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Analysis and optimization of electrochemiluminescence periodic signal processing based on singular value decomposition

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ABSTRACT

Electrochemiluminescence (ECL) detection is one of the most prevailing electrochromism approaches to test biotin and chemicals. As thorny ECL signals by impurities are devastative in judging the right substance and its concentration precisely, it is crucial to dispose the noise and process it into smooth curves without filtering essential biochemical information conveyed in the signal. This contribution investigates Singular Value Ratio (SVR) spectrum to extract periodic signals from every noise ECL signal. A novel improved method of rearranging periodic compositions from complex signals is proposed. Finally, actual ECL signal generated by $Ru(bpy)_3^{2+}$ is analyzed and optimized to demonstrate that the improved technique is efficacious and feasible.

1. Introduction

Electrochemiluminescence(ECL) detection is one of the prevailing electrochromism approaches to test biotin or chemicals [1]. It involves electron transfer between electrochemically generated radical ions in solution to produce excited species that emit light. When voltage is exerted between the working electrode and the counter electrode, elements or radicals can be exited to metastable potentials, which would be capable to transmit photon when moving back to stable valance [2]. ECL signals are unique to specific substances since wavelength and luminescence intensities are distinct [3]. In addition, the voltage of photo multiplier tube (PMT) also contributes to ECL signals [4]. Combined with electrochemical (EC) detection, we can forecast the concentration range and the substance type.

However, in practice, thorny ECL signals by impurities are devastative in judging the right substance and its concentration precisely. Since electrochemical (EC) and ECL detection devices are always integrated, both ECL and EC detections are conducted simultaneously [5]. As cyclic voltammetry serving as EC method, voltages are cycling periodically [6]. Thus the ECL signals versus time are also periodic. If impurities such as remnants in the last experiment are not obliterated, cusps or irregular oscillation will occur. Hence it is crucial to dispose the noise and change it into smooth curves for analysis.

To solve this intractable problem, we initially introduced a classic SVD method by rearranging the time sequence signal into a time hided but dependent $n \times n$ matrix [7]. However, according to the analytical and optimizing results, we found that the classical approach in processing the signal has its drawbacks such as multiple sinusoids in noisy environment. The problem of recovery of multiple sinusoids in noisy environment has been addressed by several researches in the past [8,9]. In practice, one often encounters noise signals with multiple periodic components, which are not necessarily sinusoidal but have definite unknown repeating patterns.

In paper [10], the approach using the Singular Value Ratio (SVR) spectrum is introduced in order to extract periodic signal of every noise signal. In paper [11], a method based on signal energy is proposed, which is also based on SVD and can solve such kind of problems. However, both of them may not be efficacious since the error between the forecasted results and the authentic signal can't be eliminated thoroughly. Hence we proposed a novel improved and more stable method of extracting periodic compositions from complex signals

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[12]. With the implementation of the improved method, the ECL signals were optimized to determine the substance and concentration [13]. Successful results were obtained.

2. SVD principles

2.1. Definition of SVD

The SVD of a m × n matrix A is defined [14] as

$$A = U\sum V^T \tag{1}$$

where $U = [u_1 u_2 \ldots u_m] \in R^{m\times m}$,
$V = [v_1 u_2 \ldots u_n] \in R^{n\times n}$, $U^T U = I$, $V^T V = I$ and $\sum \in R^{m\times n}$

Σ is equal to $\mathrm{diag}(\sigma_1 \sigma_2 \ldots \sigma_p 0 \ldots 0)$ and $\sigma_1 \geq \sigma_2 \geq \ldots \geq \sigma_p \geq 0$ are called non-zero singular values of matrix A. The rank of matrix A is $p(p \leq \min(m,n))$, U and V are called left and right singular matrix of matrix A respectively.

2.2. Periodic signal component detection by SVR spectrum

Suppose that the sampling interval is Δt, thus a time series is formed as$\{x(n)n = 1,2,\ldots\}$. Taking a positive integer M as the column number of a matrix to be constructed ($M \geq 2$), supposing that N segments with the same length of M points are extracted from the series consecutively, then the matrix is rearranged into N columns and N rows, as shown below:

$$A_m = \begin{bmatrix} x(1) & x(2) & \cdots & x(M) \\ x(M+1) & x(M+2) & \cdots & x(2M) \\ \vdots & \vdots & \ddots & \vdots \\ x((N-1)M+1) & x((N-1)M+2) & \cdots & x(NM) \end{bmatrix} \tag{2}$$

While the signal period is $M\Delta t$. If noise is absent, A_M will be a rank-one matrix where $\sigma_2 = 0$.

In the presence of weak noise, $\frac{\sigma_1}{\sigma_2}$ would be very high. However, a slight erroneous selection of row length would not generate a large $\frac{\sigma_1}{\sigma_2}$ due to the misalignment. Hence, the profile of variation of this ratio with row length can be employed to detect periodicity of a signal. This profile is henceforth called Singular Value Ratio (SVR) Spectrum [15]. The SVR spectrum not only detects periodicity but also determines its period length [16].

In practice, there is no strict periodic series, which may be either a quasi-periodic series or a noise periodic series. However, as long as the series contains a conspicuous periodic component, there should be an associated peak in its SVR spectrum. Reversely, in a SVR spectrum, an obvious peak indicates a periodic component in the signal series.

