Communications

Simultaneous application of spline wavelet and Riemann–Liouville transform filtration in electroanalytical chemistry

Xiao-Ping Zheng, Jin-Yuan Mo* and Pei-Xiang Cai

Department of Chemistry, Zhongshan University, Guangzhou 510275, China

The spline wavelet can be applied to the processing of signals. It is particularly appropriate for processing nonstationary signal noise. Riemann–Liouville transform (RLT) filtration can be used to remove extraneous currents from faradaic current, but it is not suitable for filtering random noise. Spline wavelet and RLT filtration are combined for the first time to filter random noise as well as extraneous currents. Signals with a signal-to-noise ratio of 0.8 can be filtered. Results of processing experimental data are satisfactory.

In electroanalytical chemistry, the collected current signals often have random noise and extraneous currents. Capactive current is the most common extraneous current. Soong and Maley[1] presented a method to separate faradaic current from capactive current in polarography. This method repeatedly performs Riemann–Liouville transformation, and is thus known as Riemann-Liouville transform (RLT) polarography. Hemstead and Oldham,[2] applied Cotrell filtration to remove extraneous currents from a faradaic signal. Zhang and Mo,[3] studied RLT filtration that could be applied in step voltammetry and normal pulse scan voltammetry. This method is very effective in removing some extraneous regularly changing currents, but it is not suitable for filtering random noise. Wavelet analysis is a technique for processing signal noise. It is particularly appropriate for processing nonstationary signal noise.[4,5] This method has some advantages over other signal processing methods: necessary information can be obtained from signals containing a large amount of noise; the signal representation of the frequency domain distribution state in the time domain and time frequency domain localization can be provided directly.

In this communication, spline wavelet and RLT filtration are combined to filter random noise and capactive current.

Theory

Wavelet transform techniques have been described in many papers.[6–9] Here only a brief description of the main equation is given.

The spline wavelet function may be expressed as follows:

$$\Psi_m(x)=\sum_{n=0}^{3m-2} q_n N_m(2x-n),$$

where,

$$q_n=\frac{(-1)^m}{2^{m-1}}\sum_{j=0}^{m}\binom{m}{j}N_{2m}(n-j+1),\ n=0,\ 1,\ 2,\ \ldots,\ 3m-2 \qquad (1)$$

According to Mallat's decomposition algorithm, the signal f_k can be decomposed to the blurred version f_{k-1} whose frequency is not greater than 2^{k-1} and pass band items $g_1, g_2, \cdots, g_{k-1}$ whose frequency is between 2^{k-1} and 2^k. That is,

$$f_k = g_{k-1}+g_{k-2}+\cdots+g_{k-1}+f_{k-1} \qquad (2)$$

Thus, the random noise (pass band items) can be filtered and the useful signal (blurred version) will be reserved.

RLTs are the integral transforms employed in fraction calculus. The principle of RLT filtration is based on the properties of fractional difference and integration:

$$\text{When } f(t)=kt^p,\ \frac{d^q}{dt^q}f(t)=\frac{d^q}{dt^q}(kt^q)=K\frac{\Gamma(p+1)}{\Gamma(p-q-1)}t^{pq} \qquad (3)$$

$$\text{If } p=q,\ \text{then } \frac{d^q}{dt^q}(kt^q)=k\Gamma(q+1) \qquad (4)$$

which upon rearrangement becomes:

$$\frac{1}{\Gamma(q+1)}\frac{d^q}{dt^q}(kt^q)=D_q(kt^q)=K \qquad (5)$$

In step voltammetry, the equation of faradaic current may be expressed as follows:[10]

$$i_J(t)=\sum_{j=1}^{J}\frac{Q_j}{\sqrt{\pi[(J-j)\tau+\tau']}}=\frac{Q_J}{\sqrt{\pi\tau'}}+\sum_{j-1}^{J-1}\frac{Q_j}{\sqrt{\pi[(J-j)\tau+\tau']}} \qquad (6)$$

where J is the different step, τ is the remaining time of each step, τ' is the sampling time at each step,

