Approximate Derivative Calculated by Using Continuous Wavelet Transform

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A novel method of calculating approximate derivative of signals in analytical chemistry by using the continuous wavelet transform (CWT) is proposed. As compared with numerical differentiation, FT method and DWT method, fast calculation, and simple mathematical operation are remarkable advantages of CWT method. The signal-to-noise ratio (SNR) of approximate derivative of signals calculated by CWT method is easily enhanced only through appropriately adjusting the dilation, even in the case of very low SNR. Therefore, CWT method is a powerful tool for performing the approximate derivative calculation of signals in analytical chemistry. Additionally, the approximate second derivative evaluated via CWT method can be used to determine the peak potentials of the overlapping square wave voltammogram (SWV) of Cd(II) and In(III), and the results are very satisfactory.

INTRODUCTION

In analytical chemistry, derivative calculation is often used as a resolution enhancement technique to facilitate the detection and location of poorly resolved components in the complicated experimental signals and also as a background compensation tool to reduce the effect of variable spectra background in quantitative spectrophotometry.[1,2] The derivative technique was applied to ultraviolet−visible (UV−vis) spectroscopy,[3,4] infrared spectrum,[5,6] and electroanalytical chemistry.[7] It is widely appreciated that the principal problem encountered by using differentiation for data analysis is the rapid degradation of the signal-to-noise ratio (SNR) as the order of derivative increases. Hence, to obtain the higher order derivative of signal, some techniques of smoothing, such as smoothing by polynomial,[8−10] sliding average,[11] and smoothing in the Fourier Domain,[12,13] are required in conjunction with the differential operations.

The wavelet transform method (WT), as proposed by Grossmann and Morlet,[15] has been used for signal and image processing.[16] Because of fast in computation with localization and quick decay properties in contrast to the fast Fourier transform (FFT),[17] large number of basis functions available and high speed data treatment, WT has been successfully applied to signal processing in chemical areas, such as flow injection analysis,[18] high performance liquid chromatography,[19] infrared spectrometry,[19] nuclear magnetic resonance spectrometry,[20] and voltammetry[21] for denoising, smoothing, and removing a large unwanted line.

There are some common methods for derivative calculation, such as numerical differentiation,[17] polynomial filters,[9,10,14] and Fourier Transform (FT).[5,6,13] Recently, some papers[17,33,34] concerning using WT for approximate derivative calculation have been reported. In refs 33 and 34, the efforts mainly focus on the applications to practical signals and different analyzing wavelet as compared with the one in the present work was used. The discrete wavelet transform (DWT) method proposed in ref 17 has a major advantage that differentiation and smooth can be carried out in the same calculation, and SNR can be enhanced for higher order derivative calculation. However, there are two limitations in DWT method: (1) because the number of the data points reduces the 50% for each derivative order computation, it requires that the number of data points available of the original signal is not too small. (2) For the SNR of signal being very low (e.g. SNR = 5), the present DWT method cannot be used. In this work, we utilize the continuous wavelet transform (CWT) to calculate the approximate derivative from another angle, and our investigations lay primarily stress on limitation of resolution, selection of the optimum dilation, and SNR enhancement. In CWT method, SNR enhancement can be conveniently achieved in each order derivative calculation only via suitably increasing the dilation, although in the case of severe interference of noise (very low SNR). Because the number of the data points does not diminish after using CWT to evaluate the approximate derivative, there is no requirement for the number of data points of the original signal in CWT method. In addition, as compared with the FT method, the calculation for derivative via our method is relatively simple and very fast due to only using the convolution operation in the whole process of derivative computation.

THE CONTINUOUS WAVELET TRANSFORM (CWT)

The continuous wavelet transform[32,33] (CWT) $Wf(a,b)$, the projection of a signal $f(x)$ on the analyzing wavelet $\psi_{a,b}(x)$, can be described by the equation as follows

$$Wf(a,b) = \int_{-\infty}^{+\infty} f(x)\cdot\psi^{*}_{a,b}(x)dx \qquad (1)$$

where the asterisk represents the complex conjugate and $f(x)$ and $\psi_{a,b}(x)$ both belong to $L^2(R)$ ($L^2(R)$ indicates the Hilbert space of measurable, square-integrable one-dimensional functions, i.e., signals of finite energy). $\psi_{a,b}(x)$ can be obtained from a single function $\psi(x)$, the mother wavelet,

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Table 1. Comparison of Three Types of Signals

type of signal	Gaussian[b]	Lorentzian	Sech^2-function
general form	$\frac{h}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(x-p)^2}{2\sigma^2}\right]$	$\frac{h}{\pi\sigma\{1+[(x-p)/\sigma]^2\}}$	$h\cdot\mathrm{sech}^2[\sigma(x-p)]$
line shape	continuous and symmetric peak shape with regard to $x = p$		
peak position	$x = p$		
fwhm[a]	$2\sigma\sqrt{2\ln 2}$	2σ	$\ln(3+\sqrt{8})/\sigma$
corresponding FT	$h\cdot\exp(-\sigma^2y^2/2)\cdot\exp(-iyp)$	$h\cdot\exp(-\lvert\sigma y\rvert)\cdot\exp(-iyp)$	$(2h/\sigma)\cdot\frac{\pi y/2\sigma}{\sinh(\pi y/2\sigma)}\cdot\exp(-iyp)$
derivative	indefinitely derivable		

[a] fwhm represents full-width at half-maximum of the peak. [b] h, σ, and p denote the parameters concerning height, width, and peak position, respectively.

by translations and dilations

$$\psi_{a,b}(x) = \frac{1}{\sqrt{a}}\,\psi\left(\frac{x-b}{a}\right) \tag{2}$$

where the parameters of translation are $b \in R$ and of dilation are $a \in R$ and $a > 0$ (R denotes real number). Inserting eq 2 into eq 1, we can recognize that

$$Wf(a,b) = \frac{1}{\sqrt{a}}\int_{-\infty}^{+\infty} f(x)\cdot\psi^*\left(\frac{x-b}{a}\right)dx = f(b)\otimes\psi_a{}^*(b) \tag{3}$$

where $\otimes$ denotes the convolution and $\psi_a{}^*(x) = 1/\sqrt{a}\;\psi^*(-x/a)$. It can be seen from eq 3 that $Wf(a,b)$ can be computed through the convolution product.

