Deriving calibration curves at early times of chronoamperograms using the chemometrically resolved net faradaic current

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ABSTRACT

In chronoamprometric methods, the current is usually measured at relatively long times, where the contribution of charging current is assumed to be negligible. Previously, we used a chemometric method to resolve numerically the total current which is composed of three pure currents namely net faradaic current, induced charging current and step charging current. In this work, we investigated the effect of analyte concentration on each current component to derive calibration curves for quantitative analyses. In potential step chronoamperometric method, a current data matrix is obtained for each concentration of the analyte. Simultaneous analysis of the data matrices obtained at different concentrations of the analyte by multivariate curve resolution–alternative least squares (MCR–ALS) analysis, produced the net contribution of three types of currents for each concentration of the analyte. Then, the calibration curves based on the faradaic and induced charging current contributions below five cell time constants were compared with the traditional calibration curve, which was based on the total current. In this manner, the linear range, limit of detection and analytical sensitivity of all kinds of calibration curves were compared with each other. The calibration curves obtained based on net faradaic current represented better analytical appraisals compared to those obtained by total current. In addition, we found that at low analyte concentrations, the induced charging currents have insignificant contribution in total current, whereas it represented very significant contribution (even larger than net faradaic current) at high analyte concentrations. Also, the obtained calibration curves were used for prediction of unknown concentrations.

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1. Introduction

Total current signal in electrochemical methods are composed of faradaic, step charging and induced charging contributions [1,2]. The existence of induced charging current in total current was demonstrated in previous studies [1]. However, finding the contribution of these kinds of current remained as a challenge in electrochemistry for years. Due to this fact, the information about the net contribution of all three kinds of current is limited. Accompany of faradaic current with residual current produces complications in quantitative analyses, such as higher detection limit and inaccurate quantification at low concentrations. To compensate the effect of residual currents, measuring current at relatively long times has been suggested since residual current decays much faster than faradaic current in this time. Very recently, we suggested using of a chemometrics method named multivariate curve resolution–alternative least squares (MCR–ALS) for separation of total current into its three components [3].

MCR–ALS is known as a soft-modeling method which can analyze great varieties of electrochemical data [4,5] such as voltammograms [6,7] and chronoamperograms [8]. Previously, resolving the contribution of all three kinds of current in total current was obtained for potential step and staircase cyclic voltammetric methods [3]. Also, the presence of these types of current for oxidation and reduction processes was investigated. So, it seems that, this approach can be used as a general method to obtain all current contributions for redox species with different mechanism of electron transfer. The next in this approach is finding the advantages of using net faradaic current rather than total current in chronoamperometric method.

Chronoamperometry is a valuable electrochemical technique which is used extensively for quantitative analysis. For construction of calibration curve by using of this method, the currents at a constant potential and after successive addition of analyte are measured. In this method, for a period of at least five times of cell constant, an appreciable contribution of charging current to the total measured current exists, and this impose a limitation on the experimental time scale [9]. To overcome this problem, usually the calibration curves are commonly plotted by using the data at times longer than about five cell time constants, where the contribution of charging current is supposed to be negligible.

Indeed, the traditional calibration curves are based on the total current contributions.

It seems that by implementation of our introduced approach [3], it is possible to construct the calibration curves based on faradaic or even induced current contribution at initial times of chronoamperograms i.e., before five cell time constants. To do so, chronoamperometric data of different concentrations of each analyte were collected and the corresponding data matrices were built as described previously [3]. In this way, for each concentration value, one data matrix was built and finally for each calibration data set, several data matrices were constructed. For simultaneous analysis of these data matrices, MCR–ALS can be employed [10]. So, after application of MCR–ALS on augmented data matrix, the calibration curves based on all kinds of current contributions could be plotted before five cell time constants. Then, the obtained curves are compared with each other and also compared with calibration curve based on the total current. In this way, the linear range, analytical sensitivity and limit of detection for all kinds of calibration curves are compared with each other. So, the advantages of using net faradaic current rather than total current can be explored.

2. Experimental

2.1. Chemicals and apparatus

Cobalt(II) chloride hexahydrate, 1,10-phenanthroline, and potassium chloride were obtained from Merck chemical company. Hexaammine ruthenium(III) chloride was purchased from Sterm Chemicals. The stock solution of 0.1 M Co(phen)$_3$Cl$_2$ in 0.1 M KCl solution was made based on previous report [10] by mixing 0.1 M CoCl$_2$.6H$_2$O and 0.3 M 1,10-phenanthroline. Then, by diluting the stock solution with 0.1 M KCl, different concentrations of Co(phen)$_3$Cl$_2$ solutions were prepared (i.e., 0.00, 2.00×10^{-6}, 4.00×10^{-6}, 9.00×10^{-6}, 1.40×10^{-5}, 4.00×10^{-5}, 9.99×10^{-5}, 2.99×10^{-4}, 9.90×10^{-4}, 1.48×10^{-3}, 3.85×10^{-3}, 6.54×10^{-3}, 9.09×10^{-3} and 1.15×10^{-2} M). Also, by using 0.1 M Ru(NH$_3$)$_6$Cl$_3$ in 0.1 M KCl as a stock solution, different aqueous solutions of Ru(NH$_3$)$_6$Cl$_3$ were prepared at different concentrations (i.e., 0.00, 5.00×10^{-6}, 1.00×10^{-5}, 1.50×10^{-5}, 2.00×10^{-5}, 4.00×10^{-5}, 9.99×10^{-5}, 2.00×10^{-4}, 4.98×10^{-4}, 9.90×10^{-4}, 2.91×10^{-3}, 5.66×10^{-3}, 9.09×10^{-3}, 1.03×10^{-2} and 1.74×10^{-2} M).