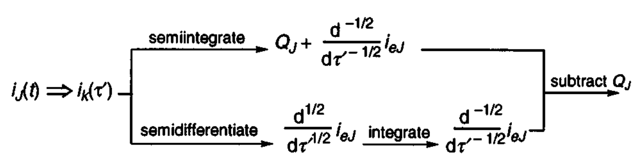
$$Q_j=nFAD^{1/2}C_0^*(\varphi_j-\varphi_{j-1}),$$

$$\varphi_j=1/\left\{1+\exp\left[\frac{nE}{RT}(E_J-E_{1/2})\right]\right\}$$

When capactive current exists:

$$i_J'(t)=\frac{Q_J}{\sqrt{\pi\tau'}}+\sum_{j=1}^{J-1}\frac{Q_j}{\sqrt{\pi[(J-j)\tau+\tau']}}+i_{xJ}=\frac{Q_J}{\sqrt{\pi\tau'}}+i_{eJ} \qquad (7)$$

The process of RLT filtration is as follows:



RLT filtration is used at every step and a series of coefficients $Q_1, Q_2, \cdots Q_J$ could be obtained. From these coefficients and eqn. (6), the current after filtration is obtained.

Experimental

Apparatus

The experiment was carried out on a microcomputer-mutual-function voltammeter supported by in-house sofware. A hanging mercury electrode working electrode, platinum auxiliary electrode and a saturated calomel reference electrode, (Analytical Apparatus Factory of Tai County, China) were used.

Chemicals

All solutions were prepared with analytical-reagent grade chemicals and doubly distilled water. Cd^{II} stock solution (0.1 mol l^{-1}) was prepared using $CdSO_4 \cdot 8H_2O$ (Chemical Reagent Factory of Jiangsu Province, China) in 2 mol l^{-1} HCl. The stock solution was diluted as necessary to prepare samples. A solution having 0.5 mol l^{-1} KNO_3 was used as a supporting electrolyte.

Results and discussion

Data processing of simulating signals

The equation for simulating signals with random noise and capactive current is

$$i_J'(t) = i_J(t) + S_N + i_c \qquad (8)$$

where $S_N = (0.5 - \text{RND})\, I_{max}/(\text{S/N})$, RND is a random number between 0 and 1, I_{max} is the theoretical $i_J(t)$ maximum, S/N is the signal-to-noise ratio and i_c is the capactive current. The current curve with extraneous signals is shown in Fig. 1.

First, the spline wavelet should be used to filter random noise from current signals. The spline wavelet basis order (m) and truncation frequency (l) will affect the results of filtration. So the processing results of different spline wavelet basis orders and truncation frequencies have been compared, the relative errors of peak current [I_p(%)] and peak potential [E_p(%)] are given in Table 1. These errors show that for m = 2–4 (S/N = 0.8, l = 3), the optimum condition is m = 3, when l = 2–5 (S/N = 0.8 and m = 3), the optimum condition is l = 3. Thus the third-order spline wavelet basis and truncation frequency l = 3 are the most effective and are chosen to process signals. The effect of different m and l values are shown in Figs. 2 and 3.

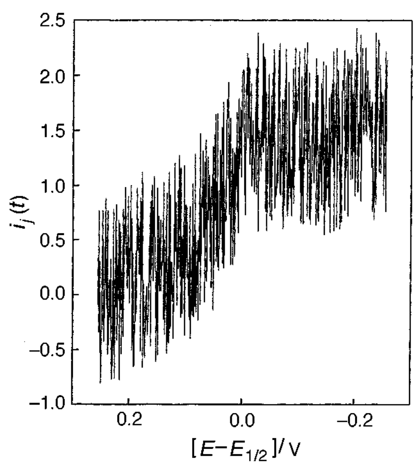


Fig. 1 Current curve with extraneous signals (S/N = 0.8).

Table 1 Relative errors of peak current and peak potential (S/N = 0.8) at different spline wavelet orders (m) (l = 3) and truncation frequencies (l) (m = 3)

	m			*l*			
	2	3	4	2	3	4	5
I_p (%)	1.74	0.82	1.15	2.83	0.82	0.90	2.11
E_p (%)	2.26	1.52	1.87	3.43	1.52	1.67	2.85

According to eqn. (6), twenty current *versus* voltage (the whole scan voltage) curves are simulated at twenty different sampling times τ′ of every step. The spline wavelet is then used to filter random noise from each curve. The useful signals can be separated from S/N = 0.8 [in Fig. 3(*c*)].