Another different form of wavelet transform (WT), the most popular one applied to the signal processing, is the discrete wavelet transform (DWT), which is based on the notion of multiresolution analysis and often leads to the construction of orthogonal bases of wavelets.[22] The aims of CWT and DWT for signal process are different. The former is a tool for analysis and feature determination,[22] and approximate derivative calculation as will be seen in the present work, while the latter is the preferred technique for data compression and denoise.

THEORY

In this paper, the signals to be analyzed include three types of signals: Gaussian, Lorentzian, and sech^2-function. The two formers are the representative line shapes in the practical spectroscopy and chromatography, while sech^2-function is often encountered in ac voltammetry (For examples, several electroanalytical techniques such as square wave voltammetry (SWV),[23] semidifferential electroanalysis,[24] and derivative neopolarography[25] can be described by sech^2-function). To perform an explicit comparison between them, the major properties concerning the three types of signals are exhibited in Table 1.

From Table 1, it can be seen that the three types of signals in analytical chemistry have some common points: (1) their line shapes are all continuous and symmetric peak shapes with respect to $x = p$, (2) the positions of maximum (peak position) all lie in $x = p$, and (3) their derivatives are all indefinitely derivable. If a signal $f(x)$, representing one of three types of signals, convolutes with a smoothing function $h(x)$ and the result is $g(x)$, which can be expressed as

$$g(x) = f(x)\otimes h(x) \tag{4}$$

After performing the n order derivative at the two sides of eq 4, we can get

$$\frac{d^n}{dx^n}g(x) = \frac{d^n}{dx^n}[f(x)\otimes h(x)] = \left[\frac{d^n}{dx^n}f(x)\right]\otimes h(x) = f(x)\otimes\left[\frac{d^n}{dx^n}h(x)\right] \tag{5}$$

eq 5 can be easily deduced by utilizing the FT. According to the convolution theorem, let perform the FT for eq 5

$$F\left[\frac{d^n}{dx^n}g(x)\right] = (\mathrm{i}y)^n[\mathrm{F}(y)\mathrm{H}(y)] = [(\mathrm{i}y)^n\mathrm{F}(y)]\mathrm{H}(y) = \mathrm{F}(y)[(\mathrm{i}y)^n\mathrm{H}(y)] \tag{6}$$

where F indicates the FT, and $\mathrm{F}(y)$ and $\mathrm{H}(y)$ denote the corresponding FTs of $f(x)$ and $h(x)$, respectively. Consequently, performing the inverse FT for eq 6, we can derive eq 5. If $d^n/dx^n\,h(x)$ can be employed as an analyzing wavelet, i.e., $\psi(x) = d^n/dx^n\,h(x)$, we can use CWT to carry out the approximate derivative calculation. Depending on the eq 3 and eq 5, we can derive

$$Wf(a,b) = f(b)\otimes\psi_a{}^*(b) = \left[\frac{d^n}{db^n}f(b)\right]\otimes[(-a)^n h_a{}^*(b)] \tag{7}$$

where $h_a{}^*(x) = h^*(-x/a)/\sqrt{a}$. Eq 7 shows that $Wf(a,b)$ (the CWT of the signal) is just the n order derivative of the signal smoothed by $h_a{}^*(x)$ at the resolution (dilation) a. This is the theoretical basis of approximate derivative of signal ($f(x)$) by utilizing CWT method. Namely, we regard the nth derivative of the signal blurred with $h_a{}^*(x)$ at the resolution (dilation) a as the approximate nth derivative of the signal. In the present work, we choose Gaussian function as the smoothing function ($h(x) = \exp[-x^2/(2\sigma^2)]$) because the n order derivative of Gaussian function can be used as wavelets.[27] Accordingly, we can utilize the CWT to compute the approximate derivative. Although higher than second order derivatives of Gaussian function can also be used as wavelets, in practical application of this work, we select the first and the second derivatives of Gaussian function (the latter is called Mexican-hat wavelet added a minus sign) as the analyzing wavelets for approximate derivative calculation. The reason is that the line shapes of higher than second-

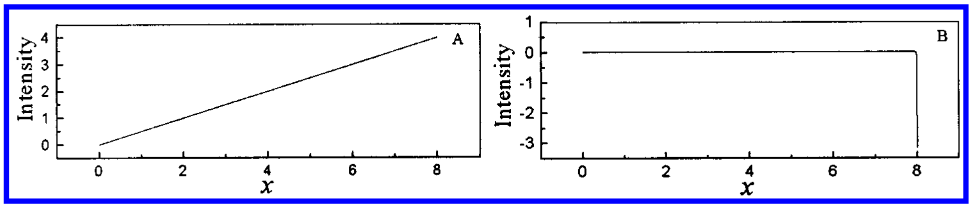

Figure 1. A slope of line (A) and its approximate derivative (B) calculated by CWT method (dilation = 1). The line is described by the function, $f(x) = 0.5x$ (data point = 1024).

order derivatives of $h_a*(x)$ (Gaussian function) cannot be fully exhibited when dilation (a) is small. As a result, this can lead to incompletely describing the approximate derivatives of original signal through the CWT method. In this paper, for the first and second derivative calculation, we adopt the first and second derivatives of a Gaussian function as the analyzing wavelets to perform calculation directly. While for the higher than second derivative calculation, e.g. fifth derivative, we can successively perform CWT twice by using the second-order derivative of a Gaussian function as analyzing wavelet and then carrying out CWT once by using the first-order derivative of a Gaussian function as the analyzing wavelet to evaluate the approximate fifth order derivative of the signal.

According to eq 7, from the mathematical point of view, it can be rigorously said that the approximate derivative calculated by the CWT method depends on the analyzing wavelet ($\psi_a(b)$). The distortion of the approximate derivative caused by the wavelet in fwhm as will be discussed below is very little under the small dilation but will be enlarged with dilation's increase.

EXPERIMENTAL SECTION

In this work, all the data processing was performed with our self-written software package of CWT algorithms (compiled with C language in DOS and UNIXOS). To test the performance of this method applied to practical signal, the overlapping square wave voltammogram (SWV) of Cd(II) and In(III) is employed.

In practical computation, the signal to be processed is often discretely sampled data, so eq 3 is necessarily discretized into

$$Wf(a,kT_s) = \frac{1}{\sqrt{a}} \sum_n f(nT_s) \cdot \psi^* \left[\frac{(n-k)T_s}{a} \right] \cdot T_s \qquad (8)$$

where $1/T_s$ is the sampling frequency. Comparing eq 3 with eq 8, we can recognize that $Wf(a,b)$, $f(x)$ and $\psi^*[(x-b)/a]$ are discretized into their corresponding terms, $Wf(a,kT_s)$, $f(nT_s)$ and $\psi^*[(n-k)T_s/a]$, respectively. n is the serial number of signal data, and k indicates the number of translation. For a given dilation (a), eq 8 is used to implement the CWT on discretely sampled data under different k and then obtain the wavelet coefficients' sequence $Wf(a,kT_s)$, which is just the approximate derivative of the signal ($f(nT_s)$).

