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Study on Resolution and Analysis Method of Stripping Voltammetric Overlapped Peaks

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For overlapped peaks in stripping voltammetric wave, put forward a post-processing analysis method which made mathematical theory combined with computer technology, namely a resolution algorithm based on nonlinear fitting. The method on the basis of the existing instrument and some experimental data, depend on certain mathematics theory, with the help of the computer powerful processing ability, to mathematical analysis the overlapped peaks data. It process mathematical decomposition aim to separate the overlapped peaks which instrument can't separate and decompose the overlapped peaks into each independent child-peak shape. By analyzing the peak position, peak height, peak width and peak area of independent child-peak, to estimate information such as the nature and content of the corresponding component. Simulation result and experiments demonstrate that the novel technique beats stripping voltammetric overlapped peaks, experimental hardware requirements relatively not so strict and the resolution effect present better performance.

1. Introduction

For the problem of multi-element measurement with serious influence each other, there are three kinds of ways to solve, one is to separates completely using chemical method before measurement, this method is considerably consuming time laborious and money, which was confirmed (KOMATSUBARA M, et al. (2009) and ZHANU Xiao-Xing, et al. (2010)); another with the aid of mathematical theory and computer technology to mathematical analysis the overlapped peaks data obtained from the existing instruments. The mathematical analysis method needs certain experimental data, the relative ease of experimental hardware requirement, and with the development of computer technology, some complex mathematical theory is no longer difficult to implement in computer, in under the guidance of certain mathematical theory, with the aid of computer powerful operation ability, can resolve overlapped peaks in high accuracy and achieves the accuracy requirement needed for the detection and analysis which was confirmed (Li Yuan-Lu, Yu Sheng-lin and Zheng Gang (2007); LUO Li-qing and ZHANG Xiu-chun (2008)).
There are many analysis methods for overlapped peaks, from the perspective of signal processing; overlapped peaks can be divided into time domain, frequency domain analysis and time-frequency analysis. Wavelet analysis is a time-frequency analysis method most commonly used, need to choose the right mother wavelet function, because of the difference of parameter selection, the processing result will be different which was confirmed (RAMAKRISHNAN S and SELVAN S (2007)); Curve fitting technique is a more effective method in time domain analysis; according to the peak shape to create a certain mathematical model and decomposes the original peaks which was confirmed (SHI You-ming, et al. (2008)) In addition to the above method, more representative processing methods of overlapped peaks also have neural network, factor analysis, Kalman filtering, signal differential which was confirmed (ZEMBATY Z (2009); GUTIERREZ J M (2008)).
Sena, et al. (2010) reported the self-simulation curve fitting and iterative curve fitting method, compared performance of the proposed method with curve fitting in the resolution of chromatographic peaks, with regard

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to the serious overlapping chromatographic peaks which the retention volume is slightly different, or keep the same volume but peak shape different, iterative method of nonlinear simultaneous equations can obtain good results. Kalman filtering is widely used in resolution of overlapped peaks from multi-component linear sweep voltammetric and square wave voltammetric, in addition to the overlapped chromatographic and overlapped spectra signal resolution which was confirmed (ZHANG Xiu-qi, et al. (2002)). Using the first order differential method, Slepchenko et al. (2004) reported that Mosaic multi-wavelength overlapped chromatographic peak was separated, and achieved better resolution results. Yong-qing zhang, et al. (2003) reported the spline convolution method to distinguish overlapped voltammetric signal, by this method to deal with many kinds of overlapped electrochemical signals obtained from cyclic voltammetric peak and adsorptive stripping voltammetry, etc, and achieved better resolution results.

For stripping voltammetric overlapped peaks, we choose using nonlinear data fitting technology to progress overlapped peak signal resolution; Through established the right mathematical model, analysis overlapped voltammetric peak resolution algorithm based on curve fitting, and processed simulation and experiment analysis.

