60 s. The anodic peak potentials of the ligand are at 0.58 V and 0.73 V, and the cathodic peak potential corresponding to the anodic peak is at 0.48 V. Therefore the reaction of ALC is quasi-reversible at the CPE. The Zr(IV)-ALC complex is oxidated at 0.81 V, no cathodic peak corresponding to the anodic peak of the complex appears, indicating the reaction of the complex is irreversible at the CPE.

The influence of potential scan rate(v) on the peak current of the complex (I_p) was examined over the 100 to 500 mV/s. A plot of I_p vs. v is linear. The above results show that the oxidation current is controlled by adsorption of the complex.

It was found from the experiments that the peak potential (E_p) of the Zr(IV)-ALC complex varies positively with increasing potential scan rate. There is a linear relation between E_p and $\lg v$ in the range of 100~500 mV/s, the linear regression equation is:

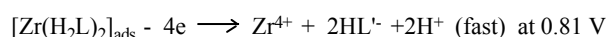
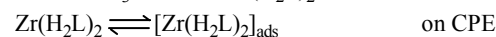
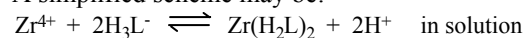
$$E_p(\text{V})=0.03 \lg v+0.8294$$

The correlation coefficient is 0.9572. From $2.303RT/\alpha nF = 0.03$, we can get $n=4$ ($\alpha=0.5, T=298 \text{ K}$).

The peak potential of the complex changes linearly with increasing pH value, and the slope is equal to $0.053 \text{ V} \cdot \text{pH}^{-1}$. The number of protons, m , taking part in the electrode reaction may be calculated as follows:

$$dE_p/d\text{pH} = -2.303 \cdot m \cdot R \cdot T / (\alpha \cdot n \cdot F) = 0.053, \text{ with } m=1.83 \approx 2.$$

A simplified scheme may be:



The experiment indicated that the ratio 4:1 (w/w) of graphite powder to silicon oil is the best ratio. Preliminary experiments were carried out with various types of buffers, such as HAc-NaAc, HAc-NH₄Ac, (CH₃)₆N₄-HCl and HCOOH-HCOONa. The results showed that HAc-NaAc is the best buffer solution. I_p is the highest and steady when pH varies over the range of 3.8~4.6, the concentration of buffer solution varies over the range of 0.04~0.28 mol/L and the concentration of ALC varies over the range of 5.0×10^{-7} ~ 2.0×10^{-8} mol/L. pH 4.3, 0.20 mol/L HAc-NaAc, 2.0×10^{-8} mol/L ALC ($C_{\text{Zr}} \leq 2.0 \times 10^{-8}$ mol/L) and 5.0×10^{-7} mol/L ALC ($C_{\text{Zr}} > 2.0 \times 10^{-8}$ mol/L) were the condition applied to trace determination of Zr(IV).

The linear range for determination of zirconium was evaluated. The peak currents increase linearly with Zr(IV) concentration over the range 6.0×10^{-10} - 2.0×10^{-8} mol/L (5.0×10^{-7} mol/L ALC) and 2.0×10^{-8} - 2.0×10^{-7} mol/L (1.0×10^{-6} mol/L ALC) for a 60 s accumulation. A detection limit was estimated to be 2.0×10^{-10} mol/L ($S/N=3$) for a 90 s accumulation.

The interference of co-existing ions on the determination of Zr(IV) was investigated. The results showed that a 1000-fold excess of K^+ , Mg^{2+} , Ca^{2+} ; 500-fold excess of Pb^{2+} ; 100-fold excess of Hg^{2+} ; 10-fold excess of Fe^{3+} , Th^{4+} , Bi^{3+} , Tb^{3+} , Sn^{4+} , Ti^{4+} , Y^{3+} , Eu^{3+} ; 2-fold excess of In^{3+} , Sc^{3+} , Cu^{2+} and 1.0×10^{-2} mol/L NaF do not interfere in the determination of 2.0×10^{-8} mol/L Zr(IV) with an error of $\leq 10\%$. The Hf(IV)-ALC complex produces a peak at -0.81 V under the same condition of the examination, the sensitivity is the same as that of zirconium.

The recommended method was applied to the determination of zirconium in ore samples. After the samples were melted, sedimentated as reference 8, the hydroxide sediment of metals was dissolved directly with 2.2 mol/L HCl, diluted to a certain concentration and measured zirconium with standard addition method. The proposed method was successfully applied to the determination of zirconium in the ore samples (**Table 1**).

Table 1 Analytic results of samples

Sample	Present method ($\mu\text{g/g}$)	Average($\mu\text{g/g}$)	RSD(%)	Reference (%)
GSD-1	0.0315, 0.0328, 0.0327	0.0323	2.2	0.0309
GSD-3	0.0236, 0.0222, 0.0213	0.0234	6.4	0.0211
GSD-7	0.0143, 0.0170, 0.0168	0.0160	9.4	0.0162

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