The multifunctional voltammetry analyzer (LK-98 Electroanalysis System) was controlled by a microcomputer and supported by self-designed software. The working electrode was a hanging mercury drop electrode, whose area was about 0.01 mm^2, which was the medium drop size used in all experiments. The counter-electrode was a platinum wire, and the Ag/AgCl electrode was used as the reference electrode. A solution containing 0.1 mol/L KCl as well as being saturated with AgCl was used as the inner solution of the reference electrode. The concentration of the KNO_3 supporting electrolyte is 0.1 mol/L.

All solutions were prepared with analytical grade chemicals and double distilled water. Stock solutions of 1.02×10^{-2} mol/L Cd(II) and 1.03×10^{-2} mol/L In(III) were prepared by utilizing Cd(II) sulfate and In(III) chloride tetrahydrate, respectively. The prepared samples were the dilute solutions containing 1.02×10^{-5} mol/L Cd(II) and 1.03×10^{-5} mol/L In(III) in the experiments.

The technique we used was square wave voltammetry (SWV). The range of scan potential was from −0.8 to −0.4 V, and the scan increment is 1 mV. The SW amplitude and the SW period are 25 mV and 0.16 s, respectively. The temperature was kept at 20 °C during the experiment. The solutions were deaerated with high purity nitrogen for 20 min prior to and between runs. Each experiment repeats five times, and the average results of five times are presented.

RESULTS AND DISCUSSION

1. Application to the Slope of Line. To give an external estimation of the CWT method for derivative calculation, we use CWT method to evaluate the approximate derivative for a slope of line. Figure 1 shows the slope of a line ($f(x) = 0.5x$, data point = 1024) and its approximate first derivative via CWT method. It is clear that most properties of the derivative of the slope of line can be retained when using CWT method for derivative calculation except side-lobe problem resulting from the starting and ending points of signal not having a common value. In practice, for the three types of signals (Gaussian, Lorentzian, and $sech^2$-function) in the present work, we can use translation-rotation transformation (TRT)[17,31] method to solve side-lobe problem.

2. Resolution Enhancement. Derivative as a tool of enhancing resolution and narrowing the peak than the original data has long been used in the analytical chemistry. However, theoretically, the resolution of the approximate derivative of the original signal calculated by means of CWT method cannot attain the one true derivative of the original signal. We can take advantage of FT to give the relevant interpretation. For a signal $f(x)$, on the basis of eq 7 and the property of $h_a(x)$ (even function), the FT of the approximate derivative obtained via CWT method can be written as

$$F[Wf(a,b)] = F\left\{ \left[\frac{d^n}{db^n} f(b) \right] \otimes [(-a)^n h_a*(b)] \right\} = (-a)^n \sqrt{a} (\mathrm{i}y)^n \mathrm{F}(y) \mathrm{H}(ay) \quad (9)$$

where the asterisk is eliminated because $h_a(x)$ and $\mathrm{H}(ay)$ (Gaussian function) are both the real functions. Without

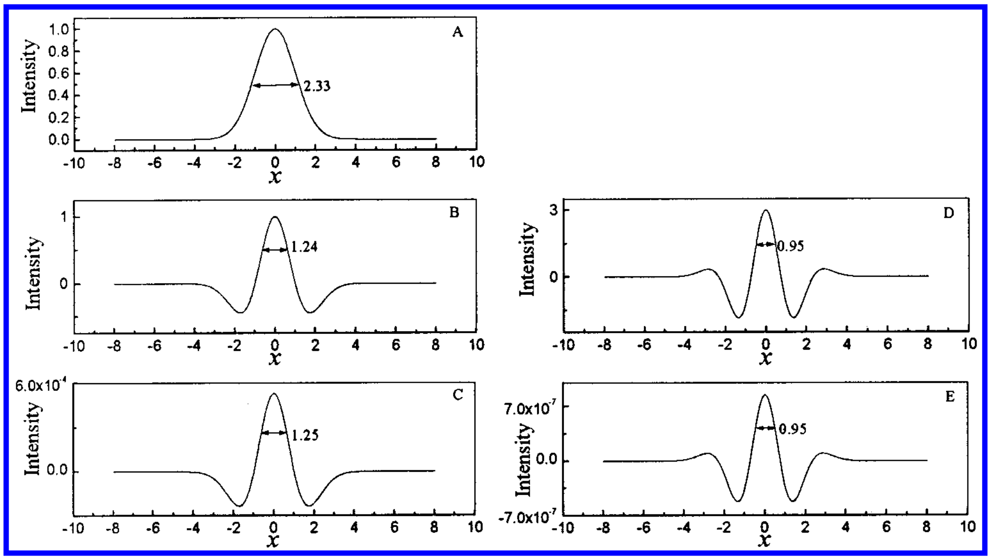

Figure 2. Comparison of fwhms of derivatives calculated by CWT method with the ones of the analytical derivatives. The simulated Gaussian peak (A) (noise-free, $f(x) = h{\cdot}\exp[-(x-p)^2/2\sigma^2]$) is made of 1024 data points, and corresponding peak position (p), peak height (h), and peak width parameter (σ) are 0, 1, and 1, respectively. The true second (multiplied by -1) and fourth derivatives of signal approximated by analytical derivatives of Gaussian peak are shown in (B) and (D), respectively. The approximate second (multiplied by -1) and fourth derivatives using CWT method (dilation = 1) are displayed in (C) and (E), individually.

considering the proportional coefficient $((-a)^n\sqrt{a})$ since it cannot influence the distribution of frequency of original signal, i.e., it has no effect on the resolution. As compared with the true derivative of the signal ($d^n/dx^n\ f(x)$ and corresponding FT, $(iy)^n F(y)$), we can recognize that $H(ay)$ is introduced in eq 9. Because $H(ay)$ is a smoothing function, some high frequencies of the original signal are suppressed. This will lead to degradation of resolution. Since the smaller the dilation is, the finer the resolution is in spatial domain and the coarser the one is in the frequency domain,[28] we can enhance resolution depending on decreasing dilation. When a trends to zeros, $H(ay)$ (Gaussian function) will have a tendency to 1. In this way, the frequency distribution of $Wf(a,b)$ will be infinitely approximate but be impossible to attain the frequency distribution of $d^n/dx^n\ f(x)$. Hence, the resolution of approximate derivative obtained by CWT method cannot reach the one true derivative of the original signal.