From the current curve at different sampling times obtained through the above operation, the current *versus* time curve at every step can be obtained. RLT filtration is then used to remove capactive current from these current signals at every step. A series of coefficients $Q_1, Q_2, \cdots Q_J$ can be obtained. According to eqn. (6) and using these coefficients, the current after filtration can be obtained. The results of the above operations can be seen in Fig. 4 (curve 1). The relative errors of the peak potential [E_{err}(%)] and peak current [I_{err}(%)] at different sampling times τ′ are shown in Table 2. The processing error X^2 is also calculated. the equation is

$$X^2 = \sum_{i=1}^{n} (y_i - y_i^*)^2$$

where y_i is the theoretical value at the ith point, and y_i* is the value after processing. From X^2, the processing result of the

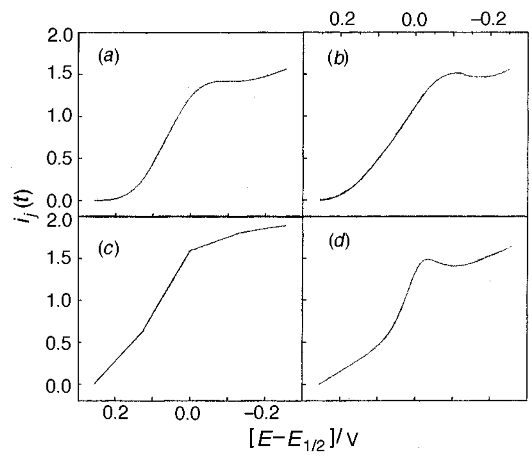


Fig. 2 Effect of different spline wavelet basis orders (m) (S/N = 0.8, 1 = 3): (*a*) m = 4; (*b*) m = 3; (*c*) m = 2; and (*d*) theoretical curve.

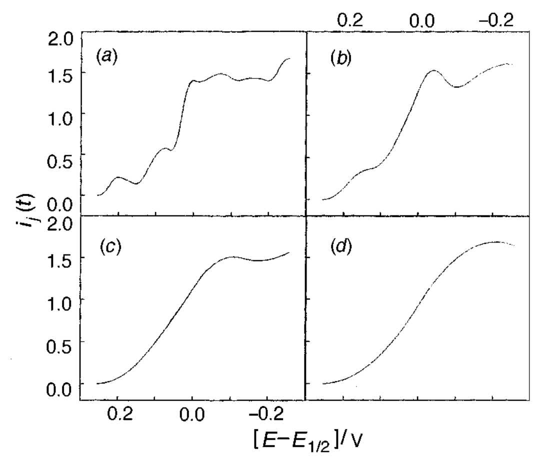


Fig. 3 Effect of different truncation frequencies (l) (S/N = 0.8, m = 3): (*a*) l = 5; (*b*) l = 4; (*c*) l = 3; and (*d*) l = 2.

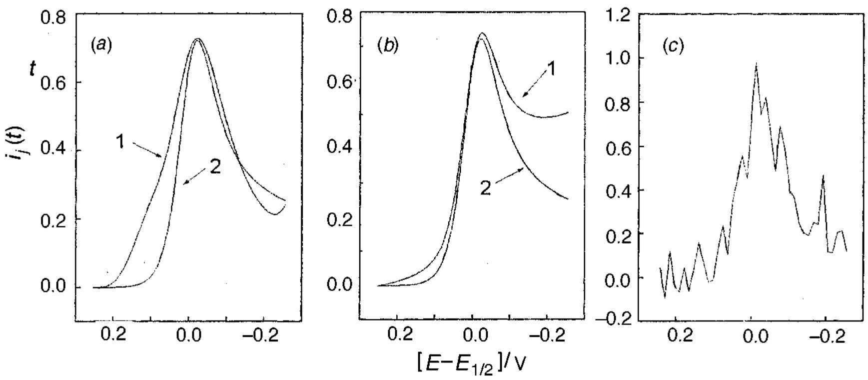


Fig. 4 Process results (*a*) curve 1, current with capacitive current and random noise processed by spline wavelet and RLT filtration; curve 2, theoretical faradaic current. (*b*) curve 1, current with capacitive current processed by RLT filtration, curve 2, theoretical faradaic current; (*c*) current with capacitive current and random noise processed by RLT filtration only.

