

Wavelet Transform: A Method for Derivative Calculation in Analytical Chemistry

Alexander Kai-man Leung,[†] Foo-tim Chau,^{*,†} and Jun-bin Gao[‡]

Union Laboratory of Asymmetric Synthesis and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P. R. China, and Department of Mathematics, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

A novel method based on wavelet transform is proposed in this work for approximate derivative calculation. An approximate first derivative of an analytical signal can be expressed as the difference between the two scale coefficients C_1 , which were generated from any two Daubechies wavelet functions. The optimal results for both synthetic and experimental data were obtained with the use of the Daubechies wavelet functions D_8 and D_{18} . Our work demonstrated that the new method can enhance the signal-to-noise ratio at higher order derivative calculation and retain all major properties of the conventional methods.

Derivative calculation is a very powerful technique in analytical chemistry for data analysis because it offers an apparent higher resolution of the differential data when compared with the original data.¹ It can be utilized for resolving spectra, sharpening peaks, eliminating unwanted background interference, and carrying out quantitative analysis.^{2,3} In analytical studies, applications of the derivative technique can be found in ultraviolet–visible (UV–vis) spectroscopy,^{3–5} chromatography,⁶ and potentiometric titration.⁷ Although the technique is a useful tool for data analysis, it has a major drawback in increasing the noise level in higher order derivative calculation.⁸ To perform higher order derivative calculation via numerical differentiation, noise reduction is usually performed between data from each order of successive derivative calculation.⁹ Commonly used methods of this kind include sliding

average, weighted average, smoothing by polynomial, and time averaging methods.³

Wavelet transform (WT) has attracted recent interest in applied mathematics for signal and image processing.¹⁰ This new mathematical technique has been demonstrated to be fast in computation with localization and quick decay properties in contrast to some existing popular methods, especially the fast Fourier transform (FFT). Since 1989, WT has been proposed for signal processing in chemical studies owing to its efficiency, large number of basis functions available, and high speed in data treatment. It has been applied successfully in flow injection analysis, high-performance liquid chromatography, infrared spectrometry, mass spectrometry, nuclear magnetic resonance spectrometry, UV–vis spectrometry, and voltammetry for data compression and smoothing.¹¹ At the end of 1997, more than 70 papers had been published on applying WT in chemical studies. In this work, WT is introduced as a novel method for approximate derivative calculation in processing analytical data. The major advantage of the proposed method is that it can perform numerical differentiation and noise reduction in the same calculation and can enhance the signal-to-noise ratio (SNR) for even higher order derivatives.

METHOD OF INVESTIGATION

Derivative Method. In analytical chemistry, the derivative method is mainly used for resolving spectra, locating peak maxima and minima in a spectrum, and detecting inflection points in the titration curve. Since it is very difficult to obtain a mathematical expression or function to represent an analytical signal \mathbf{X} ($=\{x_1, x_2, \dots, x_n\}$) or $f(x)$, the simplest way to perform derivative calculation on \mathbf{X} is by numerical differentiation.¹² The signal \mathbf{X} is usually divided equidistantly on the x -axis, and the first derivative of $\mathbf{X}^{(1)}$ is evaluated from the slope of two adjacent points by eq 1:

$$x_i^{(1)} \approx \frac{x_{i+1} - x_i}{\text{separation between } x_{i+1} \text{ and } x_i} \quad (1)$$

where i is a running index. In general, the average separation between x_{i+1} and x_i is chosen as the new coordinate on the x -axis

* To whom correspondence should be addressed. Telephone number: (852) 2766 5603. Fax number: (852) 2364 9932. E-mail address: bcftchau@polyu.edu.hk.

[†] The Hong Kong Polytechnic University.

[‡] Huazhong University of Science and Technology.

(1) Adam, M. J. *Chemometrics in Analytical Spectroscopy*; The Royal Society of Chemistry: Cambridge, UK, 1995; pp 54–62.

(2) Rojas, F. S.; Ojeda, C. B.; Cano Pavon, J. M. *Talanta* **1998**, *35*, 753–761.

(3) Talsky, G. *Derivative Spectrophotometry Low and High Order*; VCH: Weinheim, 1994.

(4) Howell, J. A.; Hargis, L. G. *Anal. Chem.* **1994**, *66*, 445R–461R.

(5) Hargis, L. G.; Howell, J. A.; Sutton, R. E. *Anal. Chem.* **1996**, *68*, 169R–183R.

(6) Strobel, H. A.; Heineman, W. R. *Chemical Instrumentation: A Systematic Approach*, 3rd ed.; John Wiley & Sons: New York, 1989; p 875.

(7) Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman Scientific & Technical: England, 1989; pp 574–578.

(8) Haswell, S. J. *Practical Guide to Chemometrics*; Marcel Dekker: New York, 1992; pp 264–267.

(9) Antonoy, L.; Stoyanov, S. *Anal. Chim. Acta* **1996**, *324*, 77–83.

(10) Wickerhauser, M. V. *Adapted Wavelet Analysis from Theory to Software*; A K Peter: Massachusetts, 1994; pp 361–423.

(11) Leung, K. M.; Chau, F. T.; Gao, J. B. *Chemom. Intell. Lab. Syst.*, in press.