Because the degradation of resolution resulting from $H(ay)$ can make the fwhm of approximate derivative via CWT method wider than the one of true derivative (the true derivative can be approximated by the analytical derivative of the signal), the second and fourth order analytical derivatives of simulated noise-free Gaussian peak ($f(x) = h{\cdot}\exp[-(x-p)^2/2\sigma^2]$, data point = 1024, $p = 0$, h and σ are both equal to 1) are employed as example to test our prediction. For the second derivative of signal, there is a phase inversion corresponding to the direction of the original peak. To compare fwhm easily and clearly, the second derivative is multiplied by -1 to inverse the direction. Figure 2 gives a comparison of fwhms of second and fourth derivatives evaluated by CWT method with the ones of analytical derivative of the signal (true derivative).

Seen from Figure 2, the increment of fwhm of the second derivative by using the CWT method is little when the dilation (a) is small, e.g. $a = 1$. It is also obvious that the shapes of the approximate derivatives via CWT method are very similar to the corresponding analytical derivatives of the signal. Moreover, almost the same results on peak central positions (one data point shift yielded by numerical computation) are obtained as compared with the ones of corresponding analytical derivatives. Therefore, the reliability of approximate derivatives calculated via CWT method can be guaranteed.

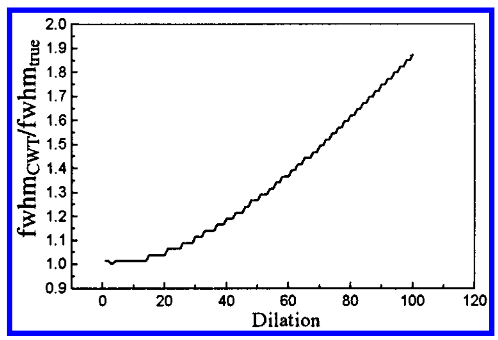

Figure 3. The influence of dilation on the fwhm of approximate second derivative calculated by CWT method. $fwhm_{CWT}$ and $fwhm_{true}$ indicate the fwhms of approximate second derivative evaluated by CWT method and the analytical derivative, respectively.

Figure 3 depicts the variation of fwhm of second derivative as an example through the CWT method with the increasing dilations (a is from 1 to 100). It is clear that fwhm will be wider as the dilation increases.

In Figure 3, when the value of dilation is less than 20, the relative error of $fwhm_{CWT}/fwhm_{true}$ is not greater than 5%.

3. Signal-to-Noise Ratio (SNR) Enhancement. In practice, the experimental signals are often corrupted by noise. Since the rapid degradation of SNR occurs in conjunction with differentiation operation, the higher derivatives cannot be evaluated except on the condition that smoothing is employed between each order of derivative calculation. Reference 11 provides us a convenient method to estimate the relative SNR of unsmoothed derivative. However, the relative SNR of derivative of sech^2-function signal was not given. According to the approach provided in ref 11, we

Table 2. Relative Signal-to-Noise Ratios of Unsmoothed Derivatives of Three Types of Signals

derivative order	line shape[a]		
	Gaussian	Lorentzian	$Sech^2$-function[b]
0	1	1	1
1	$2.02/w^1$	$1.84/w^1$	$1.90/w^1$
2	$3.26/w^2$	$4.1/w^2$	$3.29/w^2$
3	$8.1/w^3$	$16.6/w^3$	$9.62/w^3$
4	$17.7/w^4$	$64/w^4$	$25.9/w^4$
5	$52/w^5$	$390/w^5$	$105/w^5$
6	$141/w^6$	$2204/w^6$	$389/w^6$
7	$478/w^7$	$17065/w^7$	$2008/w^7$
8	$1675/w^8$	$132275/w^8$	$9542/w^8$

[a] w indicates the number of the points in the fwhm of the peak. [b] The data point of simulated $Sech^2$-function is 1024, and p, h, and σ are 0, 1, and 1, respectively.

calculated the relative SNRs of the first eight unsmoothed derivatives of $sech^2$-function signal and listed them in Table 2 as a supplement.

According to the data listed in Table 2, we can conveniently estimate the SNR at each order of derivative through the equation expressed as below[11]

$$\mathrm{SNR}_n = (C_n/w^n)\cdot \mathrm{SNR}_0 \tag{10}$$

where C_n is a constant (see Table 2), both relying on the order of derivative (n) and on the type of signal. SNR_n and SNR_0 represent the SNRs of nth and zeroth derivatives without smoothing, respectively. Because the smoothing function $h_a(x)$ (see eq 7) is introduced in the process of evaluating the approximate derivative via CWT, both smoothing and derivative calculation can be simultaneously performed. Furthermore, high SNR can be achieved in higher order derivative calculation only by appropriately increasing the dilation. To investigate the influence of dilation on the SNR enhancement, we separately generate noise-free signal and white noise and smooth each separately for facilitating the study. Since the smoothing method (convolution with a smoothing function, see eq 7) in CWT method is linear, this approach can yield the same results as when the signal and the noise are added together before smoothing. To obtain the information concerning the variation of SNR with respect to the dilation, we use the factor of SNR enhancement[8] to characterize the increment of SNR caused by smoothing, which can be described as

$$Q = \frac{\mathrm{SNR}_s}{\mathrm{SNR}_{us}} = \frac{M_s/\mathrm{std}[S_s(x)]}{M_{us}/\mathrm{std}[S_{us}(x)]} \tag{11}$$

where M_s and M_{us} indicate the peak heights after and before smoothing, respectively, and $\mathrm{std}[S_s(x)]$ and $\mathrm{std}[S_{us}(x)]$ denote the standard deviations of noise ($S(x)$, white noise) after and before smoothing individually. Equation 11 shows that the value of Q depends on the ratio of $M_s/\mathrm{std}[S_s(x)]$ (smoothed) and $M_{us}/\mathrm{std}[S_{us}(x)]$ (unsmoothed), but in essence it can be regarded as the function of dilation because SNR_s is decided by the dilation (see Figure 4).

In Figure 4, the first-order derivatives of three types of signals are employed as example. For three types of signals, the curves describing the variation of Q with respect to increasing dilation have similar tendencies. Namely, there is a certain limit to the degree of SNR enhancement via CWT method for smoothing each line shape. Seen from Figure 4, high SNR of the approximate derivative calculated via CWT method can be achieved merely by appropriately increasing the dilation.

