Direct quantitative analysis from the current curve data of pulse voltammetric techniques

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ABSTRACT

Pulse technologies have been widely employed in analytical electrochemistry systems. Double layer charging current has been an obstacle to the accurate measurement of faradaic current despite the theoretical and experimental efforts. Conventional pulse approaches record the current at a later pulse time for minimizing the capacitive effects and reducing the background currents. In this study, a method for extracting the quantitative information directly from the current curve data of pulse voltammetry is developed using trilinear decomposition algorithm. Feasibility of the proposed method is proved and an application study is performed for quantitative analysis of bovine serum albumin (BSA). The method can simultaneously obtain net faradaic current and double layer charging current directly from the measured signals, and the quantitative information can be obtained as well. Thus the performance of voltammetric techniques can be improved. Because the net signals are used, the sensitivities are increased by about 160%, 90% and 25% for normal pulse voltammetry, differential pulse voltammetry and staircase voltammetry, respectively. Quantitative determination of BSA in solutions was carried out with a calibration model of six samples. The recoveries are in a range from 98.1% to 102.9%, which may prove the reliability of the proposed method.

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1. Introduction

Pulse techniques based on controlled potential have been widely developed in analytical chemistry since the potentiostat appeared in electrochemical instrument [1]. Normal pulse voltammetry (NPV) [2,3], differential pulse voltammetry (DPV) [4,5] and staircase voltammetry (SV) [6,7] are three commonly used pulse techniques. These techniques have been widely employed in inorganic and organic analysis [8,9], mass transfer process [10–12], kinetics [13,14], electrodic adsorption studies [15], etc. The most attraction of the pulse techniques lies in the advantage of lower detection limit through minimizing the capacitive effects and reducing the background currents by sampling the current just before the potential is changed. Compared with continuous electrolysis methods such as cyclic voltammetry (CV), pulse voltammetry generally provides better signal-to-noise ratio (S/N) and a lower detection limit by controlling the extent of electrolysis prior to current measurement and discrimination against background processes [16–18]. However, reducing the charging current by

sampling the current at a later pulse time decreases the faradaic current as well. This will result in a sensitivity loss.

With the rapid development of modern analytical instruments, high-dimensional data can be easily acquired in analytical chemistry. Therefore, chemometric methods for three- or higher-dimensional data analysis appear to be attractive and have been gaining widespread acceptance in many scientific fields [19,20]. A numerous of algorithms for analyzing three-dimensional data array have been proposed to extract chemical information from the data. These algorithms can be divided into the noniterative and iterative algorithms based on the computational procedures [21]. The former refer to the generalized rank annihilation method (GRAM) [22] and the direct trilinear decomposition (DTLD) method [23], and the latter include multivariate curve resolution coupled to alternating least squares (MCR–ALS) [24], parallel factor analysis (PARAFAC) [25], alternating trilinear decomposition (ATLD) [26], alternating penalty trilinear decomposition (APTLD) [27], self-weighted alternating trilinear decomposition (SWATLD) [28], etc. Holding better tolerance to instrumental noise and model deviations, the iterative algorithms have consequently been more widely employed than the noniterative algorithms. Among the iterative algorithms, PARAFAC and ATLD have been commonly used in the resolution of three-dimensional data array. PARAFAC

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can provide unique solution and is particularly useful for the quantitative analysis of complex multicomponent samples [29]. ATLD, based on an alternating least squares principle, has a capability to converge faster and has been applied in analyzing the excitation–emission fluorescence and high performance liquid chromatography–diode array detection (HPLC–DAD) data [30,31]. Furthermore, a MATLAB graphical interface toolbox of ATLD and PARAFAC has been developed for treating high-dimensional data conveniently [32]. Before applying these algorithms, however, a three-dimensional data array needs to be constructed. There are kinds of ways for constructing a three-dimensional data array. In the electrochemical analysis, besides the two variables of potential and concentration as the two common dimensions, another variable such as pH [33], accumulation time [34], pulse height [35], waveforms [36] can be used to construct the third dimension. In our previous studies [37,38], the current sampled during the whole experiment time are recorded and a new way of constructing data array was proposed, in which pulse time is adopted as one of the dimensions.

In this work, data array was constructed using the current curves measured with the three commonly used pulse techniques of NPV, DPV and SV, and trilinear decomposition algorithm was employed to extracting high sensitive quantitative information of pulse voltammetry. Based on the different attenuation rates of faradaic and charging current versus time, trilinear decomposition algorithm can perform a well separation of the two currents. Because the net faradaic current can be extracted by the proposed method, sensitivity is increased compared with the conventional method. Moreover, direct quantitative detection can be achieved through the established trilinear model without measuring the peak height. Feasibility of the method was proved and the method was applied in quantitative analysis of bovine serum albumin (BSA).