(12) Meloun, M.; Militký, J.; Forina, M. *Chemometrics for Analytical Chemistry Volume 2: PC-Aided Regression and Related Methods*; Ellis Horwood: New York, 1994; pp 376–380.

to minimize the error of signal shifting. To obtain a higher order derivative $\mathbf{X}^{(m)}$, a step-by-step numerical differentiation is adopted:

$$x_i^{(n)} \approx \frac{x_{i+1}^{(n-1)} - x_i^{(n-1)}}{\text{separation between } x_{i+1}^{(n-1)} \text{ and } x_i^{(n-1)}}; \quad n \geq 1 \quad (2)$$

where n represents the derivative order. Other methods found in chemical studies for derivative computation include the use of Fourier transform¹³ and polynomial filters,¹⁴ such as the Savitzky–Golay polynomial filter.^{15–19}

A differentiated analytical signal has the following properties after the derivative calculation.³ (1) Peak maxima or minima give extrema in even derivatives and zero crossing in odd derivatives. (2) Peak maxima produce positive extrema in the $4n$ th derivative and negative extrema in the $(4n - 2)$ th derivative ($n = 1, 2, 3, \dots$). (3) Inflection points give zero crossing in even derivatives and extrema in odd derivatives. (4) As the derivative order increases, the number of extrema exceeds that of the fundamental curve because each inflection gives an additional extremum by differentiation. As a result, virtual extrema or satellites are observed, and they may superimpose extrema of neighboring analytical peaks in some cases. (5) As the derivative order increases, the full width at half-maximum (fwhm) becomes smaller and the peak becomes sharper. (6) Finally, the signal-to-noise ratio depends on the width or the number of points in the fwhm of the peak²⁰ with

$$\text{SNR}(n) \approx \frac{C(n)}{\text{fwhm}^n} \quad (3)$$

where C_n and n denote a constant and the derivative order, respectively. To improve the SNR for higher-order derivatives, digital signal smoothing is required between successive derivative order calculations. Commonly used methods include running averaging,²¹ least-squares polynomial smoothing,²² spline,²³ and Fourier transform.²⁴ In this work, WT is introduced as a new tool for approximate derivative calculation.

Wavelet Transform. WT involves decomposition of a signal function or vector (e.g., a spectrum of a chemical) into simpler, fixed building blocks at different scales and positions.²⁵ Different algorithms were proposed to achieve this purpose. In 1989, Mallat²⁶ introduced the multiresolution signal decomposition (MRSD) algorithm. Daubechies adopted this approach to construct families of compact supported wavelets and coupled it to

quadrature mirror filtering. This provides a general way for constructing orthogonal wavelet bases and leads to implementation of the fast wavelet transform (FWT) algorithm.

In WT, a signal \mathbf{X} or $f(x)$ is transformed linearly from its original domain to wavelet domain. The process is similar to applying the signal with Fourier transform (FT). However, in Fourier analysis, only sine and cosine functions can be adopted, which are localized in the frequency domain only. Fourier analysis has difficulty in processing a function having components that are localized in the time domain.²⁷ As a result, a small frequency change in FT produces changes everywhere in the time domain. Such difficulty can be overcome by wavelet functions, which are localized both in frequency or scale and in time via dilations and translations of the mother wavelet, respectively. This leads to a compact representation of large classes of functions and operators in the wavelet domain.

In WT treatment, all basis functions $\Psi_{a,b}(x)$ can be derived from a mother wavelet $\Psi(x)$ through the following dilation and translation processes:²⁸

$$\Psi_{a,b}(x) = a^{-1/2} \Psi\left(\frac{x-b}{a}\right) \quad a, b \in R \quad \text{and} \quad a \neq 0 \quad (4)$$

where a and b are respectively the scale and position parameters expressed in real number R . The basic idea of WT is to represent any arbitrary function $f(x)$ as a superposition of wavelets. Like FT, decomposition of \mathbf{X} with respect to the wavelet function series $\{\Psi_{j,k}(x)\}$ is described by the following formula:

$$f(x) = \sum_{j=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} c_k^{(j)} \Psi_{j,k}(x) \quad (5)$$

Therefore, the signal is represented by a set of coefficients $\{c_{j,k}\}$ in the wavelet domain. $\Psi_{j,k}(x)$ is defined by eq 4, with $a = 2^j$, $b = 2^j k$, and j as the resolution level. Implementation of the discrete WT developed by Mallat²⁹ has made the wavelet methods an effective tool for processing chemical data.

A wavelet basis is characterized by a particular set of numbers, called wavelet filter coefficients. The discrete WT treatment involves performing two related convolutions on a signal, with one being a low-pass filter $\mathbf{L} (= \{l_k\})$ and the other a high-pass filter $\mathbf{H} (= \{h_k\})$. The signal is then converted into two bases with equal size of

$$c_{j,k} = \sqrt{2} \sum_N c_{j-1,N} l_{N-2k} \quad (6)$$

and

$$d_{j,k} = \sqrt{2} \sum_N c_{j-1,N} h_{N-2k} \quad (7)$$

with $N = -\infty$ to $+\infty$ and k being the length of the wavelet filters.

(13) Horlick, G. *Anal. Chem.* **1972**, *44*, 943–947.

(14) Barak, P. *Anal. Chem.* **1995**, *67*, 2758–2762.

(15) Savitzky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627–1639.

(16) Steinier, J.; Termonia, Y.; Deltour, J. *Anal. Chem.* **1972**, *44*, 1906–1909.

(17) Madden, H. H. *Anal. Chem.* **1978**, *50*, 1383–1386.

(18) Gorry, P. A. *Anal. Chem.* **1990**, *62*, 570–573.

(19) Rzhetskii, A. M.; Mardilovich, P. P. *Appl. Spectrosc.* **1994**, *48*, 13–20.

(20) O'Haver, T. C.; Begley, T. *Anal. Chem.* **1981**, *53*, 1876–1878.

(21) O'Haver, T. C. *J. Chem. Educ.* **1991**, *68*, A147–A150.

(22) Willson, P. D.; Edwards, T. H. *Appl. Spectrosc. Rev.* **1976**, *12*, 1–81.

(23) Losev, A. J. *Electron Spectrosc. Relat. Phenom.* **1990**, *50*, c19–c23.

(24) Lee, O.; Wade, A. P. *Anal. Chem.* **1994**, *66*, 4507–4513.

(25) Dai, X. D.; Joseph, B.; Motard, R. L. In *Wavelet Application in Chemical Engineering*; Motard, R. L., Joseph B., Eds.; Kluwer Academic Publishers: Boston, MA, 1994; pp 1–32.

(26) Mallat, S. *IEEE Trans. Acoust. Speech Signal Process.* **1989**, *37*, 2091–2110.

(27) Cody, M. A. *Dr. Dobbs's J.* **1992**, *17* (4), 16–28; 100–101.

(28) Daubechies, I. *Ten Lectures on Wavelets*; SIAM Press: Philadelphia, PA, 1992.

(29) Mallat, S.; Hwang, W. *IEEE Trans. Inf. Theory* **1992**, *38*, 617–643.

The variables l_k and h_k in eqs 6 and 7 denote the coefficients of the low-pass and high-pass filters, respectively, with the following properties:

$$h_k = (-1)^k l_{-k} \quad (8)$$

with

$$\sum_k l_k = 1 \quad \text{and} \quad \sum_k h_k = 0 \quad (9)$$

In the above formulas, the outputs of \mathbf{L} and \mathbf{H} are referred to respectively the smoothed or scale coefficients (major information), $\mathbf{C}_j (= \{c_{j,k}\})$, and the differential or wavelet coefficients (detail information), $\mathbf{D}_j (= \{d_{j,k}\})$, of the signal data.

Different wavelet functions such as the Daubechies wavelet, Meyer wavelet, Coiflet wavelet, spline wavelet, orthogonal wavelet, local cosine basis, and others^{28,30} were proposed by various workers. Different bases face different tradeoffs, such as how compactly these functions are localized in space and how smooth they are. In chemical studies, both the Daubechies and spline wavelet functions have been widely used for data compression and smoothing. Here, the Daubechies family of wavelets D_{2m} , with m being any positive integer from 1 to 10, were chosen for approximate derivative calculation. The approximate first derivative of \mathbf{X} is assigned to be equal to the difference between two scale coefficients at the first resolution level (eq 10) as

$$\mathbf{X}^{(1)} \approx \mathbf{C}_{1,D_{2m}} - \mathbf{C}_{1,D_{2\tilde{m}}} \quad m \neq \tilde{m} \quad (10)$$

where D_{2m} and $D_{2\tilde{m}}$ represent any two Daubechies wavelet functions, with m and \tilde{m} being any positive integer. Any higher order derivative computation can be achieved by using the result obtained from the lower derivative calculation as an input for WT calculation. Then eq 10 is applied again to determine the approximate derivative at the next higher order. To generalize the approximate derivative calculation, such an iteration process can be expressed as follows:

$$\mathbf{X}^{(n)} \approx \mathbf{C}_{1,D_{2m}} - \mathbf{C}_{1,D_{2\tilde{m}}} \quad m \neq \tilde{m} \quad \text{and} \quad n \geq 1 \quad (11)$$

with $\mathbf{C}_{1,D_{2m}}$ and $\mathbf{C}_{1,D_{2\tilde{m}}}$ obtained from WT treatment of $\mathbf{X}^{(n-1)}$ at the first resolution level with Daubechies wavelet functions D_{2m} and $D_{2\tilde{m}}$.

EXPERIMENTAL SECTION

All data simulations and computations were carried out by using the wavelet toolbox, WTderiv, which was developed by us. It was coded in MATLAB Version 5.1 (The MathWorks Inc., MA) under Microsoft Windows 95 environment on a PC compatible with a 133 MHz Pentium processor.

To test the performance of the proposed WT algorithm in the real situation, it was applied to process an experimental chromatogram which was obtained through a HP 1050 HPLC-DAD

system equipped with a 20-mL sample loop and a HP LiChrosomb (200 × 4.6 mm i.d., 5 mm) C₁₈ RP column (Hewlett-Packard, Germany). The mobile phase was a mixture of methanol–water (30:70 v/v), and it was adjusted purposely to such a ratio that partial overlapping of the peaks was observed. The flow rate was 0.5 mL/min. The spectra were collected in the wavelength range from 250 to 600 nm with a spectral resolution of 2 nm. The data sets obtained were converted to ASCII text files with the macro program, 3DATA.MAC, developed by us, under the HP Chem-Station Revision A.03.01 environment (Hewlett-Packard, Germany). The macro can be used to extract a particular range of a spectrochromatogram for subsequent data analysis.

All solvents used were of HPLC grade quality (Lab-Scan, Ireland), and double deionized water (Millipore-Waters, MA) was utilized. Food dye samples of Red 2G and Allura Red, employed in this study, were provided by the Hong Kong Government Laboratory. A two-component sample solution consisting of 20 ppm of Red 2G and 20 ppm of Allura Red was prepared by dissolving them directly in the mobile phase. Ten milliliters of sample solution was injected into the HPLC-DAD system for analysis.

RESULTS AND DISCUSSION

Optimum Daubechies Wavelet Functions Selection. In this work, the proposed method for derivative calculation was tested with different simulated signals such as Gaussian function,³¹ Lorentzian function,³² and sigmoid function.³³ To apply FWT successfully on the analytical data \mathbf{X} , the signals needed to be extended periodically at the two extremes. However, in practice, the starting and ending points of the signal do not have a common value. As a result, side-lobe problem will be encountered and affect the signal reconstruction and derivative calculation. To solve such a problem, the translation–rotation transformation (TRT) method was adopted.^{34,35} The TRT algorithm involves subtraction of the data vector $\mathbf{C} (= \mathbf{X})$ by selected quantities \mathbf{B} to give a rotated array by

$$c_{0,j}^{\text{TRT}} = c_{0,j} - b_i \quad (12)$$

with

$$b_i = c_{0,1} + \frac{(c_{0,n} - c_{0,1})i}{n} \quad (13)$$

where i and n denote the running index and the length of the data, respectively. After the TRT treatment, both $c_{0,1}^{\text{TRT}}$ and $c_{0,n}^{\text{TRT}}$ have the same value. Then $\mathbf{C}_0^{\text{TRT}}$ is extended periodically at the two extremes in the following manner:

$$\{\dots, c_{0,n-1}, c_{0,n}, c_{0,1}, c_{0,2}, \dots, c_{0,n-1}, c_{0,n}, c_{0,1}, c_{0,2}, \dots\} \quad (14)$$

Details of the TRT method can be found in ref 35. Besides, FWT

(31) Meyer, V. R. *LC-GC Int.* **1994**, 7, 590–596.

(32) Fell, A. F. *UV Spectrom. Group Bull.* **1980**, 8, 5–31.

(33) Zupan, J.; Gasteiger, J. *Neural Networks for Chemists: An Introduction*; VCH: Weinheim, 1993; pp 23–28.

(34) Hayes, J. W.; Glover, D. E.; Smith, D. E.; Overton, M. W. *Anal. Chem.* **1973**, 45, 277–284.

(35) Chau, F. T.; Shih, T. M.; Gao, J. B.; Chan, C. K. *Appl. Spectrosc.* **1996**, 50, 339–349.

(30) Chui, C. K. *An Introduction to Wavelets*; Academic Press: New York, 1992; p 49.

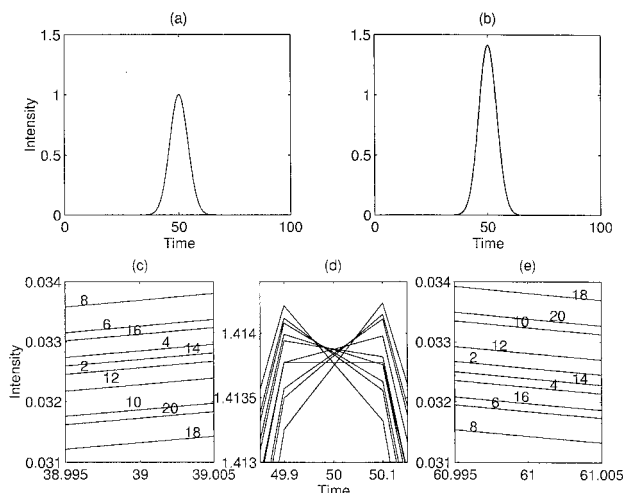


Figure 1. (a) Simulated Gaussian signal with 1000 data points which was generated by using the peak center (P_C), peak height (P_H), and peak width (P_σ) having values of 50, 1, and 4, respectively, for WT derivative calculation. (b) A spatial delay plot which was obtained by applying the TRT method and the Daubechies wavelet functions D_{2m} with $m = 1, 2, \dots, 10$ to the Gaussian signal as shown in (a). The lower part shows the magnified spatial delay plot (c) in the positive slope region, (d) near the peak maxima, and (e) in the negative slope region.

was developed to process data with a length of L equal to 2^p , with p being any positive integer. In practice, it is not easy for a chemical instrument to generate 2^p data exactly. To cope with this problem, the coefficient position retaining (CPR) method which was developed in our previous work³⁶ was used in the present wavelet calculations.

To apply eq 11 successfully for approximate derivative calculation, we needed to choose two different Daubechies wavelet functions. It was found on comparing $C_{1,D_{2m,n}}$ and $C_{1,D_{2\bar{m},n}}$ which were computed from two different Daubechies wavelet functions D_{2m} and $D_{2\bar{m}}$, respectively, that they had a similar shape and magnitude in the y -axes and a very small spatial shift was observed in the x -axes. These shifts of the two signals that followed by the subtraction process gives an approximate first derivative of the original signal.³ Figure 1b–e shows the spatial shifts of the scale coefficients $C_{1,D_{2m,n}}$ which were obtained by processing the Gaussian signal (Figure 1a) with D_{2m} , $m = 1, 2, \dots, 10$. The peak center (P_C), peak height (P_H), and peak width (P_σ) have values of 50, 1, and 4, respectively. Daubechies wavelet functions with m greater than 11 are not accurate and are not commonly used in signal processing. Table 1 shows the percentage shifts of the peak maxima and their associated values in the y -axis as compared with the original Gaussian function (Figure 1a). In most cases, the shifts were not greater than 0.2%. In Figure 1b,d, a special pattern of Daubechies wavelet functions was observed in the regions with position and negative slopes. In the positive slope region (Figure 1c), the D_{2m} functions were arranged in a special order with $2m = 8, 6, 16, 4, 14, 2, 12, 10, 20$, and 18 and in decreasing intensity at a given value on the x -axis. The opposite trend was observed in the negative slope region (Figure 1e). Besides, the same pattern was also discerned in the position slope

Table 1. Percentage of the Shift of the Peak Maximum of the Gaussian Signal As Shown in Figure 1b with WT Treatment When Compared with the Gaussian Peak (Figure 1a)^a

| Daubechies wavelet function used | position of the peak maximum | shift of the peak maximum (%) | maximum peak height |
|------------------------------------|------------------------------|-------------------------------|---------------------|
| original Gaussian peak (Figure 1a) | 50.0 | | 1.0000 |
| D_2 | 50.0 | 0.0 | 1.4138 |
| D_4 | 49.9 | −0.2 | 1.4140 |
| D_6 | 49.9 | −0.2 | 1.4141 |
| D_8 | 49.9 | −0.2 | 1.4142 |
| D_{10} | 50.1 | 0.2 | 1.4141 |
| D_{12} | 50.1 | 0.2 | 1.4139 |
| D_{14} | 49.9 | −0.2 | 1.4143 |
| D_{16} | 49.9 | −0.2 | 1.4141 |
| D_{18} | 50.1 | 0.2 | 1.4142 |
| D_{20} | 50.1 | 0.2 | 1.4142 |

^a The x -axes were rescaled to that of the original signal for comparison.

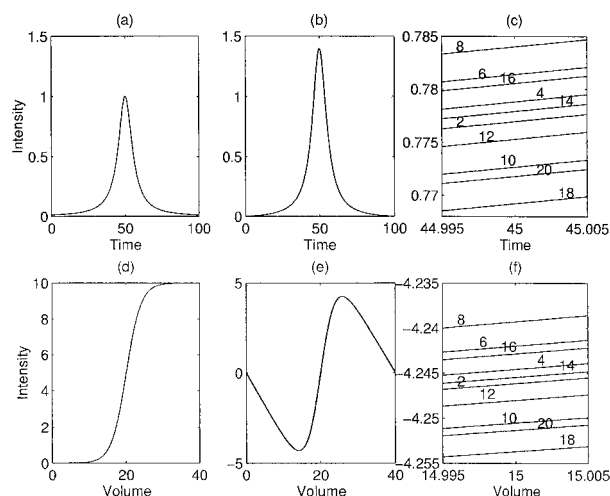


Figure 2. (a) Simulated Lorentzian function with 1000 data points which were produced by using $P_C = 50$, $P_H = 1$, and $P_\sigma = 2$, and (b) a simulated sigmoid function with 1000 data points for WT derivative calculation. The spatial delay plots (b and e) were obtained by applying the TRT method and the Daubechies wavelet function D_{2m} with $m = 1, 2, \dots, 10$ to the Lorentzian and sigmoid functions respectively, with the corresponding magnified spatial delay plots (c and f) at the positive slope region of (b) and (e).

regions when the Lorentzian and the sigmoid functions were used (Figure 2c,f). To perform approximate derivative calculation, we need to choose D_{2m} and $D_{2\bar{m}}$ from the upper and lower sections of Figure 1b. For example, the difference

$$X^{(1)} \approx C_{1,D_{16}} - C_{1,D_2} \quad (15)$$

can be adopted to evaluate the first derivative of X . In Figures 1c, 2c,f, it can be seen that a combination of D_8 and D_{18} should give the optimal result for the derivative calculation because it gives the largest difference or highest values for the first derivative. Besides, we have found that in this study the SNR value of the first derivative is the highest with the use of such a

(36) Leung, K. M.; Chau, F. T.; Gao, J. B.; Shih T. M. *Chemom. Intell. Lab. Syst.*, in press.

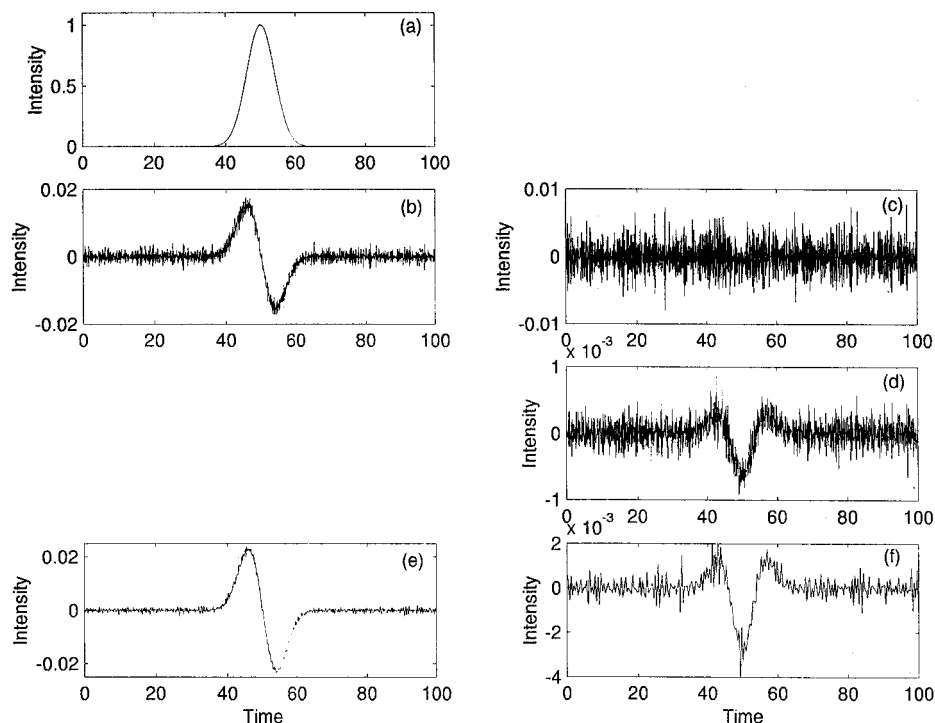


Figure 3. (a) Simulated Gaussian signal as shown in Figure 1a with white noise having a value of 0.001 (SNR = 500) for WT derivative calculation. (b and c) First and second derivatives plots, respectively, deduced from the conventional method without smoothing. (d) The result of the second derivative derived from the traditional method with smoothing. (e and f) The first and second derivatives obtained from the wavelet transform treatment with the use of the D_8 and D_{18} functions.

combination. In this approach, eq 11 can be rewritten as follows:

$$X^{(n)} \approx C_{1,D_{8,n}} - C_{1,D_{18,n}} \quad \text{and } n \geq 1 \quad (16)$$

with $C_{1,D_{8,n}}$ and $C_{1,D_{18,n}}$ being obtained from WT for $X^{(n-1)}$ at the lower derivative.

Comparison with the Conventional Derivative Calculation.

Traditionally, smoothing is required between each order of derivative calculation because unwanted noise is introduced into the derivative data. It involves a convolution of the data series with a smoothing function which consists of a set of weighting coefficients to control the increase of noise magnitude or SNR. Various smoothing methods proposed differ only in how the coefficients are calculated.² The Daubechies wavelet function is also a kind of filter. As different values of m are chosen, different sets of weighting coefficients are generated for data smoothing. There are two major advantages of employing WT for approximate derivative calculation. First, both derivative and smoothing calculations can be performed in the same calculation. Second, SNR can be improved in higher order derivative calculations as described below.

As stated before, the relative SNR of an unsmoothed derivative signal is inversely proportional to the power n of the width or the number points in the fwhm of the peak (eq 3). Table 2 shows typical values of the relative SNRs of unsmoothed differentiated Gaussian and Lorentzian signals.²⁰ If the width or the number of points in the fwhm of the peak can be reduced, the SNR can be improved. Figure 3b–f shows a comparison between the first and second derivatives of a Gaussian signal (Figure 3a) with white noise (SNR = 500) from conventional derivative calculation

Table 2. List of C Values for Derivative Orders from 0 to 8 As Used for Eq 3 in SNR Calculation of the Unsmoothed Derivative Gaussian and Lorentzian Signals

| derivative order n | constant C | |
|----------------------|-----------------|-------------------|
| | Gaussian signal | Lorentzian signal |
| 0 | 1 | 1 |
| 1 | 2.02 | 1.84 |
| 2 | 3.26 | 4.1 |
| 3 | 8.1 | 16.6 |
| 4 | 17.7 | 64 |
| 5 | 52 | 390 |
| 6 | 141 | 2204 |
| 7 | 478 | 17065 |
| 8 | 1675 | 132275 |

without smoothing and WT treatment with optimum D_8 and D_{18} functions. From the results of conventional derivative calculation, the SNR of the first derivative is about 4.9 (Figure 3b). However, if no smoothing is performed on the first derivative data before the second derivative calculation, the SNR of the second derivative is very low, and the signal is masked with the noise completely (Figure 3c). So, in the conventional derivative calculation, the first derivative data must be denoised or smoothed with a suitable filter prior to the second derivative calculation. Savitzky–Golay polynomial filter and Fourier transform are the denoising filters widely used in chemical studies. But, the former method requires a proper polynomial to be chosen, while the latter involves complex number calculation. When the first derivative was smoothed with a Savitzky–Golay 17-point filter, the SNR of the second derivative was about 2.4 (Figure 3d). On the other hand, the SNR of the first and second derivatives from our WT derivative

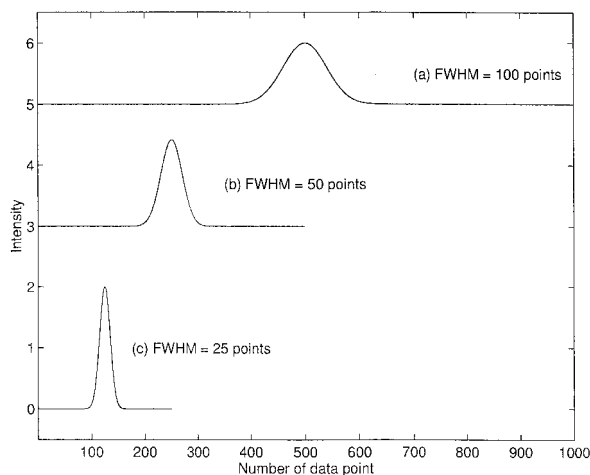


Figure 4. (a) Simulated Gaussian signal in Figure 1a with white noise having a value of 0.001 (SNR = 500) for WT derivative calculation. (b) The simulated Gaussian signal which was processed with WT at resolution level 1 with the D_8 wavelet function. (c) The simulated Gaussian signal which was obtained with WT at resolution 2 with the D_8 wavelet function.

calculation are about 11.4 and 3.5, respectively (Figure 3e,f). The x -axes on the first and second derivative plots of Figure 3e,f were rescaled for visual comparison. When compared with the conventional methods, no complex number was involved, and only simple matrix operations were required in our wavelet derivative calculation. By using WT derivative calculation, the data length of the first derivative is reduced by 50%. The result indicated that the proposed WT method is better than the conventional method.

Such an improvement on SNR using WT method over the conventional methods as mentioned above can be explained in view of the number of data points represented for the fwhm of the Gaussian peak adopted in this work (Figure 3a). Figure 4b,c shows respectively the number of points for fwhm at resolution levels 1 and 2 which correspond to two separated WT calculations on the original signal (Figure 3a). The fwhm values are reduced by 50% at each WT treatment. Therefore, the SNR in the WT derivative calculation is enhanced. By using WT, the data length of the first derivative is equal to 50% of the original data. This is because the first derivative was derived from the difference of the scale coefficients $C_{1,D_{8,1}}$ and $C_{1,D_{16,1}}$ (Figure 4b). Their data lengths are equal to 50% of that of the original data. In the second derivative calculation, the coefficients from the first derivative are used as inputs for WT computation. As a result, a further 50% of data length is reduced, and the data length of the second derivative is equal to 25% of the original data.

Since the proposed WT method was used to perform approximate derivative calculations in this work, most of the properties in the conventional method are retained. Figure 5 shows a comparison between the conventional and wavelet methods for a synthetic signal with overlapped peaks. The first derivative obtained from the traditional method was smoothed with the Savitzky–Golay 17-point filter for the second derivative calculation (Figure 5c). In the first derivative plots (Figure 5b,d), the two methods give the same results on the position of peak maximum and turning point. Moreover, in the second derivative plots (Figure 5c,e), both give similar results on the peak center position. The major difference between the two methods were

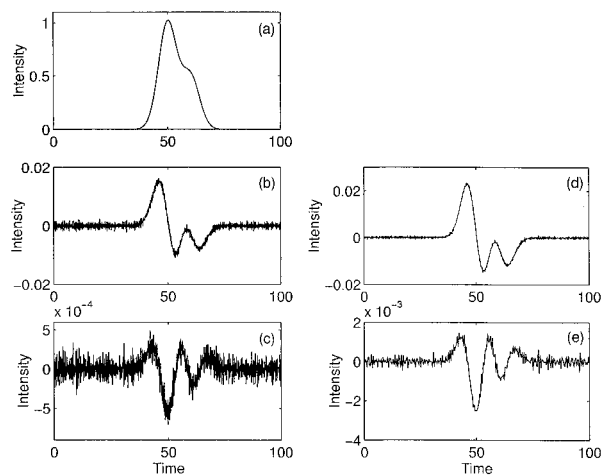


Figure 5. (a) Simulated signal with 1000 data points which were produced by overlapping peak 1 with $P_C = 50$, $P_H = 1$, and $P_o = 4$, and peak 2 with $P_C = 60$, $P_H = 2$, and $P_o = 4$, with white noise having a value of 0.001 (SNR = 500 for peak 1 250 for peak 2) for WT derivative calculation. The first derivative (b) and the second derivative (c) of the signal are obtained by using the conventional method. The first derivative (d) and the second derivative (e) of the signal are obtained by the proposed WT method using D_8 and D_{16} .

the SNR on the first and second derivatives and the number of coefficients of each derivative, as can be seen from the plots. Figure 6a shows the experimental chromatogram of a mixture of Red 2G and Allura Red obtained at 506.5 nm. The first and the second derivative plot of the chromatogram as derived from the proposed approximate WT derivative method are depicted in Figure 6b,c, respectively. These results are much smoother than those from the conventional method (Figure 6d,e). The second derivative plot as shown in Figure 6e was obtained by smoothing the data in Figure 6d with the Savitzky–Golay 17-point filter before numerical differentiation.