2. Overlapped peaks resolution based on curve fitting

As a very powerful data processing method, Curve fitting can to process discrete data with function model easily, and applied to noise elimination, signals identification (overlapped signals resolution), etc. which was confirmed (ZHAO Lin, et al. (2011)). It means that had two or more independent mathematical function, through optimize and solve the undetermined parameter in the mathematical model (function), and get the optimal parameter estimates, then confirm the optimized mathematical function of each independent signal, and finally, achieve the resolution of overlapped signals into individual signals and obtain the relevant information of each signal which was confirmed (HU Yao-gai, et al. (2012)).

A. The establishment of mathematical model for voltammetric peak

Stripping voltammetric peak can be simulated by gaussian function, lorenz function or combination function with gaussian and lorentz function. Here, we adopt gaussian function as a simulation on a single voltammetric peak, and for other simulation function forms, the corresponding algorithm can be derived by adopting the idea of completely similar.

The simulation functions for stripping voltammetric peak is as follows:

$$y = \sum_{n=1}^{n} \frac{d}{dx}\left\{\frac{A_i}{1+\exp[B_i(x-C_i)]}\right\} \tag{1}$$

In the above type, the height of the peak shape is controlled by parameter A; half peak width is controlled by parameter B; parameter C decides the peak position; and parameter n represents the number of independent peaks contained in the overlapped peak.

Single peak gaussian function expression is as follows:

$$\mathrm{g(x)} = \mathrm{Ae}\frac{-(\mathrm{x}-\alpha)^2}{2\sigma^2} \tag{2}$$

It can be known from above type, if the peak type is known, as long as gets the three parameters, namely parameter A(peak's intensity), μ (peak's position) and σ(peak's width), and the complete information about the gaussian peaks can be obtained.

Towards the overlapped peak composed by two adjacent independent peaks, its separation degree can be represented as:

$$\mathrm{R_g} = 2(\mathrm{v_2} - \mathrm{v_1})/(\mathrm{W_1} + \mathrm{W_2}) \tag{3}$$

In above type, v_1 and v_2 as peak position; and W_1 and W_2 as half peak width of the two independent peak.

Separation degrees and overlapped degrees belong to the inverse relationship, namely, the smaller separation degree means the two peaks with serious overlapped, and resolving the overlapped peaks successfully will be difficult; Conversely, bigger separation degree represents smaller overlapped degree, and resolving the overlapped peaks is easier to success.

The so-called half peak width refers to that when the peak height reach halfway its peak width. By the formula (6-2), gaussian peaks’ half peak width can be inferred that as follows:

$$w = 2\sqrt{-2ln0.5}\sigma \approx 2.3548\sigma \tag{4}$$

Combined with the formula (6-3) can be further concluded that the gaussian peak - gaussian peaks separation degree as follows:

$$\mathrm{R_{gg}} = \frac{\alpha_2-\alpha_1}{1.1774(\sigma_1+\sigma_2)} \tag{5}$$

Based on gaussian function, the overlapped peaks simulation signal model can be represented as:

$$f(x) = f_1(x, A_1, \alpha_1, \sigma_1) + f_2(x, A_2, \alpha_2, \sigma_2) + \cdots + f_N(x, A_N, \alpha_N, \sigma_N) = \sum_{i=1}^{N} A_i e^{\frac{-(x-\alpha_i)}{2\sigma_i^2}} \quad (6)$$

Among above, N expresses the number of independent peaks.

Under discrete statement, the error-squares-sum function of any point in the actual measurement $f^*(j), j = 1,2, \ldots L$ with the fitting value $f(j)$ can be represented as:

$$E = \frac{1}{2}\sum_{j=1}^{L}(f^*(j) - f(j))^2 \quad (7)$$

To solve optimal function $f(x)$, actually is to seek the minimum of objective function E according to the principle of least squares.

By the formula (6), (7) shows that the objective function E is nonlinear multi-function about Ai,αi,σi(i=1,2,…,N), to seek it's extreme, analytic method and numerical iteration can be usually used, but the former cannot calculates the extreme directly, so the numerical iteration is used here.

