

Studies on Alternating Pulse Current-Chronopotentiometric Stripping Analysis

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Abstract: Alternating pulses current – chronopotentiometric stripping analysis (APC-CPSA) is a new method as a variant of chronopotentiometric stripping analysis (CPSA). During the stripping step an alternating pulse current with a high frequency in a square wave mode is imposed on the electrode system. Thus, τ and sensitivity of APC-CPSA is increased a lot. The τ , $E \sim t$ equation and its reciprocal derivative equation for APC-CPSA are derived and verified by the experimental results.

Keywords: Chronopotentiometric stripping analysis, alternating pulse current-chronopotentiometric stripping analysis.

Based on the first ideas presented by Beck¹, a new method called alternating pulse current - chronopotentiometric stripping analysis (APC-CPSA) has been developed. In this technique, during the stripping step the current imposed on the electrolysis cell comprises of an alternating pulse current (APC) and the inherent direct current of CPSA. The APC is operated with a high frequency in a square wave mode. i_S and i_R is defined as the anodic and cathodic pulse current, respectively, t_S and t_R is the time for which these currents flow. So, when i_S and i_R alternates, parts of the stripped species undergo "re-deposition-reoxidation" cycles. As a result, the transition time τ and the sensitivity of APC-CPSA are considerably increased. It is necessary to control $t_S+t_R \ll \tau$ and $|i_S t_S| > |i_R t_R|$ to ensure that the entire reaction occurs for stripping.

In this paper, the transition time equation, potential-time curve and reciprocal derivative equation for APC-CPSA are derived theoretically as following:

Solving Fick's diffusion law of metal within the mercury film by conventional Laplace transform, the transition time equation can be obtained as:

$$\tau' = \frac{C_M^* l}{\lambda'} \quad (1)$$

where l is the mercury-film thickness, C_M^* is the concentration of amalgam after the pre-electrolysis, $\lambda' = [(K_1 i_S t_S + K_2 i_S t_R) / (t_S + t_R) n F A]$. In the system, inevitably, there is interference from charging current, background current and diffusion of metal ions, which leads to K_1 ($0 < K_1 < 1$) and K_2 ($0 < K_2 < 1$). K_1 and K_2 represent the stripping

efficiency of i_S and deposition efficiency of i_R respectively.

This is the theoretical basis for quantitative analysis of alternating pulse current-chronopotentiometric stripping analysis (APC-CPSA).

$$\text{The amplification factor } K_A = \frac{\tau'}{\tau} = \frac{\lambda}{\lambda'} = \frac{1 + v_t}{K_2 v_i + K_1 v_t} \quad (2)$$

where $v_i = i_R / i_S$, $v_t = t_S / t_R$, τ is the transition time of normal PSA². K_A does not depend on the absolute values of i_S , i_R , t_S and t_R , but only on v_i and v_t . As indicated in Eqn.2, $v_i < 0$ results in $K_A > 1$. In addition, the greater K_2 is, the greater K_A is. So, increasing deposition efficiency K_2 avails on the enhancement of sensitivity for APC-CPSA.

If $K_1 = K_2 = 1$, theoretical equations above are ideal which deviate from the realistic equations, *e.g.*, the ideal amplification factor is greater than the realistic values, especially for $|v_i| \rightarrow v_t$. This conclusion is supported by the experimental results.

By solving Fick's law of metal ions on the surface of electrode, we can obtain the concentration of metal ions. Substituting it and Eqn.1 into the Nernst equation yields the potential-time curve for APC-CPSA:

$$E = E^0 + \frac{0.059}{n} \lg \left[\frac{2l}{(\pi D_{M^+})^{1/2}} \right] + \frac{0.059}{n} \lg \left(\frac{t^{1/2}}{\tau' - t} \right) = E' + \frac{0.059}{n} \lg \left(\frac{t^{1/2}}{\tau' - t} \right) \quad (3)$$

D_{M^+} is the diffusion coefficient of metal ions. The reciprocal derivative equation³ is:

$$\text{When } t \approx \tau'/2: (dt/dE)_{\max} \approx \frac{nF}{RT} \cdot \frac{\tau'}{3} = \frac{nF}{3RT} \cdot \frac{C_M^* l}{\lambda'} \quad (4)$$

This is the quantitative relationship between peak-height and concentration after reciprocal derivative procedure. At $T=298\text{k}$, $nF \tau' / 3RT = 13.35n \tau'$, *i.e.*, the sensitivity for reciprocal derivative APC-CPSA is greater by an order of magnitude than that for APC-CPSA. Experimental results have also proved that the sensitivity of reciprocal derivative APC-CPSA is improved by about an order of magnitude.

References

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