Owing to the down-sampling property of WT, the data length of the first and second derivatives (Figure 6b,c) are reduced by 50% and 75%. It may be unfair to compare the results on the quality of derivative calculation directly with those from the conventional method with smoothing only. So, data resampling was introduced in another calculation for comparison. In Figure 6f, the first derivative of the chromatogram was deduced by applying the conventional method to a reduced data set of Figure 6a as obtained by selecting alternative data points. The first derivative was then denoised with the Savitzky–Golay 17-point filter. The second derivative (Figure 6g) was obtained similarly to the first derivative with data resampling. By comparing Figure 6f,g with the corresponding data from the proposed WT algorithm, similar results are obtained. Yet plots from the proposed WT method still have a higher SNR value.

Limitations of the Proposed Method. Wavelet transform is a powerful method for approximate derivative calculation, as demonstrated in this work. However, the proposed method suffers from some limitations. First, the derivative order depends on the number of data points available in the original signal. If the number of data points is too small, for example 100 points, then only the first two derivatives can be obtained with acceptable results, and the higher derivative order calculations are impossible. It is because the number of data point diminishes by 50% for each

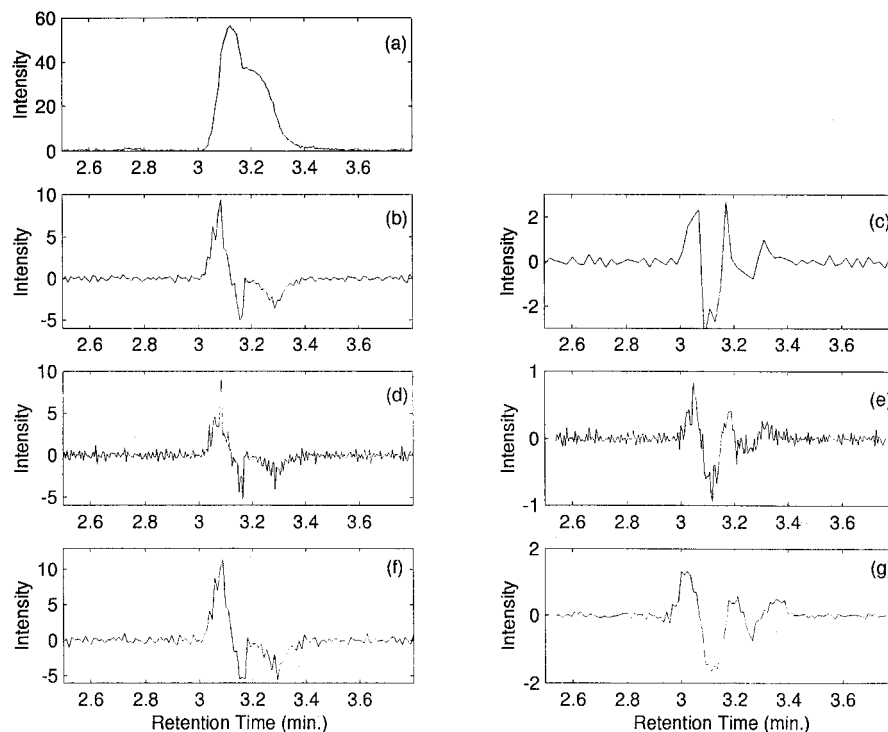


Figure 6. (a) Experimental chromatogram of a mixture of Red 2G and Allura Red recorded at 506.5 nm. (b) The first and (c) the second derivative of the chromatogram as deduced from the proposed WT method. (d) The first and (e) the second derivative of the chromatogram through numerical differentiation with Savitzky–Golay denoising treatment. (f) The first and (g) the second derivative of the chromatogram through numerical differentiation with resampling and Savitzky–Golay denoising treatment.