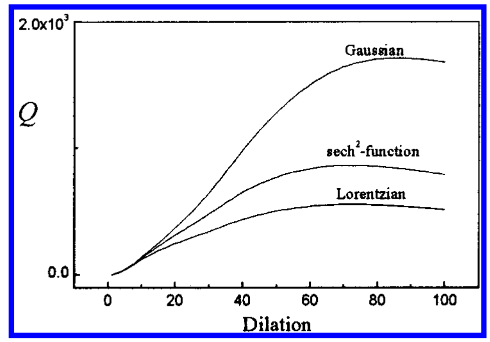

Figure 4. The effect of dilations on the factor of SNR enhancement (Q).

4. Selection of the Dilation. In the process of calculating the approximate derivative through CWT method, selection of an appropriate dilation (a) cannot only make the important information of original data exhibit enough but also suppress some unuseful information. Although the dilation's increase can make the SNR enhanced, the distortion of the signal and degradation of the resolution can be yielded in conjunction with the dilation's increase. For the sake of finding the optimum dilation to obtain a tradeoff between the high resolution and good SNR, in this work, we use the correlation coefficient as a criterion to choose the optimum dilation, which can be expressed as[29]

$$r = \frac{\sum_{i=1}^{N} x_i y_i - \frac{1}{N}(\sum_{i=1}^{N} x_i)(\sum_{i=1}^{N} y_i)}{\sqrt{\sum_{i=1}^{N} x_i^2 - \frac{1}{N}(\sum_{i=1}^{N} x_i)^2}\cdot\sqrt{\sum_{i=1}^{N} y_i^2 - \frac{1}{N}(\sum_{i=1}^{N} y_i)^2}} \tag{12}$$

where x_i and y_i represent the ith elements of the vectors, $\boldsymbol{X}$ and $\boldsymbol{Y}$, respectively. N refers to the length of the vector (the number of the elements). The larger the value of r is, the more similar the two vectors are. The maximum of r is equal to 1. When $r = 1$, the two vectors of $\boldsymbol{X}$ and $\boldsymbol{Y}$ are completely similar. To find the optimum dilation, we can first calculate the approximate derivatives of original signal by using CWT method under different dilations and then compute the correlation coefficients of approximate derivatives under different dilations with the analytical derivative of pure signal. Finally, the dilation corresponding to the maximum of correlation coefficients is the optimum dilation. In fact, among all the approximate derivatives evaluated by CWT method under different dilations, the approximate derivative obtained under the optimum dilation is the most similar to the analytical derivative of pure signal. Using the simulated Gaussian signal (SNR = 20, 1024 data points, p, h, and σ are 0, 1, and 1, respectively) as an example, we calculate the approximate second derivatives via CWT method under the different dilations and the curve describing r with regard to different dilations is plotted in Figure 5.

In Figure 5, the optimum dilation is 19 and corresponding $r = 0.9952$. Correlation coefficient can as a whole give an

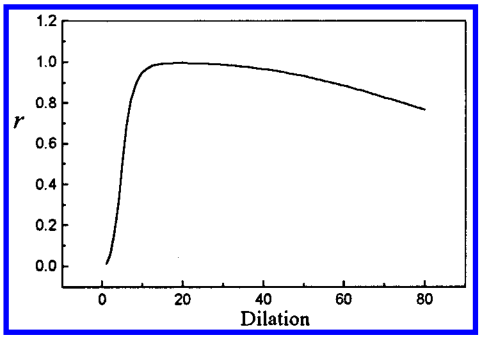

Figure 5. Correlation coefficients (r) of the analytical derivative of pure signal and approximate second derivative of original signal calculated by CWT method under different dilations. The original signal is simulated by Gaussian function (SNR = 20, 1024 data points, p, h, and σ are all same as the ones in Figure 2A). Pure signal denotes the signal without adding white noise.

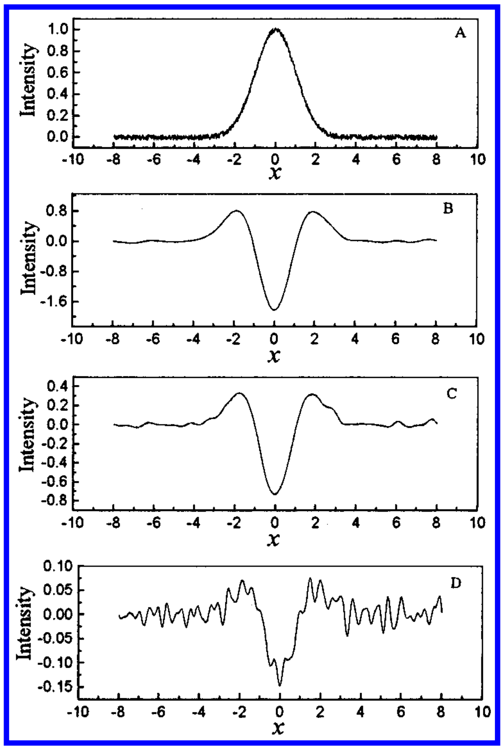

Figure 6. The original signal (A) (white noise added, SNR = 20, 1024 data points, and p, h, and σ are the same as in Figure 2A) and the corresponding approximate second derivatives evaluated by CWT method under the relative small dilation ($a = 9$) (D), the optimum dilation ($a = 19$) (C), and the relative large dilation ($a = 29$) (B), respectively.

estimation of similarity for the two vectors. In terms of the present example as shown in Figure 6, when the approximate derivative is obtained under the dilation (Figure 6D) less than the optimum dilation, the degradation of SNR can lead to reducing the similarity. In contrast, relative smooth can be achieved under the relative large dilation (Figure 6B) at the expense of the loss of resolution, but the increase of fwhm can cause the whole similarity reduced (fwhm of the approximate second derivative multiplied -1 is 1.35 under the optimum dilation and 1.38 under the relative large dilation). The approximate derivative calculated under the optimum dilation has high resolution as well as good SNR (Figure 6C). Therefore, correlation coefficient can be used as a criterion to indicate the compromise between high resolution and good SNR.

There are the different optimum dilations depending on different SNRs. Table 3 provides optimum dilations for a single peak (the first two derivatives of Gaussian function as example) in the case of different SNRs. In addition, the optimum dilation is also related to peak width and number of data points of the signal (see Table 4). When the peak width (σ) is fixed, the optimum dilation will become larger with the number of data points increasing. And the analogous relationship that the increase of the optimum dilation associated with peak width growing also exists in the case of unchanged number of data points.