Assume that the positive integer corresponding to an obvious peak in the SVR spectrum is P, and the analogical period of the related periodic component would be $P\Delta t$, where error is more than half a sample interval Δt. In SVR spectrum, the unit of the positive integer M is a sampling interval.

The above definition of the SVR spectrum sounds quite reasonable. However, the SVR spectrum usually appears disabled when detecting and extracting the signal periodic component [17]. The main reason is that there exists a period estimation error ΔT between the accurate period T of the periodic component and $M\Delta t$. With more rows constructing matrix, the error will be accumulated. Such process will lead to SVR spectrum failure.

To solve this problem, Li [18] introduces an improved method to reconstruct SVD matrix from a series. For a series $\{x(n)n = 1,2\ldots\}$ with the sampling interval Δt, extract positive real number m ($m \leq 2$). Let $M = \mathrm{round}\ (m)$, $m_k = \mathrm{round}(km), k = 0,1,\ldots,N-1$, where round is to approximate the value into the nearest integer. A_m for SVD is reconstructed as follows:

$$A_m = \begin{bmatrix} x(1) & x(2) & \cdots & x(M) \\ x(m_1+1) & x(m_1+1) & \cdots & x(m_1+M) \\ \vdots & \vdots & \ddots & \vdots \\ x(m_{N-1}+1) & x(m_{N-1}+2) & \cdots & x(m_{n-1}+M) \end{bmatrix} \tag{3}$$

The difference between (2) and (1) is that each row is not strictly followed by the latter row in series x(n). Notice that the above definition of the starting point of each row segment is in (2). The modification from (1) to (2) is to avoid the error accumulation between the predicted period and the real period. However, the simulation will prove that the improved method also possesses certain defects which can't eradicate noise signal thoroughly.

2.3. Determination of period length by SVD energy

Suppose there is a time sequence: $x_1, x_2, x_3\ldots$ An m × n dimension matrix can be constructed as follows [19]:

$$D_m^{(1)} = \begin{bmatrix} x_1^{(1)} & x_2^{(1)} & \cdots & x_n^{(1)} \\ x_2^{(1)} & x_3^{(1)} & \cdots & x_{n+1}^{(1)} \\ \vdots & \vdots & \ddots & \vdots \\ x_m^{(1)} & x_m^{(1)} & \cdots & x_{m+n-1}^{(1)} \end{bmatrix} \tag{4}$$

where $D_m^{(1)}$ suggests that the constructed matrix has m rows and its elements belong to the first period. This also implies that the period of the signal can be assumed as $T = (m+n-1) \times \Delta t$, where Δt is the sampling interval.

While keeping the length of rows constant, each time the mis-added by 1 and the period is added by Δt. Considering the (k − 1)th period is adopted to predict the kth period, ith sample points are acquired in the kth period, the matrix should be reconstructed as follows [20]:

$$D_m^{(k,i)} = \begin{bmatrix} x_1^{(k)} & x_2^{(k)} & \cdots & x_i^{(k)} & x_{i+1}^{(k-1)} & \cdots & x_n^{(k-1)} \\ x_2^{(k)} & x_3^{(k)} & \cdots & x_{i+1}^{(k-1)} & x_{i+2}^{(k-1)} & \cdots & x_{n+1}^{(k-1)} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ x_i^{(k)} & x_{i+1}^{(k-1)} & \cdots & x_{2i-1}^{(k-1)} & x_{2i}^{(k-1)} & \cdots & x_{n+i-1}^{(k-1)} \\ x_{i+1}^{(k-1)} & x_{i+2}^{(k-1)} & \cdots & x_{2i}^{(k-1)} & x_{2i+1}^{(k-1)} & \cdots & x_{n+i}^{(k-1)} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ x_m^{(k-1)} & x_{m+1}^{(k-1)} & \cdots & x_{m+i-1}^{(k-1)} & x_{m+i}^{(k-1)} & \cdots & x_{m+n-1}^{(k-1)} \end{bmatrix} \tag{4}$$

Obviously, suppose that many segments with same length of m + n − 1 points are cut consecutively from the series, and every segment is regarded as a holistic period. We can check the extent of signal repetition by thus approach. Because if the constructed dimension is appropriate and no error exists between the predicted period and the real one, a series of matrix will be formed,

$$D_m^{(1)}, D_m^{(2,1)}, D_m^{(2,2)}, \cdots, D_m^{(2,m+n-1)}, D_m^{(3,1)}, \cdots, D_m^{(3,m+n-1)}, \cdots, D_m^{(k,1)}, \cdots, D_m^{(k,i)}, \cdots \tag{5}$$

Once operating SVD, we can procure their singular values. Frobenious norm of the corresponding matrix reflects the variation of the signal intensity [21]. If the predicted period is precise, the magnitude of Frobenious norm belongs to a little fixed range. If it is not precise, the magnitude of Frobenious norm will distribute in a larger range. The width of the distributing range reflects the period of the signal. In fact, (5) can be regarded as a “sliding energy window”. Within its energy range, we can decide whether the size of the window is appropriate.

Algorithm for a general value of m can be summarized in the following steps: