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Applications of electrochemical data analysis by multivariate curve resolution-alternating least squares

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ABSTRACT

Electrochemistry studies the relationship between electricity and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice-versa. Chemometrics is the chemical discipline that uses mathematical and statistical methods to design or select optimal procedures and experiments, and to provide maximum chemical information by analyzing chemical data. Multivariate curve resolution-alternating least squares (MCR-ALS) has become a popular chemometric method used for data analysis in many different application fields. This article intends to propose a comprehensive review on different applications of MCR-ALS in electrochemistry such as complexation studies, small molecule-biomacromolecule interactions, minimization of electrodic adsorption, separation of the faradic current contribution from total current to enhance the sensitivity of the electroanalytical techniques, quantification and spectroelectrochemistry. This review was written from both electrochemical and chemometrical points of view with the aim of providing useful information for the electrochemists and to promote the use of MCR-ALS in electrochemistry.

1. Introduction

Electrochemistry is a branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. In fact, the field of electrochemistry encompasses a huge array of different phenomena (e.g.,

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Abbreviations: MLR, multiple linear regression; KF, Kalman filter; PCA, principal component analysis; PCR, principal component regression; EFA, evolving factor analysis; PLS, partial least squares; FT, Fourier transform; ANN, artificial neural networks; MCR, multivariate curve resolution; ICA, independent component analysis; MCR-ALS, multivariate curve resolution-alternating least squares; SVD, singular value decomposition; lof, lack of fit; SIMPLISMA, simple-to-use interactive self-modeling mixture analysis; DPV, differential pulse voltammetry; DPP, differential pulse polarography; COW, correlation optimized warping; icoshift, interval correlation optimised shifting; GPA, Gaussian peak adjustment; GPA2D, Gaussian peak adjustment with transversal constraints; ALPA, asymmetric logistic peak adjustment; FFT, Fast Fourier Transform; PAFFT, peak alignment by Fast Fourier Transform; RAFFT, recursive alignment by Fast Fourier Transform; PSF, parametric signal fitting; ALPA, asymmetric logistic peak adjustment; AsLSSR, asymmetric least squares splines regression; GSH, glutathione; Cys, cysteine; homo-Cys, homocysteine; MT, metallothioneins; ASV, anodic stripping voltammetry; SCP, stripping chronopotentiometry; AdSCP, adsorptive accumulation stripping chronopotentiometry; ESI-MS, electrospray ionization mass spectrometry; BiSPCE, bismuth film screen-printed carbon electrodes; DA, dopamine; CD, β-cyclodextrin; LSV, linear sweep voltammetry; GCE, glassy carbon electrode; SeMet, selenomethionine; SeCyst, selenocystine; EVLS, elimination voltammetry with linear scan; HSA, human serum albumin; BSA, bovine serum albumin; NFR, nuclear fast red; CD, carbidopa; dsDNA, double-stranded calf thymus DNA; FLR/GCE, fullerene-C_{60}/glassy carbon electrode; CV, cyclic voltammetry; SWV, square wave voltammetry; NPV, normal pulse voltammetry; RPV, reverse pulse voltammetry; PMA, polymethacrylic acid; IUPAC, international union of pure and applied chemistry; Trp, tryptophan; tyrosine, Tyr; Au NPs/GCE, gold nanoparticles decorated multiwalled carbon nanotube modified glassy carbon electrode; Bet, betaxolol; Ate, atenolol; MWCNT/CPE, multi-walled carbon nanotube modified carbon paste electrode; CCRD, central composite rotatable design; RSM, response surface methodology; EP, epinephrine; SMT, sulfamethizole; SPY, sulfapyridine; FSMW-EFA, fixed size moving window-evolving factor analysis; SMX, sulfamethoxazole; SMT, sulfamethizole; NE, norepinephrine; AC, paracetamol; UA, uric acid; FA, pteroylglutamic acid; OGCE, oxidized glassy carbon electrode; AsLSSR, asymmetric least squares spline regression; EJCR, elliptical joint confidence region; AQ, 9,10-anthraquinone; OTTLE, optically transparent thin layer electrode; DMF, dimethylformamide.

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electrophoresis and corrosion), devices (electrochromic displays, electro analytical sensors, batteries, and fuel cells), and technologies (the electroplating of metals) [1].

Chemometrics is a chemical discipline that uses mathematics, statistics, and formal logic to (a) either design or select optimal experimental procedures; (b) provide maximum relevant chemical information by analyzing chemical data; and (c) obtain knowledge about chemical systems [2]. Chemometrics assist electrochemists to solve many complicated problems in electrochemistry [3,4]. The application of chemometrics to electrochemical data is rather scarce and very recent, especially when compared to its use with spectroscopic data, but has been growing steadily over the past twenty years. In 1993, Brown et al. have published a review of the then applications of chemometrics in electrochemistry [5]. This review showed that chemometrics methods such as multiple linear regression (MLR), Kalman filter (KF), principal component analysis (PCA), principal component regression (PCR), evolving factor analysis (EFA), partial least squares (PLS), Fourier transform (FT), and artificial neural networks (ANNs) have been applied in electrochemical area to facilitate parameter estimation, optimization, signal processing, and pattern recognition. The authors pointed out that considerable progress had been made in applying chemometrics to electrochemical problems, but there was much to be explored in the future. These comments have to be appreciated against the background of the early work in the application of chemometrics in electrochemistry as a whole, and electroanalysis, in particular. The initial studies seem to have appeared in the early 1980s [6–8] and emphasized the application of the KF or the FT transform methods for the resolution of electrochemical peaks, while a typical study of multivariate calibration modelling prior to 1993 is illustrated by the polarographic determination of pyrazines with the aid of the MLR, PCR and PLS methods [9].