2. Experimental

2.1. Reagents

All chemical reagents were of analytical grade. Emodin purchased from Aladdin (Shanghai, China) is a standard substance for high performance liquid chromatography. BSA was purchased from Sigma–Aldrich Corporation (Saint Louis, Missouri, USA) and used without further purification. Potassium ferricyanide, anhydrous sodium sulfate, orthophosphoric acid, acetic acid and orthoboric acid were purchased from Guangfu Chemical Co., Ltd. (Tianjin, China). Potassium ferricyanide was prepared with 0.1 M sodium sulfate. All the emodin, BSA and emodin–BSA solutions were prepared with 0.04 M Britton–Robinson buffer (pH = 4.0). Doubly distilled water was used in preparation of the samples.

2.2. Instrument and measurement

A self-made electrochemical workstation was employed for the experiment, consisting of a data acquisition card (NI USB-6211, National Instruments Corporation, Texas, USA), potentiostat circuit board (Lanlike Chemistry & Electron High Technology Co., Ltd., Tianjin, China) and personal computer (Lenovo, Beijing, China). The control programs were written in MATLAB (The MathWorks Inc., USA). Three-electrode system with a 3-mm-diameter bare glassy carbon electrode (working electrode), a saturated calomel electrode (reference electrode) and a platinum sheet electrode (auxiliary electrode) was used for all the measurements. All potentials were referred to the saturated calomel electrode (SCE). All experiments were carried out at room temperature.

Potassium ferricyanide was used for investigating the feasibility of the proposed method. In the experiments, the potential ranges from 0.6 V to −0.2 V increased by −0.02 V. A pulse width of 60 ms and interval of 1.0 s between successive pulses were used. For emodin–BSA complex solution, the potential ranges from −0.1 V to −0.9 V increased by −0.01 V and the solution was kept stirring for adsorption for 90 s before each measurement. A pulse width of 40 ms and interval of 0.5 s between successive pulses were used. Sampling rate is 20,000 points per second. All solutions were carefully degassed with high-purity nitrogen for 5 min before the measurements in order to remove the oxygen. A two-dimensional data matrix corresponding to each sample can be constructed by taking the decaying current in each pulse as a row, and joining the signals of a group samples together yields a three-dimensional data array.

2.3. Construction of the trilinear data array

The three commonly used pulse technologies (NPV, DPV and SV) were investigated in this work. The waveforms for the three methods are shown in Fig. 1(a), (c), and (e). For NPV, the initial baseline potential is kept unchanged and the pulse amplitude is linearly increased in each successive pulse. For DPV, the pulse amplitude remains constant and the initial baseline potential in each pulse is linearly increased. For SV, the potential sweep is a series of stair steps. The current curves sampled in the measurement of the three pulse technologies are depicted in Fig. 1(b), (d), and (f). Taking the curve of a pulse as a line vector, the curves measured in different pulses form a two-dimensional data matrix, and the matrices of different samples form a three-dimensional data array. The three dimensions, therefore, are sampling time, potential, and sample index (or concentration), respectively. The clear physical significances of the three dimensions make the trilinear decomposition results of the array have strong electrochemical interpretation, which represent the relative decaying current in each pulse, the relative current at each potential (voltammogram) and the relative concentration in each sample.

2.4. Calculation

For pulse technologies, the measured response current is used to construct a three-dimensional data array $\mathbf{X}$ of dimension $I \times J \times K$, in which I, J, K represent the number of data point sampled in a pulse, the number of pulses, and the number of samples, respectively, and the trilinear model can be depicted as:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk} \quad (i = 1, \ldots, I; \ j = 1, \ldots, J; \ k = 1, \ldots, K)$$

(1)

where x_{ijk} is an element (i, j, k) of $\mathbf{X}$, the value of which is the measured current at ith time of jth pulse for kth sample; N denotes the number of factors, which means the number of components (faradaic and charging current) in the measured signal; a_{in}, b_{jn} and c_{kn} are the elements in the vector of the relative decaying current curve, the relative weight of decaying current in each pulse (voltammogram) and the relative concentration in each sample, respectively; e_{ijk} is the residual of the element (i, j, k) of $\mathbf{X}$.

Several methods like ATLD and PARAFAC can be used for decomposing a three-dimensional data array $\mathbf{X}$ into the components of its factors. In this study, ATLD was adopted and two factors (faradaic and charging current), i.e., $N = 2$, were used in the calculation. From the measured data $\mathbf{X}$, two vectors can be obtained for $\mathbf{A}$ ($\boldsymbol{a}_1$ and $\boldsymbol{a}_2$), $\mathbf{B}$ ($\boldsymbol{b}_1$ and $\boldsymbol{b}_2$) and $\mathbf{C}$ ($\boldsymbol{c}_1$ and $\boldsymbol{c}_2$), respectively. Clearly, the two vectors in $\mathbf{A}$ are the relative decaying current curves of the faradaic and charging current. One vector in $\mathbf{B}$