

Indirect Differential Pulse Voltammetric Determination of Aluminum by a Pyrocatechol Violet-Modified Electrode

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Abstract: A PCV-modified electrode was simply prepared by dip-coating a pyrolytic graphite electrode in a NaAc-HAc buffer solution of PCV. The peak currents of differential pulse voltammograms (DPV) decrease with the addition of Al and the peak potentials remain the same. The decreasing of Δi_p is linear with Al concentration in the range of $1 \times 10^{-8} \sim 1 \times 10^{-7}$ mol/L. The detection limit is 5×10^{-9} mol/L and the relative standard deviation for 4×10^{-8} mol/L Al is 2.9% ($n=8$). No serious interference was found. The determination of Al in water samples is reported.

Keywords: Pyrocatechol violet (PCV); aluminum; chemically modified electrode; differential pulse voltammetry; indirect determination; drinking water.

Aluminum has been considered to be a causative agent for various neurological disorders¹. During the last decade, considerable attention has been paid to the electrochemical determination of Al for its distinguished merits of high sensitivity, easy manipulation and simple instrumentation². Among them, mostly used method is adsorption stripping voltammetry (ASV). However, ASV uses hanging mercury drop electrode (HMDE) as working electrode which is harmful to one's health. During the detection, procedures of preconcentration and deaeration are often required. All of these cause some limits in its practical application. Recently, Barisci *et al*³ and Downard *et al*⁴ have fabricated chemically modified electrodes (CME) to determine Al, but the sensitivity is not high enough and the practical applications are still lacking. PCV is a good complexation ligand for Al. The PCV spectrophotometric method for determining Al has been widely used in environmental analysis⁵. PCV possesses good electrochemical characteristics^{6, 7}. In this paper, we report an indirect DPV determination of Al by a PCV modified pyrolytic graphite electrode.

Experimental

0.02 mol/L Pyrocatechol violet (PCV) solution; 0.02865 mol/L aluminum stock solution (4.0×10^{-4} mol/L Al standard solution for analytical work was prepared by the dilution of the stock solution with a pH 2.0 HCl solution); 0.2 mol/L NaAc-HAc buffer solution (pH 4.8). All chemicals were of analytical grade and all solutions were prepared with double-distilled water from quartz.

A three-electrode system (BAS electrochemical system) was used in which the PCV-modified pyrolytic graphite electrode was used as working electrode, a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The differential-pulse mode parameters are: scan rate 20 mV/s, pulse amplitude 50 mV and pulse width 60ms. The experiments were performed at room temperature.

A PCV-modified electrode was prepared with following procedure: The pyrolytic graphite electrode was polished with an abrasive paper from 400 to 1200 mesh and ultrasonically cleaned in water. It was then dipped into a newly prepared 0.02 mol/L PCV solution for a certain time and rinsed with water to remove the untightly absorbed materials.

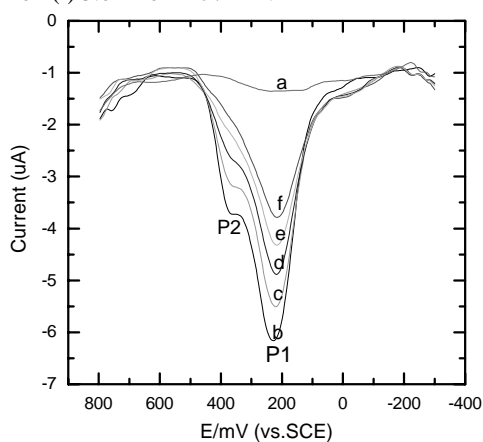
Put the electrodes into the blank buffer solution and apply the differential-pulse mode with potential scanning from -300 to 800 mV. Then add Al solution with different concentration into the solution and record the DPVs. Optimum experimental conditions including a 0.2 mol/L NaAc-HAc buffer solution of pH 4.8 and a PCV concentration of 0.02 mol/L were used to modify the electrode.

Results and Discussion

1. DPV current response of Al at PCV-modified electrode

Figure 1 is the DPVs of the pyrolytic graphite electrode in NaAc-HAc buffer solution (pH 4.8) under different conditions. It shows that there is no peak on the bare electrode. After modifying the electrode, there are two oxidation peaks at the potential of $E_{pa1}=+0.22\text{V}$ (P1) and $E_{pa2}=+0.38\text{V}$ (P2) respectively. By adding Al into the buffer solution, both of the peak currents decrease and the peak potentials remain the same. Only P1 was chosen for quantitative analysis because P2 is much smaller than P1.

Figure 1. The differential-pulse voltammograms of (a) bare electrode, (b~f) PCV-modified electrode in 0.2 mol/L HAC-NaAc buffer solution (pH 4.8) in the presence of (a, b) 0, (c) 3.0×10^{-8} (d) 6.0×10^{-8} (e) 1.0×10^{-7} (f) 5.0×10^{-7} mol/L Al.



Within a certain concentration range, the decrease of the peak current Δi_p ($\Delta i_p = i_{p \text{ bare}} - i_{p \text{ CAl} \neq 0}$) is linear to the Al concentration and can be used to determine Al.