Multivariate curve resolution (MCR) is a widespread and powerful methodology for the analysis and modeling of chemical data in many different application fields, the most prominent being process monitoring. This methodology provides a bilinear description of the observed data variation which is kept within the borders of the chemical realm through the implementation of adequate constraints. Multivariate resolution encompasses in its wider definition all the methods that aim at the decomposition of a data matrix into a linear model of dyads (the bilinear model). From this perspective, PCA, independent component analysis (ICA) and MCR methods can be considered to share the same overall objective: the resolution of complex mixtures into pure-components contributions in situations where no or little prior information is available. However, interpretation of PCA loadings vectors is often not so straightforward, as these vectors may represent combinations of different phenomena described by the data. On the other hand, each ICA “loadings vector” (source signal) describes one independent phenomenon [10]. This difference is due to the intrinsic properties of the two methods: while PCA is based on determining the orthogonal directions of maximum dispersion of the samples in the multidimensional space defined by the variables, the aim of ICA is to recover the pure source signals mixed together in the observed signals. There is no reason why the variations in one pure signal should in any way be related to the variations in another pure signal. Hence, by calculating independent latent variables, it should be possible to find the pure source signals. The term “pure” should be clarified at this point: for example, in the case of a process where one compound A disappears to yield another compound B, the two compounds are inter-dependent, as the appearance of B occurs at the same time as the disappearance of A. The signals of these two compounds are not independent, so they will contribute to the same IC. This IC does not correspond to the signal of a pure compound, but rather describes a single phenomenon occurring during the process. This is an important difference compared to MCR, which aim to extract different signals for A and for B [10].

Currently, the most popular and flexible MCR algorithm is undoubtedly multivariate curve resolution-alternating least squares (MCR-ALS), proposed by Tauler in 1995 [11]. The MCR-ALS has become a popular chemometric method used for the resolution of multiple component responses in unknown and unresolved mixtures [12]. On one hand, this recognition is due to the great variety of data sets that can be analyzed by MCR methods; essentially, any multi-component system that gives as a result data tables or data matrices that can be described by a bilinear model [12,13]. This description includes all kinds of processes and mixtures monitored by diverse multivariate responses, such electrochemical measurements. On the other hand, other reasons for the acceptance of MCR-ALS are its ability to deal with multiple data matrices simultaneously (reducing factor analysis intrinsic ambiguities [11,14,15] and/or data rank deficiencies [16,17]) and the diversity and flexible application of constraints to help and improve the resolution results.

The MCR-ALS was originally developed by Tauler for spectroscopic data (obeys Beer's law) and it was shown to be a very powerful chemometric tool for spectroscopic studies. Later, the method was applied for voltammetric studies, and some modifications were introduced in order to adapt it to the characteristics of voltammetric data [18]. The conditions for the application of MCR-ALS to voltammetric data can be summarized as: (a) experimental currents must be measured at equally spaced potentials that are always identical, and (b) the currents should be linearly dependent on the concentration of the electroactive species present in the investigated system. In order to obtain high-quality data, the voltammograms used for data treatment should ideally correspond to the average of several consecutive experimental curves obtained using different electrodes. Moreover, a point-by-point subtraction of the background current (obtained for supporting electrolyte) from the total currents obtained in the presence of the studied system must be performed. This charging current subtraction assumes that the electrode double-layer capacitance does not change greatly in the presence of the test compound. Furthermore, a new interpretation about the concept of component in MCR-ALS must be applied to electrochemical data in relation to the concept as used with spectroscopic data [19]. This conceptual difference is crucial for the interpretation of MCR-ALS results from electrochemical data. The concept of component is a critical point, for spectroscopic data component is associated to pure chemical species in solution [14,20], but for electrochemical data component must be associated to a single electrochemical process giving a signal, including not only redox processes but also some other possible phenomena like, for instance, electrode adsorption of a species [18,21] or capacitive currents due to the charging of the electrical double layer at the electrode surface. Anyway, in many situations, a single electrochemical process is produced by a single species. The number of components of each submatrix can be evaluated by singular value decomposition (SVD) [18,21]. Although this tool can be only considered as a guide since sometimes a component could be neglected if its concentration profile or its response vector is a lineal combination of others. Another issue with electrochemical data is the distinctive response (peak shape) of electrochemical methods (voltammetric methods) to every species which needs applying the signal-shape constrain, introduced for MCR-ALS of voltammetric data [19], that restricts pure signals to the expected peak shape by fitting it to a proper parametric equation, e.g. asymmetric logistic peak or logistic power peak. Comparative studies with different voltammetric techniques [22] have shown that the best results with MCR-ALS are obtained with peak-shaped signals (as compared with sigmoidal-shaped ones) with practically equal baselines at both sides of the peaks. As mentioned before, the