and a more efficient algorithm that is suitable for large application can be found in [3].

2 Experimental

Experiment was carried out in a MEC-12A microcomputer-based electrochemical analyzer (made in China) with Epson Lx-800 Recorde(made in Japan). The working electrode was a SME-84 static mercury electrode equipped with a platinum auxiliary electrode and an Ag/AgCl(saturated KCl) reference electrode, a scanning rate of 50 mV/s, drop time of 1.0 s and sampling time of 20 ms were used throughout determination. All measurements were made at 20± 0.2℃. Ion strength was maintained constant at _= 0.12($NaNO_3$). The concentration of Cd^{2+} ion used for all the data reported were 2.0×10^{-4} mol/L, reagent grade chemicals and distilled water were employed in all cases.

3 Results and Discussion

We used computer with our self-writing software package of WMCD to compute and compare processing deconvolution voltammetric curves in order to select the optimal wavelet basis. Results(as shown in Fig. 1) are ① cubic B-spline $N_3(t)$ is better basis and ② if cubic B-spline wavelet basis and $0.5 < S/N < 100$ are selected, the parameter $l = 4$ is more suitable. Fig. 1-a is result processed from equation (4) and Fig. 1-b is processed experimental data from Cd(Ⅱ)-Succ-Ox complex system. From fig. 1 we can find that the WMCD with cubic-spline wavelet basis is desirable way to extract useful information.

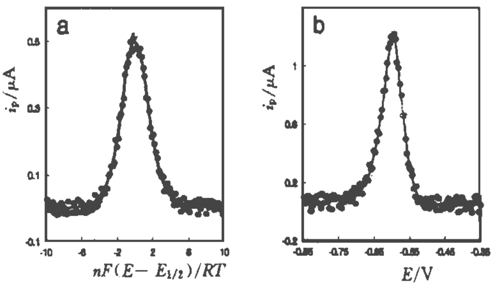

Fig. 1 The processing results of WMCD with 3rd order B-spline wavelet basis $l = 4$, $S/N = 10$
a: simulation data form(4) at $q = 1$,
b: experimental data from Cd(Ⅱ)-Succ-Ox complex system

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高噪声伏安信号的样条小波多通道滤波分析

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摘 要 阐述了样条小波多通道分解法(WMCD)在电分析化学中的应用,提出了高噪声伏安信号中有用信息提取的新方法,讨论了基于样条函数的小波多通道分解方法.

关键词 样条小波,多通道分解,伏安法
分类号 O 177.6, O 657.1

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Spline Wavelet Multifrequency Channel Filters for High Noise Digital Signal Processing in Voltammetry*

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The application of Fourier Analysis (FA) and Kalman Filter(KF) in analytical chemistry such as smoothing, interpolation and enhancement of resolution has been greatly refined in recent 20 years[1]. Because one of keys of FA is to determine the frequency separation value of signal with the noise in both frequency and time domain, it is impossible to obtain the precise frequency separation value and the signal separation. Thus FA can only be used to process signal containing certain noise. Recently, the subject of wavelet analysis has attracted much attention from mathematicians and other scientists alike. In this paper the exploring research of the application of wavelet analysis in voltammetry is presented as the most up-to-date signal processing method.

1 Theory

The purpose of wavelet transform procedure is to decompose a signal into localized contributions that are characterized by a so-called scale parameter. The mathematical technique to perform this decomposition has been described in a number of papers[2]. Suppose that the introduced disturbance is random noise,

$$S_n(t) = M(0.5 - \mathrm{RND}) \tag{1}$$

where M is the amplitude of noise and RND is any random data between 0 and 1, $r(t)$ represents a simulation function of voltammetry. It was showed as following

$$r(t) = \frac{H}{[1 + S\exp(t-p)]} \tag{2}$$

If the equation (2) is q-times, it can represent all voltammetric curves. The discrete expression is

$$S_u = \frac{\mathrm{d}^q}{\mathrm{d}t^q} r(t_i) = \frac{N^q t_k^{-q}}{\Gamma(-q)} \sum_{j=0}^{N-1} \frac{\Gamma(j-q)}{(j+1)} r\left(t_i - \frac{j t_i}{N}\right) \tag{3}$$

where $t_i = a + [(b-a)(i-1)]/N$, $i = 1, 2, 3\cdots, N$, a is initial potential and b is final potential, the equation of voltammetry with noise is described as follows.

$$S(t) = S_u(t) + S_n(t) \tag{4}$$

To any signal $S(t) \in L^2(R)$, V_k instead of $L^2(R)$, the bigger the value k, the closer the V_k is to $L^2(R)$, so $S_k(t) \in V_k$ can be found obviously to represent $S(t)$ approximately, $S(t) \approx S_k(t)$. We have decomposed $S_k(t)$ into blurred version $S_{k-1}(t)$ whose frequency is not bigger than 2^{k-1} and pass-band items G_{k-1} whose frequency is between 2^{k-1} and 2^k. For the digital signal, blurred version S_{k-1} is useful information separated from noise. More details

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