According to the formula (7) in this article, due to the derivative of the objective function exists and easy to calculate, so here adopts the derivative method to evaluate the optimal solutions.

Formals partial derivative with A_i, μ_i, σ_i for Objective function E, and formulas as follows:

$$\frac{\partial E}{\partial A_i} = \sum_{j=1}^{L}[f(j) - f^*(j)]e^{-(j-\alpha_i)^2/2\sigma_i^2} \quad (8)$$

$$\frac{\partial E}{\partial \alpha_i} = \sum_{j=1}^{L}[f(j) - f^*(j)]e^{-(j-\alpha_i)^2/2\sigma_i^2}\frac{A_i(j-\alpha_i)}{\sigma_i^2} \quad (9)$$

$$\frac{\partial E}{\partial \sigma_i} = \sum_{j=1}^{L}[f(j) - f^*(j)]e^{-(j-\alpha_i)^2/2\sigma_i^2}\frac{A_i(j-\alpha_i)}{\sigma_i^3} \quad (10)$$

To guarantee the stability of the iterative convergence, inertia gene k and step length adjustment parameter p are introduced into optimization procedure, the after adjustment formulas as follows:

$$\Delta A_i(t+1) = -p_A\frac{\partial E}{\partial A_i} + k_A\Delta A_i(t) \quad (11)$$

$$\Delta\alpha_i(t+1) = -p_\alpha\frac{\partial E}{\partial \alpha_i} + k_\alpha\Delta\alpha_i(t) \quad (12)$$

$$\Delta\sigma_i(t+1) = -p_\sigma\frac{\partial E}{\partial \sigma_i} + k_\sigma\Delta\sigma_i(t) \quad (13)$$

In above type, $\Delta A_i(t), \Delta A_i(t+1)$ is iterative adjustment quantity of at the moment of $t, t+1$; p_A, k_A is the step change size and inertial factor of A_i respectively. The meanings of $\Delta\alpha_i(t)$, $\Delta\alpha_i(t+1), p_\alpha, k_\alpha$; $\Delta\sigma_i(t), \Delta\sigma_i(t+1)$, p_σ,k_σ parameters in the same way.

B. Resolution algorithm of overlapped peaks based on curve fitting

In the process of curve fitting, the selection of initial value of A_i, α_i, σ_i (*i=1,2,…,N*), p and k parameter, have important influence in iterative efficiency and fitting results.

Firstly, give initial values to $A_i$and σ_i, which are random numbers from the scope of (0, 1), α_i is the estimated values from the scope of (1, L), if all the experimental data can be convergent, then such value is reasonable.

Besides, inertial factor k and step length adjustment parameter p, large step p can improve the convergence speed, but too large will make the convergence process produces shock phenomenon, cause only local optimal solution, and cannot get the stable and global optimal solution;

However, too small step length p will reduce the convergence efficiency, slow convergence and increase the number of iterations, increase data computation, lead to converge into local optimum easily and can't jump out.

So, in the actual application, choose the appropriate inertia factor k and step length adjustment parameter p is crucial. Experiments show that selection step p between 0.1-0.6, k from the range of 0.03-0.3, convergence effect is ideal.

Using the curve fitting technology to process overlapped peaks resolution, its basic steps as follows:

(1) To estimate the fitting iterative maximum times T_{max}, in order to avoid the blindness of human choice.

(2) Find peak position; determine the number of independent peaks. Using the generic algorithm can realize the determination of the maximum and non-maximum overlapped peak site, which expands comparing radius and enlarges peak intensity threshold gradually.

(3) Optimize peak intensity and peak width. Optimize the peak height and adjust peak width, to minimize the fitting error.

(4) Reconstruction and peak resolution. In each step of the above, it is the basic iterative computations that using the formulas (7) to (13) to seek the error function E and calculate partial derivatives for A_i, μ_i, σ_i respectively.