2. The Linear Range, Detection Limit, Relative Standard Deviation And Stability

Under optimum conditions, the linear regression equation for the working curve is: $\Delta i_p (\mu A) = 0.09 + 0.18 \times C_{Al} (\times 10^{-8} \text{ mol/L})$, $r = 0.994$ ($1 \times 10^{-8} \sim 1 \times 10^{-7} \text{ mol/L}$). The detection limit is $5 \times 10^{-9} \text{ mol/L}$. The relative standard deviation for $4 \times 10^{-8} \text{ mol/L}$ Al is 2.9% ($n = 8$). The stability of this modified electrode is satisfactory (the current response for $1 \times 10^{-7} \text{ mol/L}$ Al is $\Delta i_p = 1.83 \pm 0.09 \mu A$ in one week).

3. Study On Interfering Ions In Drinking Water Samples

A number of foreign ions for interference were inspected. For the determination of $1 \times 10^{-7} \text{ mol/L}$ Al, the results showed that a 5000-fold excess of K (I), Na (I), Ca (II), Mg (II), Si (IV), Sr (II), Cl^- , SO_4^{2-} , ClO_3^- or NO_3^- , 3000-fold F^- , 1000-fold Co (II), Ni (II), Sn (II), Tl (I), 500-fold Zn (II), Ba (II), Mn (II), Ce (IV), I^- , 300-fold Zr (IV), NO_2^- , 200-fold Fe (II), 100-fold Fe (III), Mo (VI), V (V), Cr (VI), SCN^- and 50-fold Ga (III), In (III), PO_4^{3-} do not interfere; but 20-fold Hg (II), Ag (I), Bi (III) and 10-fold Cu (II), Pb (II) interfere.

Table 1. Determination of aluminum in real water samples ($n = 4$)

No.	Samples	Al concentration (mol/L)	
		This Method	ICP-AES
1	Robust mineral water	3.66×10^{-7}	$\leq 3.70 \times 10^{-7}$
2	Jinlu mineral water	5.00×10^{-6}	5.00×10^{-6}
3	Wahaha mineral water	4.44×10^{-6}	4.44×10^{-6}
4	Kangshifu pure water	3.67×10^{-7}	$\leq 3.70 \times 10^{-7}$
5	Kadila pure water	3.70×10^{-7}	$\leq 3.70 \times 10^{-7}$
6	Jiuzhaigou mineral water	5.37×10^{-6}	5.48×10^{-6}
7	Chengde natural mineral water1	4.50×10^{-6}	4.44×10^{-6}
8	Chengde natural mineral water2	4.36×10^{-6}	4.44×10^{-6}
9	Chengde natural mineral water3	6.50×10^{-6}	6.66×10^{-6}
10	Boiled distilled water (10min)	2.64×10^{-6}	2.59×10^{-6}
11	Boiled distilled water (20min)	5.48×10^{-6}	5.55×10^{-6}
12	Boiled tap water (20min)	4.30×10^{-5}	4.20×10^{-5}

The amounts of the major interfering elements present in drinking waters are so low compared with Al that in practice they will not cause any interference for determining Al. Table 1 gives the results for determining Al in real water samples by the proposed method. They are in good agreement with those obtained by ICP-AES method.

4. Proposed mechanism of indirect determination of Al

From the cyclic voltammograms, we can determine the electron number n , the surface coverage Γ_T and the charge transfer coefficient α , the apparent electron transfer rate constant k_s using the same method as in ref. (6). (1) In the absence of Al, $n = 2$ and $\Gamma_T = 2.58 \times 10^{-10} \text{ mol.cm}^{-2}$ which implies that the electrode is monolayer absorbed, $\alpha = 0.45$ and $k_s = 0.51$. The electrode behavior is the redox reaction of PCV which may be expressed as:

$\text{PCV} + 2\text{e} + 2\text{H}^+ \rightleftharpoons \text{PCV}^*$. (2) In the presence of Al, $\alpha=0.43$ and $k_s=0.53$. This indicates that the electrode process still shows the electrochemical behavior of PCV. (3) Because Al can form a stable complex with PCV with the ratio of 1:1 at pH 4.8⁷, the Al-PCV complex is electroinactive adsorbed on the CME, it covers the electroactive point resulting in the decrease of the peak current. As described in ref. (8), the current response $\Delta i_p = i_p \cdot K_m C_{\text{Al}} / (1 + K_m C_{\text{Al}})$ (K_m is the stability constant of Al-PCV complex, $K_m = 1.1 \times 10^{-6}$). In the low Al concentration range, $K_m C_{\text{Al}} \ll 1$, the equation can be written as $\Delta i_p = i_p \cdot K_m C_{\text{Al}}$; This is the basis of quantitative determination of Al.

Conclusion

A very simple and sensitive method for determination of Al by a PCV modified electrode was developed. Compared with ordinary polarography and ASV, the main advantages of the proposed method are: (1) Possible analyzing Al in air-saturated samples, no specific organic reagents are required and no preconcentration step is needed. (2) The detection system is relatively simple. The selectivity and sensitivity of this modified electrode are satisfactory. No serious interference is observed. (3) HMDE is no longer used as working electrode. This method can be expected to be applied to the practical flow-analysis and automation.

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