Table 2 Relative errors of peak current and peak potential at different sampling times τ′

τ′/ms	1	3	5	7	9	11	13	15	17	19
I_{err} (%)	0.80	2.75	3.46	2.80	4.17	4.01	3.60	3.77	2.92	4.00
E_{err} (%)	0	0.36	0.69	0.33	0.32	0.31	0.31	0.32	0.62	0.30

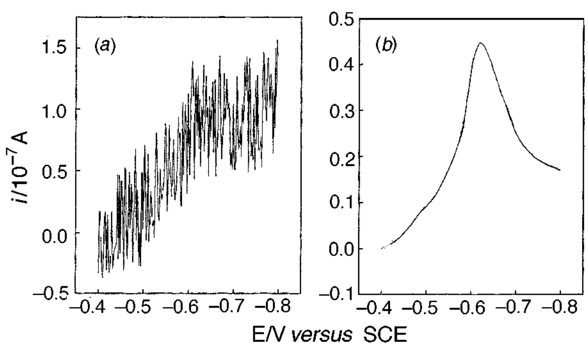


Fig. 5 Current curve of step voltammetry: (*a*) without processing; and (*b*) after processing.

whole curve can be easily seen. The value of X^2 between curves 1 and 2 is 2.2366.

Comparison of the above procedure with other methods has been made. In refs. 1–3, RLT filtration only was used to remove extraneous currents. When RLT filtration only is used to process current signals without random noise, having only capacitive current, the results is satisfactory [Fig. 4(*b*)]. When RLT filtration only is used (without use of the spline wavelet) to process signals with capacitive current and random noise (S/N = 0.8), the processing result is shown in Fig. 4(*c*). It is clear that there are still many fluctuations on the processed curve. The random noise has not been entirely removed. A curve such as this could not be used for further research like quantity and quality analysis. Thus, RLT filtration is very effective in removing capacitive current, but not suitable for random noise. It is essential for those current signals having capacitive current and random noise to use spline wavelet and RLT filtration simultaneously to filter those extraneous signals.

Experimental results

The scan voltage was from −0.40 to −0.80 V, holding time, τ, at every step was 40 ms, ΔE = 20 mV. Current signals were collected at different sampling times, τ′. These signals were processed by the above methods and the results are given in Fig. 5. The concentration of Cd^{II} was 1.00×10^{-8} mol l^{-1}. I_p was 2.27%, E_p was 1.44%. The theoretical peak current was calculated from eqn. (6) and the theoretical peak potential was based on the value given in ref. 3.

Different Cd^{II} concentrations have also been studied. The relationship between the concentration and the peak currents is linear (r = 0.9925). A reduction in the determination limit could be achieved.

Conclusion

The simultaneous application of spline wavelet and RLT filtration in electroanalytical signals to filter random noise and capacitive current proved to be very effective. The errors of the peak current are less than 5.0% and those of the peak potential are less than 1.0%.

This project was supported by the National Natural Science Foundation of China.

References

1 Soong Fu-Chin, and Maloy, J. T. *J. Electroanal. Chem.*, 1983, **153**, 29.
2 Hemstead, M. R., and Oldham, K. B., *J. Electroanal. Chem.*, 1984, **162**, 1.
3 Zhang, M., and Mo, J. Y., *The Conference Processings of Electroanaltyical Chemistry*, 1987, B30.
4 Zou, X. Y., and Mo, J. Y., *Anal. Chim. Acta*, 1997, **340**, 115.
5 Zou, X. Y., and Mo, J. Y., *Chinese Sci. Bull.*, 1997, **42**(8), 640.
6 Chui, C. K., and Wang, J. Z., *Trans. Aner. Math. Soc.*, 1992, **330**(2), 903.
7 Liu, G. Z., and Di, S. L., *Wavelet and Its Application*, Xi'an University Press, Xi'an, 1992 (in Chinese).
8 Wang, J. Z., *Advances in Mathematics*, 1992, **21**(3), 289.
9 Chui, C. K., and Wang, J. Z., *Proc. Am. Math. Soc.*, 1991, **113**, 758.
10 Mo, J. Y., and Zheng, J. L., *Acta Chim. Sin.*, 1991, **49**, 237 (in Chinese).

Paper 8/00267C
Accepted January 5, 1998