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State-transition-algorithm-based resolution for overlapping linear sweep voltammetric peaks with high signal ratio

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ABSTRACT

To resolve the overlapping linear sweep voltammetric peaks (LSVPs) in the case of small signals overlapping to a very big one, a parameter optimization method based on state-transition-algorithm (STA) is investigated. First, four special state transformation operators of STA are introduced and a parameter optimization method is proposed. Then, the overlapping LSVPs are obtained by simultaneously determining trace amounts of Cd^{2+} and Co^{2+} in the presence of a high concentration of Zn^{2+} based on optimized reagents. Finally, overlapping LSVPs are resolved into independent sub-peaks using the proposed method. The resolution results show that the goodness-of-fit of fitting curve in describing the overlapping LSVPs is more than 97%. It indicates that the proposed method is reasonable and effective for the resolution of overlapping LSVPs in the case of high signal ratio which is more than 50.

1. Introduction

The accurate on-line simultaneous determination of trace ions of many different metals, such as Cd^{2+} and Co^{2+} that coexist in zinc sulfate solution between leaching and purification process, is required for optimal control in zinc hydrometallurgy [1–5], which can provide effective feedback information. Linear sweep voltammetry (LSV) is an especially suitable on-line determination method due to its superior properties (i.e., simple, rapid, stable, sensitive, selective, reproducible and accurate) [6,7]. More importantly, the working electrode of LSV doesn't have to be replaced during the determining process, which can realize continuous on-line determination. However, the concentration ratio between the matrix (Zn^{2+}) and the impurities (Cd^{2+} and Co^{2+}) in the zinc sulfate solution is more than 10^6, which leads to the voltammetric signals of impurities being easily covered by the matrix peak due to high signal ratio. Therefore, many studies are focused on reagent for simultaneously determining ions of many different metals with high signal ratio [8,9]. Nevertheless, overlapping peaks are unavoidably generated due to the small difference in the half-wave potentials [10], and that is the main challenge in the accurate on-line simultaneous determination of trace ions in zinc sulfate solution.

Resolution methods of overlapping peaks have made great efforts and developed in recent years. Romà Tauler et al. evaluated the performance of multivariate curve resolution-alternating least squares (MCR-ALS) in the resolution and quantitation of overlapped voltammetric peaks obtained in the analysis of binary and quaternary mixtures of Cd^{2+}, In^{3+}, Pb^{2+} and Tl^{+} metal ions by anodic stripping voltammetry. [11]. Yi-zeng Liang et al. examined the developments in self-modeling curve resolution (SMCR) that utilize a certain mathematical decomposition to deconvolve the two-way signals from instrumentally unresolved multi-component mixtures into factors for single species, and reported spectroscopic and chromatographic examples of applications of SMCR [12,13]. S.V. Romanenko suggested an algorithm based on curve fitting method for the resolution of the overlapping peaks in the case of linear sweep anodic stripping voltammetry, and showed the effectiveness on modeling elements Cd^{2+} and Tl^{+}; Tl^{+} and Pb^{2+} at various proportions in a mixture [14]. The component number in overlapping multicomponent chromatogram was determined by wavelet transform in Ref. [15], and simulated data sets and a seriously overlapping 5-component chromatogram were investigated by the method. Xue-guang Shao et al. investigated the resolution of overlapping chromatograms using a novel immune algorithm and genetic algorithm. Both simulated and experimental data sets were investigated by this method [16]. Based on the fractional-order differential, Yuan-lu Li et al. proposed a new method for the resolution of the simulated overlapping Tsallis and Lorenztian peaks, and detected overlapping voltammetric peak signals [17].

In addition, Xiaoli Wei et al. developed spectrum deconvolution method based on a data dependent peak model (DDPM) for analysis of high resolution LC-MS data [18,19]. Kurajica et al. created new computer programs OVERPEAK and KINSOLID for separating overlapping DTA (DSC) peaks if the proposed mathematical model corresponds to the kinetic process [20,21]. Alfonso Fernández-González and Jose Manuel Montejo-Bernardo proposed a natural logarithm derivative method (NLDM) to accurately estimate peak positions based on a

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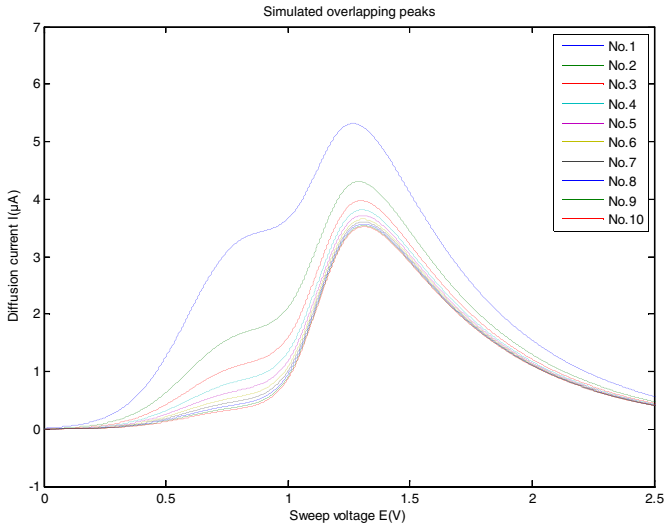

Fig. 1. Simulated overlapping LSVPs with different signal ratios. There are LSVPs on [0.5, 1.0] and [1.0, 1.5], respectively.

linearization of Gaussian curves. The method was used to detect to a certain extent overlapping peaks [22]. Gao et al. investigated non-negative matrix factorization and proposed a novel trilinear decomposition algorithm for resolving overlapping spectra [23,24]. The application of multilayer perceptron artificial neural networks (MLP ANN) based on genetic input selection for quantification of the unresolved peaks in micellar electrokinetic capillary chromatography (MECC) was reported in Ref. [25]. Mean-field independent component analysis (MF-ICA) was investigated to resolve the overlapping gas chromatographic-mass spectrometric (GC–MS) signals in Ref. [26]. Goicoechea et al. overviewed the different chemometric strategies for enhancing the chromatographic methodologies with second-order data analysis of compounds when peaks are overlapped [27].

These previous works provide inspiration and motivation for the resolution of overlapping peaks in this paper. Note that previous research focused on the ions with low signal ratio. To the best of the authors' knowledge, few studies have reported high signal ratio overlapping peaks resolution. However, the voltammetric signal ratio between the matrix (Zn^{2+}) and the impurities (Cd^{2+} and Co^{2+}) in the zinc sulfate solution is high (more than 50 even with the aid of optimized reagents), which leads to the overlapping peaks becoming much worst and the small signals being difficultly resolved. Fortunately, curve fitting based on parameter optimization is a doable method for overlapping peaks resolution, and the modern global optimization algorithms, such as genetic algorithm (GA) [28,29], particle swarm optimization (PSO) [30,31] and differential evolution (DE) [32,33], have been successfully applied in various parameter optimization problems. Although GA, PSO and DE are alternative approaches for the problem, they always encounter premature convergence and their convergence rates are not so satisfactory when dealing with some complex or multimodal functions. State-transition-algorithm (STA) is a novel

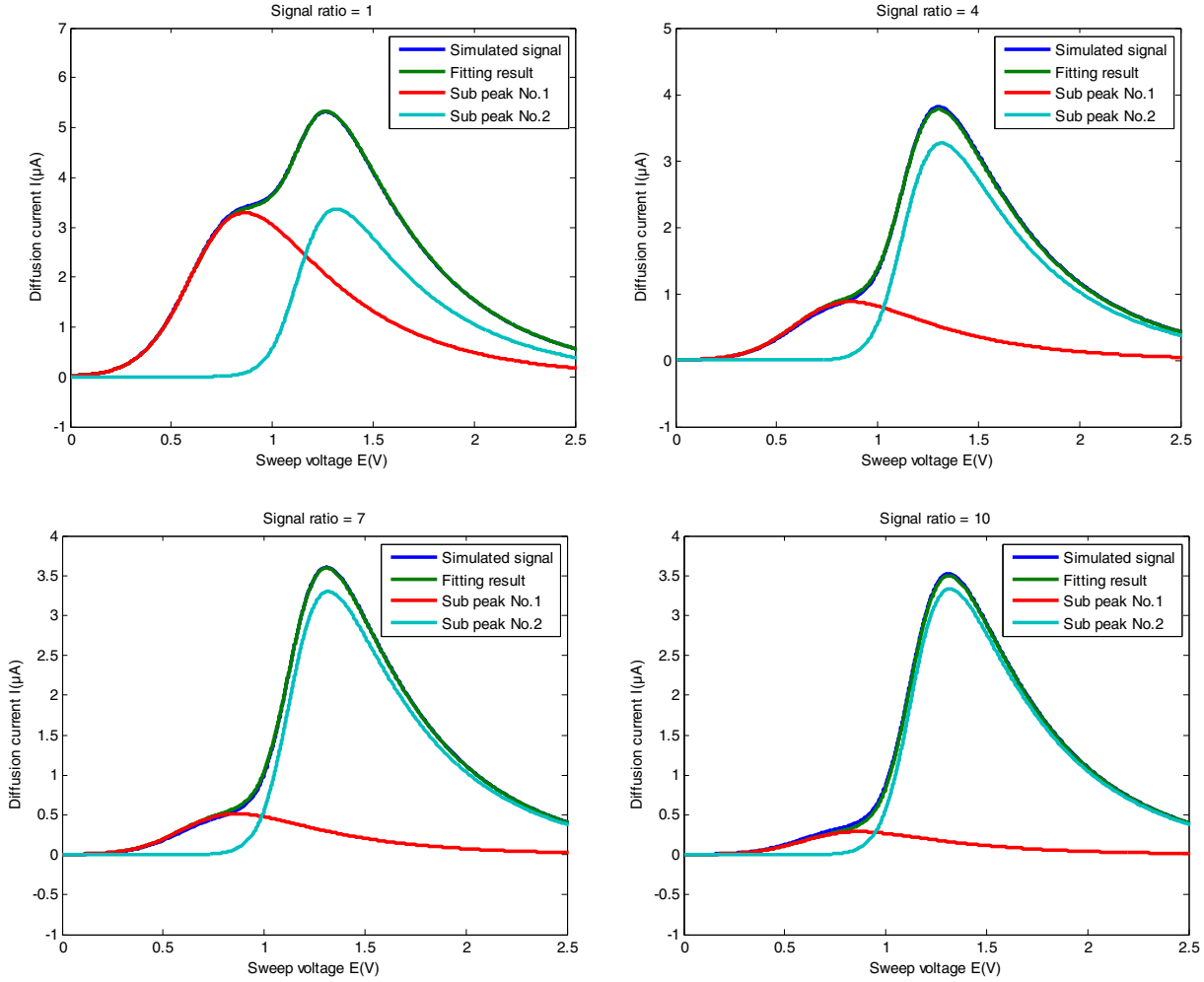

Fig. 2. Typical resolution results of simulated overlapping LSVPs. The four curves in each sub-figure are the simulated signal, fitting result and two sub-peaks, respectively.