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Oscillographic Chronopotentiometry with High and Low Frequency Current

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Abstract: A novel electroanalytical method, oscillographic chronopotentiometry with high and low frequency current, is presented in this paper. With this method, the sensitivity of almost all kinds of oscillographic chronopotentiometry can be enhanced about one order.

Keywords: Stripping, on-line preconcentration, oscillographic chronopotentiometry.

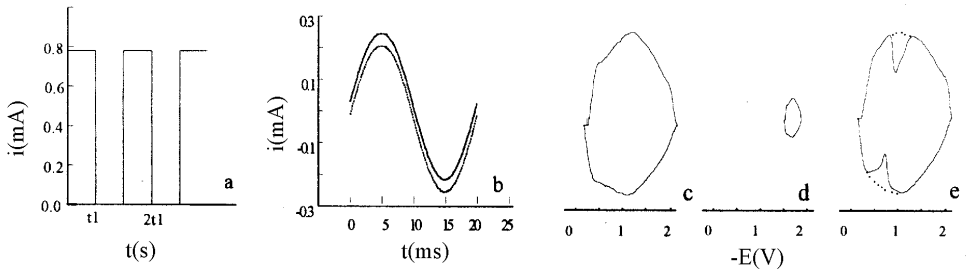
The key, by which oscillographic titration may well be involved into oscillographic analysis, is to enhance the reproducibility, sensitivity and resolution of oscillogram. When it comes to the reproducibility, it can be improved by improving the experimental circuit, varying stability of polarized current, and developing a static oscillographic analysis into a dynamic oscillographic analysis[1,2]. In respect of resolving, we may resort to some signal processing techniques, such as wavelet transform and Fourier transform[3-5]. So far as sensitivity is concerned, there are many ways to increase it, for instance, improving the method, changing a waveform of polarized current, as well as choosing some high sensitivity systems. In spite of all these methods, preconcentration and stripping is still a main way to highly enhance the sensitivity of oscillographic method[6]. Therefore, in this paper, a new on-line preconcentration and stripping method, oscillographic chronopotentiometry with high and low frequency current, is described, and the principle has been studied.

Principle

Figure 1 shows the variation of oscillogram and alternating current during the preconcentration and stripping process using the oscillographic chronopotentiometry method with high and low frequency current. The preconcentration starts after super low frequency pulse wave of alternating current is added and oscillogram contracts to negative end point of –2V(shown in **Figure 1** real line of a, b and d). After concentration has been performed about t_1 seconds (t_1=0.5(1/f) s), the stripping begins in the time range of $2t_1>t> t_1$ (shown in **Figure 1** a, e). So, the preconcentration and the stripping will take place periodically with the periodic changing of the pulse wave. In this procedure, the alternating current ($i_0 \sin \omega t$), which passes through the electrolytic cell, just shifts to

negative direction while the amplitude retains a fixed value (shown in **Figure 1**). Consequently, this method is one kind of on-line preconcentrating and stripping technique.

Figure 1. Change of current and oscillograms in preconcentrating and stripping process



Results and discussion

The effect of the interval of high and low frequency alternating current

In alternating current frequency range of 50 Hz to 0.01 Hz, the system of 5×10^{-6} mol/L Cd^{2+}+ 0.5 mol/L HAc-NaAc was studied by reducing high frequency and increasing low

Table 1 Effect of the interval of high and low frequency alternating current

High frequency/Hz	Low frequency/Hz	$i_0(i_1)$ /mA Preconcentration	Stripping	Peak height*/V	Experimental phenomenon
50.0	0.01	0.326(0.963)	0.325(0.095)	0.21	The oscillograms are stable
25.3	0.01	0.326(0.963)	0.319(0.095)	0.24	The peak height increases while the peak width
12.4	0.01	0.327(0.971)	0.318(0.110)	0.25	narrows with the decrease
4.90	0.01	-	-	-	of the high frequency
50.0	0.04	0.326(0.963)	0.320(0.105)	0.16	The peak height decreases
50.0	0.10	0.322(0.955)	0.319(0.110)	0.11	with the increase of low frequency

*based on 3.5 order differential chronopotentiometry

Increasing low frequency. The results are shown in **Table 1**. Not only is the sensitivity of oscillograms enhanced, but the retaining time of depolarizer is also prolonged with the decreasing of the high frequency. In this respect, it is suitable for the oscillographic determination. However, when the high frequency alternating current is less than 12 Hz, the stability of oscillograms is reduced. On the other hand, the stability of oscillograms decreases with the increase of low frequency.