For the overlapping signals in analytical chemistry, correlation coefficient can also be used to find the optimum dilation. We utilize the degree of separation to indicate the degree of overlap, which can be expressed as

$$R = \frac{p_2 - p_1}{\mathrm{FWHM}_1 + \mathrm{FWHM}_2} \tag{13}$$

where p_2 and p_1 refer to the positions of the first and the second peaks, respectively, and fwhm_1 and fwhm_2 denote the fwhms of the first and second peaks individually. The smaller R is, the greater the degree of overlap is. Figure 7 (parts A and B) shows the three overlapping peaks (described by Gaussian function) and the approximate second derivative under the optimum dilation, respectively. It can be seen from Figure 7 that the approximate second derivative obtained by CWT method under the optimum dilation has high resolution as well as good SNR.

In practice, however, the true derivative of pure signal is unknown. We can use the optimum dilation shown in Table 3 as reference and then progressively adjust dilations and simultaneously monitor the SNR and resolution of the derivative signal within the certain range of dilations. Finally, the selection of appropriate dilation still depends on the shape of the approximate derivative. Namely, "expert eye"[30] (i.e. an insight based on experience to know whether the shape of derivative is suitable for analyzing) is included in the process of selecting the appropriate dilation.

Generally, the selection of the suitable dilation need to rely on what the derivative technique is used for. For the signal severely corrupted by noise, it is important for signal analysis to improve the SNR and obtain useful information from the noisy signals, so the approximate derivative of the original data should be evaluated by CWT method under the larger dilations. Whereas, when the derivative is only employed for resolution enhancement, e.g. to resolve the overlapping signals, the approximate derivative should be calculated under the relative small dilation to ensure the little loss of resolution. However, at this time, the degradation of SNR has to be tolerated.

4. COMPARISON OF DIFFERENT METHODS

4.1. Comparison with Numerical Differentiation.[17] Numerical differentiation is an easy and convenient method to calculate the each order derivative of signal in analytical chemistry. However, since the rapid degradation of SNR accompanying with differentiation, numerical differentiation is difficult to straightforwardly apply to the real signal, especially for higher order derivative calculation except on the condition that smoothing is required. While CWT method

Table 3. Corresponding Optimum Dilations under the Different SNR for the First Two Derivatives

		SNR							
		5	10	20	50	100	300	500	1000
first derivative	optimum dilation	20	17	14	11	8	6	5	4
	correlation coefficient (r)	0.9953	0.9978	0.9990	0.9997	0.9998	0.9999	0.9999	0.9999
second derivative	optimum dilation	27	24	19	16	13	10	9	8
	correlation coefficient (r)	0.9843	0.9916	0.9952	0.9979	0.9989	0.9995	0.9997	0.9998

Table 4. Optimum Dilation Related to the Peak Width and the Number of Data Points[a]

		no. of data points		
		512	1024	1536
Peak Width (σ)				
0.5	optimum dilation	5	8	12
	correlation coefficient (r)	0.9968	0.9980	0.9984
1	optimum dilation	8	14	19
	correlation coefficient (r)	0.9986	0.9990	0.9991
1.5	optimum dilation	10	18	27
	correlation coefficient (r)	0.9990	0.9993	0.9993

[a] The approximate first derivative of simulated Gaussian function calculated by CWT method is used as example. SNR = 20, the parameters h and p are 1 and 0, respectively.

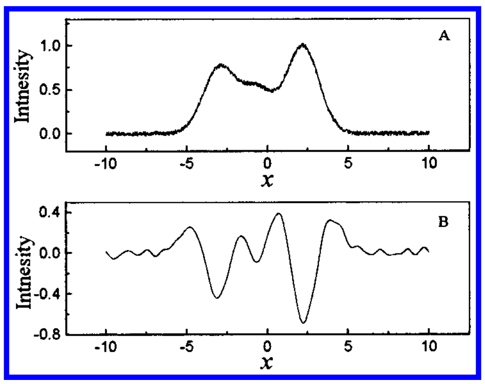

Figure 7. The original signal (A) (white noise added, SNR = 20, data point = 1024) and the corresponding approximate second derivative (B) calculated by CWT under the optimum dilation (a = 16). The peak heights of three Gaussian peaks are 1.5, 1, and 2, respectively. The parameters concerning the peak width are all equal to 1 for three Gaussian peaks. The first peak position is −3, and R, which refers to the difference of the peak positions, is equal to 0.5 for the first and the second peaks, and is 0.6 for the second and the third peaks, respectively.

is utilized for computing the approximate derivative of signal, smoothing is also performed simultaneously. Hence, using CWT method can conveniently obtain the high SNR of approximate derivative of original signal, which is very significant for the practical signal. Figure 8 illustrates the comparison between the numerical differentiation (left differentiation used in this work) and CWT method to calculate the first and second derivatives of signal (SNR = 300).

In Figure 8, the SNR of derivative signal evaluated by numerical differentiation without smoothing are very low (SNR of the first and second derivatives are about 4.0 and 0.04), especially for the second derivative, the information concerning the derivative signal is completely submerged by noise. While, as contrast, the approximate derivatives calculated by the CWT method have good line shape and comparatively high SNR (about 176.9 and 81.8 for the approximate first and second derivatives), and the information about the derivatives of signal can be easily obtained. From the Figure 8, it can be seen that the CWT method has a powerful capability of derivative calculation for the noisy signal.

4.2. Comparison with FT Method.[5,6] The derivative of signal can be obtained through the FT method. Generally, it can be done in three steps: the FT of the original signal is first performed and then multiplied by $(iy)^n$ in the FT domain. Finally, after the inverse FT is carried out, the derivative of original signal can be acquired. For three types of signals involved in this paper, since they are all symmetric, their odd or even order derivative can also be evaluated by using sine or cosine transform, respectively. Using the FT method can calculate the true derivative of signal, but, in practice, the signal is often influenced by a certain noise, so a smoothing function is required. Details referring to the derivative evaluated by the FT method can be found in refs 5 and 6.

For the noisy original signal as shown in Figure 8, the first and second derivatives via FT method are exhibited in Figure 9.

Seen from Figure 9, good results can also be achieved by using the FT method to calculate the derivative of signal. However, in the process of calculating the derivative via the FT method, because the complex number is introduced, the operation becomes relatively complicated as compared with the CWT method. Additionally, in the FT method, FT and inverse FT required can comparatively slow the speed of calculation. While, since the convolution operation is only used in the process of evaluating derivative via the CWT method, fast calculation and simple operation are remarkable advantages of the CWT method as compared with the FT method.