3. The simulation analysis of overlapped peaks resolution

Here, a mixed-peaks simulated signal is constructed by combination of multi-Gaussian peak signals, and ensures that contain overlapped peaks, and on this basis, appropriate to add a certain amount of noise signal, then to process the mixed-peaks simulated signal using the curve fitting resolution algorithm, aim to verify the effectiveness of the algorithm.

A. Construction of mixed-peaks simulated signal

The mixed-peaks simulated signal composed with 6 gauss peaks and a random noise signal, its expression as follows:

$$f(x) = f_1(x, A_1, \alpha_1, \sigma_1) + \cdots + f_6(x, A_6, \alpha_6, \sigma_6) + Noise(x) = 3e^{-\frac{(x-30)^2}{2\times5^2}} + 5e^{-\frac{(x-60)^2}{2\times3^2}} + 2e^{-\frac{(x-100)^2}{2\times6^2}} + 2e^{-\frac{(x-120)^2}{2\times6^2}} + e^{-\frac{(x-180)^2}{2\times8^2}} + 1.5e^{-\frac{(x-210)^2}{2\times6^2}} + Noise(x), (x = 1,2,\ldots,250) \quad (14)$$

The wave spectrogram diagram of mixed-peaks simulated signal as shown in the below figures. Figure 1 shows scatter diagram of mixed-signal; Figure 2 shows the after preprocessing peak charts diagram of mixed-signal.

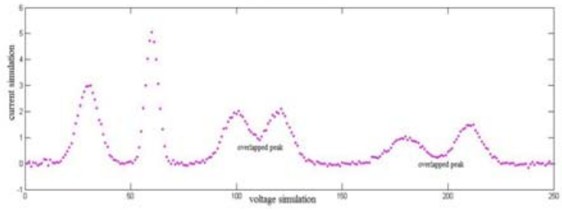


Figure 1: Scatter diagram of original signal

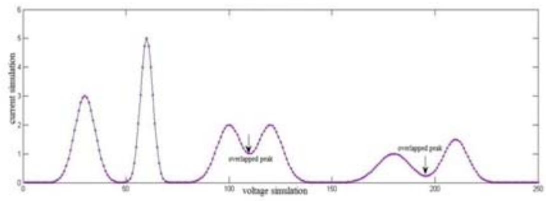


Figure 2: The after preprocessing peak charts diagram

In figure 2, each peak shape was assigned a number from left to right in turn; it is clear that No. 1 and No. 2 were independent peak shapes, but overlapped peaks appeared at the group of No. 3 and No. 4, and group of No. 5 and No. 6; according to the formula (5) to calculate the degree of two groups overlapped peaks, respectively as follows:

$$R_{34} = \frac{\alpha_4 - \alpha_3}{1.1774(\sigma_3 + \sigma_4)} \approx 1.4150 \qquad R_{56} = \frac{\alpha_6 - \alpha_5}{1.1774(\sigma_5 + \sigma_6)} \approx 1.8199$$

B. The simulation results and discussion for peaks resolution

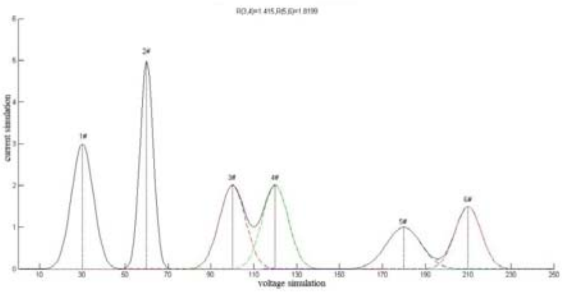


Figure 3: Separation results of R(3,4)=1.415,R(5,6)=1.8199

Using resolution algorithm of overlapped peaks and according to the prior knowledge set some parameters got the peaks resolution results as below figure 3, the corresponding error statistics data shown in table 1.