The effect of amplitude of alternating current and direct current

The system of 5×10^{-6} mol/L Cd^{2+} + 0.5 mol/L HAc - NaAc was used in the study. The results show that the sensitivity of the oscillographic determination and the stability of the oscillogram are affected highly by varying the direct or high frequency alternating

Table 2 The effect of the low frequency current

Alternating current /mA		Peak height* /V
Preconcentration	Stripping	
-0.700	-0.189	0.21
-0.936	-0.095	0.28
-1.063	-0.000	0.30

*based on 3.5 order differential oscillogram

current. The effects of changing low frequency alternating current on the sensitivity of the oscillographic determination in preconcentration and stripping processes are shown in **Table 2**.

Sensitivity

The sensitivity of high and low frequency oscillographic chronopotentiometry is shown in **Table 3**. From **Table 3**, it is obvious that the sensitivity of almost all kinds of oscillographic chronopotentiometry can be enhanced about one order with this method.

Table 3 The sensitivity of high and low frequency oscillographic chronopotentiometry

Depolarizer	Base solution	The sensitivity ($\times 10^{-6}$ mol/L)		
		Y-E	$Y^{2.5}$-E	$Y^{3.5}$-E
In^{3+}	0.5mol/ L HAc-NaAc	0.9	0.2	0.05
Cd^{2+}	0.5mol L HAc-NaAc	0.5	0.1	0.08
Pb^{2+}	0.5mol/ L NaOH	0.6	0.08	0.03
Rh^{3+}	0.1mol/ L HCl-0.6 mol/L KBr	0.3	0.1	0.04

Reproducibility

5×10^{-6}mol/L Cd^{2+} in 0.5mol/L HAc-NaAc is preconcentrated first, then determined with 3.5 order differential oscillographic chronopotentiometry. The reproducibility is shown in **Table 4**. Clearly, the oscillograms exhibit good reproducibility.

Table 4 The reproducibility of the oscillogram

Experimental condition	Peak height /mV	Mean /mV	R.S.D. / %
i_0= 0.321mA	210		
	213		
i_{1max}= -0.963 mA	219	213.8	3.7
i_{1min}= -0.095 mA	216		
	211		

Conclusion

This method shows one order higher sensitivity over the classic oscillographic method. When the method is employed in oscillographic titration, the oscillogram can be adjusted either by using the same method used in the oscilloghaphic determination, or by adjusting direct current or high and low frequency alternating current to get the oscillogram in the state, which is familiar to normal oscillographic determination. However, both end points of the oscillogram may vibrate slightly.

Compared with former potential controlled and current controlled preconcentration and stripping method, constant sinusoidal high frequency alternating current exists when

the oscillographic chronopotentiometry with high and low frequency current is applied to the process of preconcentration or stripping. Therefore, high and low frequency oscillographic chronopotentiometry belongs to on-line concentration.

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References

1. J. B. Zheng, P. Liu, S. H. Shi. *Chemical J. of Chinese Universities*, **1995**, *16*(7), 1106.
2. J. B. Zheng, H. Gao. *J. of Northwest University,* **1995**, *25*(4), 309.
3. H. B. Zhong, J. B. Zheng, Z. X. Pan, H. Gao. *Chemical J. of Chinese Universities*, **1998**, *19*(4), 547.
4. H. B. Zhong, J. B. Zheng, Z. X. Pan, H. Gao. *Chemical J. of Chinese Universities*, **1998**, *19*(4), 547.
5. J. B. Zheng, H. B. Zhong, H. Q. Zhang, Z. X. Pan, H. Gao. *Chinese J. of Analytical Chemistry,* **1998**, *26*(1), 25.
6. J. J. Zhu, J. B. Zheng, J. Hu, H. Gao. *Chemical J. of Chinese Universities*, **1994**, *15*(7), 994.

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