4.3. Comparison with the DWT Method.[17] This method adopts two different Daubechies wavelet functions ($\boldsymbol{D}_8$ and $\boldsymbol{D}_{18}$) to decompose the original signal, and the difference between two scale coefficients ($\boldsymbol{C}_{1,\boldsymbol{D}8,1}$ and $\boldsymbol{C}_{1,\boldsymbol{D}18,1}$) obtained by decomposition at the first resolution level is regarded as approximate first derivative. Any higher order derivatives can be evaluated by using the results secured from the lower derivatives as inputs for DWT calculation. More details concerning the DWT method can be found in ref 17. Since the scale coefficient obtained after smoothing and the number points of fwhm of scale coefficient are reduced by 50% at each DWT treatment (see eq 10), the SNR of the derivative calculated by the DWT method can be enhanced. However, because of one-half of the data points diminished for each derivative calculation, in the case of the relatively small number of data points of original signal (for example 100 points), higher than second order derivative cannot be evaluated owing to most of important information in the computation being removed. While using the CWT method cannot reduce the number of data points in derivative calculation, for a relatively small number of original data, the important information can be mainly retained under

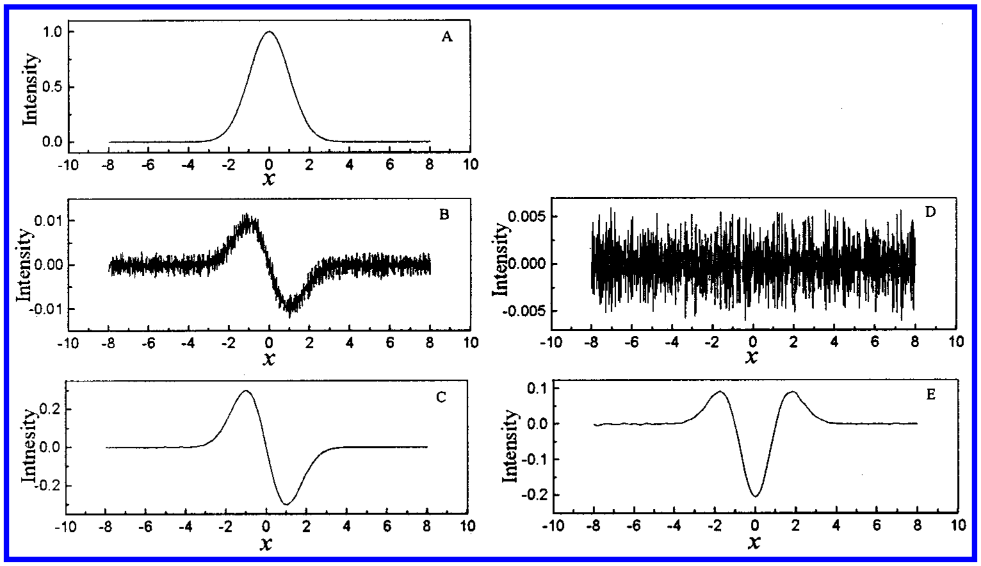

Figure 8. The original signal (A) (white noise added, SNR = 300, other parameters as Figure 2A) and the corresponding first and second derivatives obtained by different methods. (B) and (D) are the first and second derivatives of original signal calculated by numerical differentiation, respectively. (C) and (E) are the approximate first and second derivatives via CWT method under the optimum dilations (a = 6 and 11, respectively, for first and second derivatives), individually.

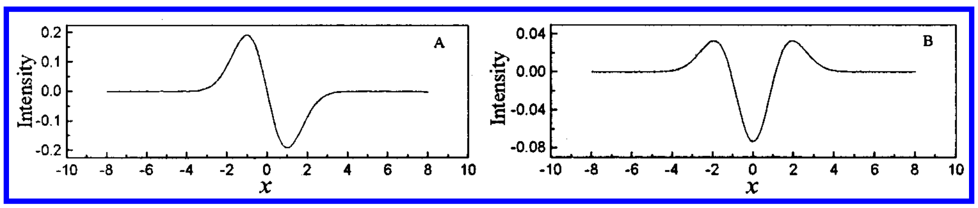

Figure 9. The first (A) and the second (B) derivatives of signal calculated by FT method. The original signal is the same as the one in Figure 8A.

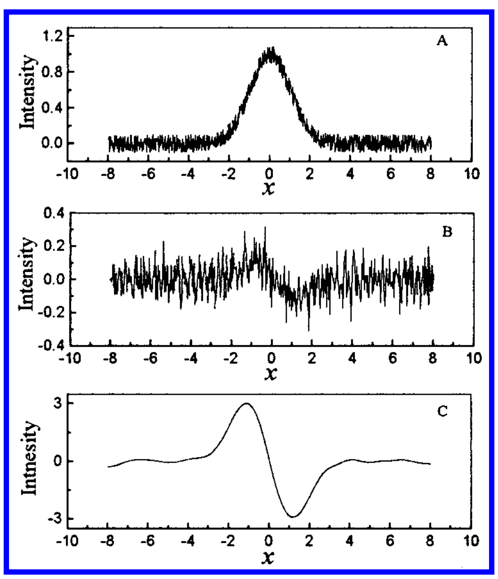

Figure 10. Comparison of first derivative calculated by CWT method (C) with the one evaluated by DWT method (B). The original signal is shown in (A) (synthesized Gaussian peak as example, white noise added, SNR = 5, other parameters concerning the signal are same as the ones in Figure 2A).

suitable dilation. Moreover, if the SNR of a signal is very low (e.g. SNR = 5, see Figure 10A), the DWT method cannot be used (see Figure 10B, the first derivative calculated by DWT method), whereas our proposed method can still be applied to the signal of a very low SNR (shown in Figure 10C, the first derivative calculated by CWT method under dilation = 32). Good results can be achieved only appropriately increasing the dilation, because the commonly observed degradation of SNR in conjunction with differentiation is not a necessary consequence and can be avoided if sufficient smoothing is employed.[2,11]

5. Application to Experimental Signal. To check the capability of our method to apply to the real signal, the overlapping square wave voltammogram of Cd(II) and In(III) is employed. Theoretically, using the same mathematical method in our previous work[32] can prove that when the $h_a^*(x)$ (see eq 7) is Gaussian function, for the single peak described by one of three types of signals in this paper, the position of the minimum (peak center position) of the approximate second derivative calculated by the CWT method is the same as the peak position (peak potential) of the original signal, and this relationship is irrelevant to dilation. For the overlapping peaks, the errors of the components' peak positions located by approximate derivative with regards to the dilations are very small when the dilation is small. In Figure 11, part A shows simulated overlapping peaks described by sech^2-function (SNR = 500), and the approximate second derivative calculated via the CWT method under dilation = 5 as an example is exhibited in Figure 11B. The relative errors of the peak positions are displayed in Figure 11C. a is from 5 to 38. When $a > 38$, the first peak position cannot be definitely determined and when $a < 5$, the SNR of approximate second derivative is relatively low.