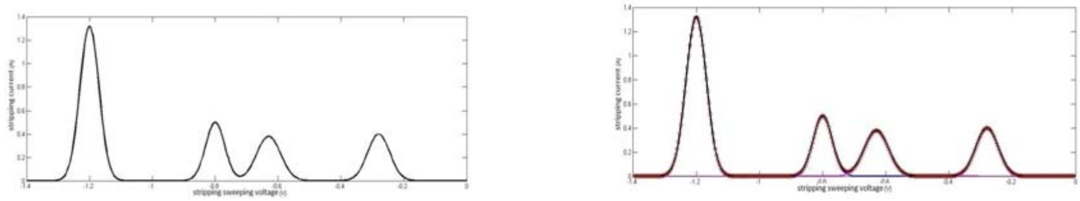
Table 1: Error statistics of Separation results (R(3,4)=1.415,R(5,6)=1.8199)

No.	Peak Height A			Peak Position α			Peak Width σ		
	Truth Value	Fitting Value	Relative Error %	Truth Value	Fitting Value	Relative Error %	Truth Value	Fitting Value	Relative Error %
1#	3	2.9273	2.42	30	30	0.00	5	5.0608	1.22
2#	5	4.8965	2.07	60	60	0.00	3	3.0403	1.34
3#	2	1.9102	4.49	100	100.8	0.80	6	6.2549	4.25
4#	2	1.8754	6.23	120	119.4	0.50	6	5.7304	4.49
5#	1	0.9666	3.34	180	179.6	0.22	8	7.8082	2.40
6#	1.5	1.4518	3.21	210	210.88	0.42	6	6.1652	2.75

Through the above data it can be seen that the maximum error appears in the position of No. 3 and No. 4, followed by No. 5 and No. 6. The relative errors of peak height, peak position and peak width parameters were 6.23%, 0.8% and 4.49% relatively, in conclusion that the analytical precision present better performance.

4. The practice of algorithm

The resolution algorithm of overlapped peak based on nonlinear curve fitting was applied to the practical application of heavy metal elements analysis in water by stripping voltammetry. Under certain experimental conditions, a group heavy metal stripping data from mixed liquor can be obtained, this mixed liquor contained Zn, Cd, Pb and Cu element, after data preprocessing, got a set of multi-peaks curve, as shown in figure 4(a). It can be seen in the graph, the curve have overlap (in the position of Cd and Pb), using overlapped peak fitting algorithm, and got each clear curve independently, as shown in figure 4(b).
The fitting algorithm completed resolution of overlapped peak, at the same time, also analyzed the private parameters of each peak separated from multi-peaks curve, those parameters include peak height, peak position and peak width, resolution data were shown in table 2. With thesevalue of parameters, can determine the nature of the peak quickly, and provide fast and accurate basis for further quantitative analysis.



a. Mixed liquor stripping curve with overlapped peaks *b. resolution results of overlapped peaks*

Figure 4: Overlapped peaks and resolution results of mixed liquor stripping curve

Table 2: The parameters obtained from the overlapping peaks parsed data

No.	Species	Peak Height A	Peak Position α	Peak Width σ
1	Zn2+	1.32	-1.2	0.032
2	Cd2+	0.50	-0.8	0.030
3	Pb2+	0.38	-0.63	0.038
4	Cu2+	0.40	-0.28	0.035

5. Conclusions

For overlapped peaks in stripping wave by linear sweep stripping voltammetry, we proposed a resolution algorithm based on nonlinear fitting. By the aid of computer technology, with mathematical theory, the algorithm is used to mathematical analysis for overlapped peaks data. Large amount of experimental verified that the resolution ability of algorithm presented in this paper reached the 0.4 level, namely for the overlapped peaks with separation degree greater than 0.4, all of them can be separated successfully. In conclusion, overlapped peak processing algorithm proposed in this paper, its mathematical model is simple; the algorithm is efficiency and fitness in application, superior performance in dealing with stripping voltammetric overlapped peaks. At the same time, the algorithm for resolution of other types of overlapped peaks provided valuable reference.

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