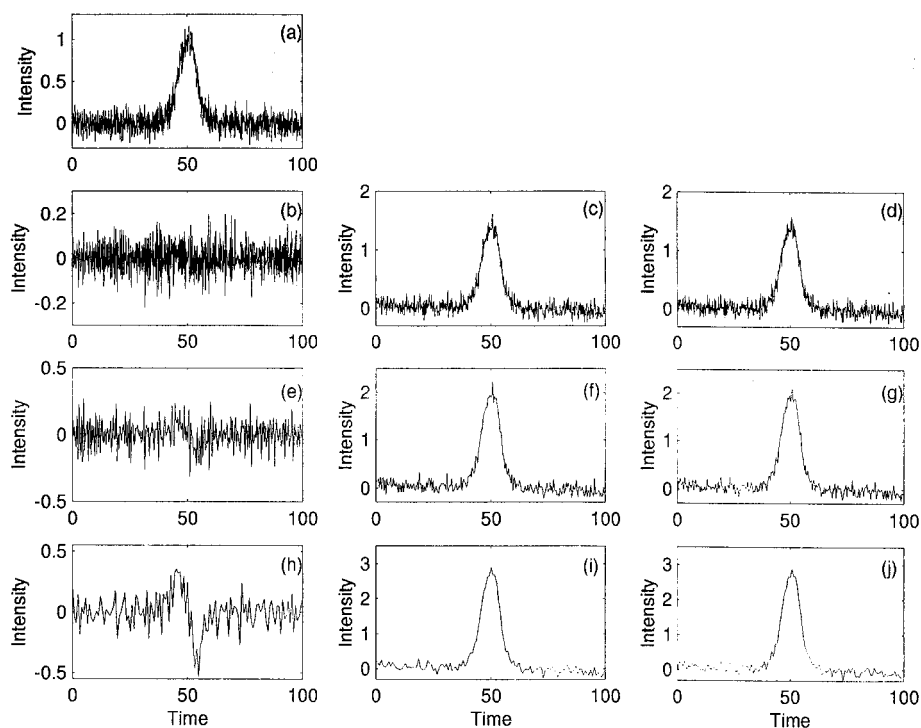


Figure 7. (a) Simulated Gaussian signal in Figure 1a with white noise having a value of 0.10 (SNR = 5) for WT derivative calculation. (b) The first derivatives of (a) as obtained with the proposed method and the corresponding scale coefficient C obtained by using (c) D_8 and (d) D_{18} wavelet functions at resolution level 1. (e) The first derivatives of (a) as obtained with the proposed method and the corresponding scale coefficient C obtained by using (f) D_8 and (g) D_{18} wavelet functions at resolution level 2. (h) The first derivatives of (a) as obtained with the proposed method and the corresponding scale coefficient C by using (i) D_8 and (j) D_{18} wavelet functions at resolution level 3.

derivative order computation as mentioned previously (Figure 4). If the higher order derivative is conducted on this reduced data set, most of the important information will be removed in the

computation. To resolve this problem, data interpolation such as linear interpolation, polynomial interpolation, and spline interpolation methods could be employed to increase the number of data

points in each derivative calculation back to the original value.¹ However, the interpolation method will inevitably introduce a certain amount of noise to the data. Second, if the SNR of the signal to be processed is very low, our approximate derivative method cannot be used (Figure 7). Hence, we recommend using the scale coefficients C at higher resolution level for derivative calculation in this case. Figure 7a gives a noisy Gaussian signal. As shown in Figure 7b, a very noisy first derivative plot was obtained from Figure 7a when the calculation was performed at resolution level 1. This is because a certain portion of relatively high frequency signals still remains in the scale coefficients C_{1,D_8} and $C_{1,D_{18}}$ at resolution level 1 (Figure 7c,d). They come from the middle frequency range in the original signal which cannot be filtered completely with the high-pass filter H in the wavelet treatment for just one pass. They are regarded as noise in the scale coefficients and suppress the first derivative signal in this case. To improve this situation, we need to treat the signal with WT at a higher resolution level and utilize the scale coefficients C at this resolution level for approximate derivative calculation. Figure 7e,h shows the results of the first derivative as obtained at resolution levels 2 and 3, respectively, using the proposed WT method. It can be seen that at these higher resolution levels, more relatively high frequency signals are removed from the scale coefficients (Figure 7f,g,i,j). Then, a more noise-free first derivative plot can be obtained. As compared with the conventional method, peak shifting was also observed in higher order derivative plots. The shift will slightly affect the accuracy of some peak parameters, such as peak center position.

Future Perspectives. Presently, most modern analytical instruments such as UV-vis or IR spectrometers have a routine to output a derivative spectra. Analog (electronic) and digital (numeric) differentiation were commonly used in these instruments.³ Up to now, only two works were reported on incorporating WT in an analytical instrument for chemical data processing and analysis.^{37,38} We think that WT will become a popular method for data analysis in chemical studies and our proposed method can be incorporated in many types of analytical instruments with the help of newly developed technology in the future.

CONCLUSION

In this work, wavelet transform was proposed as a tool for approximate derivative calculation. The difference between the scale coefficients as obtained from WT treatment at resolution level 1 using the Daubechies wavelet functions D_8 and D_{18} was equal to the approximate first derivative of a particular signal. The result indicated that the new method could enhance the signal-to-noise ratio even at higher derivative order calculation without

extra effort in data manipulation. Additionally, both the derivative and smoothing calculations could be combined in a single step. When compared with the conventional derivative methods, most of the properties found in these methods are retained in the new method.

ACKNOWLEDGMENT

This work was supported by Research Grant Council (RGC) of Hong Kong Special Administrative Region (Grant No. HKP 45/94E) and the Research Committee of the Hong Kong Polytechnic University (Grant No. 350/529).

GLOSSARY: LIST OF NOTATIONS ADOPTED IN THIS WORK

| | |
|------------------------|--|
| a | scale (dilation) parameter in WT |
| b | position (translation) parameter in WT |
| b_i | coefficients generated from TRT treatment. |
| $c_{j,k}$ | k th scale coefficient obtained at resolution level j in the WT computation |
| $c_{0,i}^{\text{TRT}}$ | 0th scale coefficient obtained at resolution level 0 after the TRT treatment |
| $d_{j,k}$ | k th wavelet coefficient obtained at resolution level j in the WT computation |
| h_k | k th coefficient of the low-pass filter H for WT |
| l_k | k th coefficient of the high-pass filter L for WT |
| (j) | j th resolution level in the WT computation |
| x_i | i th data coefficient of the analytical signal |
| i, j, k, m, p | positive integers |
| n | length of the analytical signal |
| C_j | scale coefficients generated at resolution level j in WT |
| $C_{1,D_{2m,n}}$ | scale coefficients at resolution level 1 which are derived from the Daubechies D_{2m} wavelet function for the n th-order approximate derivative calculation |
| $C(n)$ | constant for the n th-order derivative |
| D_j | wavelet coefficients generated at resolution level j in WT |
| $D_{2m}, D_{2\bar{m}}$ | daubechies wavelet function |
| fwhm | full width at half-maximum |
| SNR(m) | signal-to-noise ratio for the m th-order derivative |
| $X, f(x)$ | analytical or original signal |
| $X^{(m)}$ | m th-order derivative of the analytical signal X |
| $\Psi_{a,b}$ | Mother wavelet function |

Received for review April 2, 1998. Accepted September 28, 1998.

AC9803737

(37) Shew, S. L. U.S. Patent 5,436,477, July 25, 1995; Government Printing Office: Washington, DC, 1995.

(38) Yan, L.; Mo, J. Y. *Chin. Sci. Bull.* **1995**, *40*, 1567–1570 (in Chinese).