As the dilation increases, the absolute value of Epeak1 also as a whole increases, while the absolute value of Epeak2

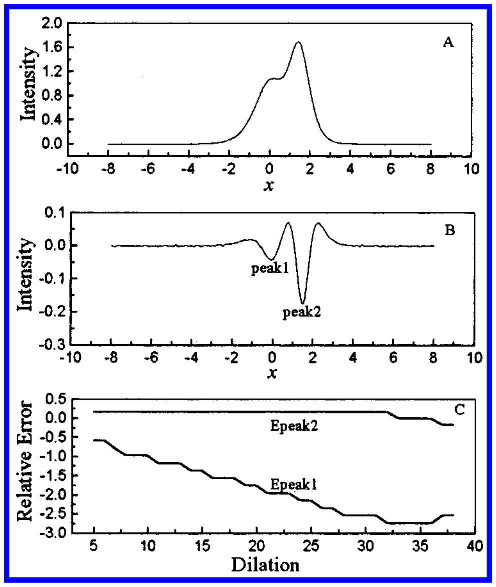

Figure 11. The simulated overlapping peaks described by sech^2-function (A), the approximate second derivative using CWT method under dilation = 5 as an example (B), and the relative errors of the peak positions determined by the approximate second derivative obtained via CWT method with regards to the different dilations (C). The white noise is added, the SNR of the overlapping peaks is 500, and the parameters of the first peak, p, h, and σ are 0, 1, and 1, respectively. The parameters of the second peak, h and σ, are 1.5 and 1.5, and p of the second peak depends on the degree of separation ($R = 0.5$). Peak 1 and peak 2 in (B) denote the positions of the first and the second peaks, respectively. Epeak1 and Epeak2 in (C) represent the relative errors of peak1 and peak2 determined by the approximate second derivative calculated by using CWT method.

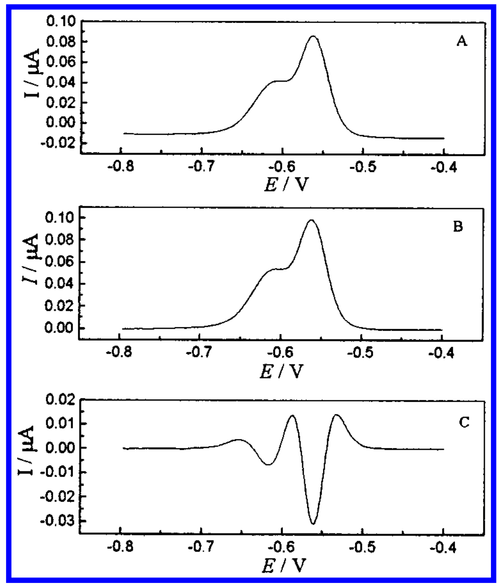

Figure 12. The overlapping square wave voltammogram (SWV) of Cd(II) and In(III) (A), the SWV (shown in (A)) modified by TRT method (B), and the approximate second derivative of modified SWV (shown in (B)) calculated by CWT method (C).

Table 5. Peak Potentials of Cd(II) and In(III) Obtained from the Approximate Second Derivative of the Overlapping SWV (Modified by TRT Method) Calculated by Using CWT and Their Relative Errors[a]

	E_p^0 (V)	E_p^{CWT} (V)	E_p(%)
Cd(II)	−0.615	−0.617	0.33
In(III)	−0.563	−0.561	−0.36

[a] E_p^0, as the theoretical potential value, denotes the peak potential of Cd(II) or In(III) which solitarily exist in solution. E_p^{CWT} indicates the peak potential obtained from the approximate second derivative calculated by using CWT method. E_p(%) refers to the relative error of peak potential.

almost keeps unchanged. When a is less than 10, the absolute value of Epeak1 is very small, within 1%. Therefore, the approximate derivative evaluated by CWT method can be used to locate the peak positions of the two components of original signal, which are significant for qualitative analysis. Because of the small difference in the half-wave potentials of Cd(II) and In(III), considerable overlap, shown in Figure 12A, exists in the SWV. From Figure 12A, it can be seen that the peak potentials of the two components are difficult to be detected accurately. In practice, since the starting and the ending points of the signal do not have the same value, the side-lobe problem will be encountered in the process of derivative calculation. So TRT method is adopted to avoid this problem (see Figure 12B). Figure 12C shows the second derivative of the overlapping SWV using the CWT method under the dilation = 5. As exhibited in Figure 12C, the peak potentials of the first and second components are easily located. Table 5 lists the peak potentials of Cd(II) and In(III) determined by the approximate second derivative calculated by CWT method.

Table 5 demonstrates that the peak potentials of Cd(II) and In(III) obtained from the approximate second derivative calculated by using CWT are very satisfactory. Hence, the approximate second derivative evaluated via the CWT method can be used as an efficient approach to detect the components' peak positions of the overlapping signals.

CONCLUSIONS

In this work, the method to calculate the approximate derivative through CWT is proposed. Compared with the true derivative (approximated by analytical derivative) of the signal, although the resolution of CWT method cannot reach the one of true derivative, the difference of resolution is little when the dilation is very small (e.g. dilation = 1). Since the smoothing function is introduced, the CWT method becomes more applicable than numerical differentiation for the practical signal. The remarkable advantages of CWT method as compared with FT method are fast calculation and simple operation due to only convolution operation used in the whole process of computation, and no complex numbers are introduced. Moreover, when an approximate derivative is calculated by using the CWT method, the number of data points cannot have 50% of reduction as compared with the DWT method; for a relatively small number of original data, the important information can be mostly retained under suitable dilation. In addition, for the signal corrupted severely (SNR = 5) by noise, our CWT method can still be applied. Only suitably adjusting the dilation, good results of approximate derivative can be achieved. Therefore, it can be said that the CWT method is an efficient approach to calculate the approximate derivative of the signal.

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