Chronoamperometric experiments were performed using a PGSTAT-12 electrochemical system (Eco-Chemie, Utrecht, the Netherlands) equipped with GPES software. A three-electrode system was used; a glassy carbon with 1.8-mm diameter was used as a working electrode, the reference electrode was an Ag/AgCl/KCl (3 M) (Metrohm), and a Pt electrode was used as an auxiliary electrode. Before each experiment, the glassy carbon electrode was polished with alumina slurry (0.3 μm) and then rinsed thoroughly with double distilled water. The cleanliness of the electrode was checked with 1.0 mM solution of K$_3$[Fe(CN)$_6$] in 0.1 M KCl.

All experiments were carried out at room temperature. Chronoamperograms were recorded at 10 ms intervals with sampling time of 0.05 ms at different potential steps. For each analyte, starting potential was selected where the peak current was not observed in cyclic voltammogram of the analyte and continued with proper increments until it reached the switching potential of its CV. So, the chronoamperograms of Co(phen)$_3$Cl$_2$ solution with different concentrations were recorded at 15 oxidation potential steps of 0.05, 0.10, 0.11, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22, 0.24, 0.26, 0.28, 0.30, 0.37 and 0.45 V. For Ru(NH$_3$)$_6$Cl$_3$ solutions, 15 reduction potential steps were selected as -0.01, -0.03, -0.05, -0.07, -0.08, -0.09, -0.10, -0.11, -0.12, -0.13, -0.14, -0.16, -0.18, -0.22 and -0.27 V.

2.2. Data analysis

Two data sets of Co(phen)$_3$Cl$_2$ and Ru(NH$_3$)$_6$Cl$_3$ were analyzed. The matrix of current data for each analyte concentration was obtained

based on our previous report [3]. Briefly, for each solution, after application of each potential step, the current was sampled as a function of time in 10 ms intervals and the current data were collected in a vector array of data. Then, the current vector arrays of all applied step potentials were collected in a data matrix **D**. The rows of **D** represent i/t curves at a specified potential step and the columns represent i/E curves at a specified time. Based on previous report [3], after applying MCR–ALS on data matrix (**D**), the pure voltammograms (**V**) and chronoamperograms (**I**) of each components can be obtained. Decomposition of **D** can be written in the matrix notation as $\mathbf{D} = \mathbf{VI^T} + \mathbf{E}$ where **E** is an error matrix. For applying the column-wise augmentation process, the data matrices obtained for different concentrations of the analyte were put over each other in a column-wise manner. Also, in the case of row-wise augmentation process, the data matrices were arranged besides each other.

The codes for MCR–ALS analysis were downloaded from the homepage of MCR–ALS (http://www.mcrals.info/). MCR–ALS needs an initial estimate of **V** or **I** matrices to start calculation. In this work, they were calculated by SIMPLISMA (simple-to-use interactive self-modeling mixture analysis). It extracts the pure variables from the current mixture data. For each pure component in the mixture, the pure variable (e.g., potential, time) represents significant contributions of that variable in the mixture data set [11]. After the use of MCR–ALS, the initial data matrix can be separated into two main matrices including the i/E and i/t curves.

Analytical sensitivity of each calibration curve was calculated by dividing the slope of calibration curve by the standard deviation about the regression (or total residual error) of the corresponding calibration curve. The standard deviation about the regression was calculated by

$S = \sqrt{\frac{\sum_i (I_i - \widehat{I_i})}{n-2}}$ where I$_i$ is the ith current value, $\hat{I}_i$ is the corresponding value predicted by the regression line and n is number of the samples. Also limit of detection (LOD) was calculated as 3S$_b$/m where S$_b$ and m are standard deviation of blank and slope of calibration curve, respectively.

3. Results and discussion

It was shown that by MCR–ALS analysis of the potential step-chronoamperometric experiment, the net faradaic current, which is free from the interfering contribution of the induced and step charging currents, can be easily extracted [3]. This net faradaic current, which is related to the analyte concentration, can be used as a response variable for drawing the calibration curve in analytical applications. To test the applicability of this approach, two probes of Co(phen)$_3$Cl$_2$ and Ru(NH$_3$)$_6$Cl$_3$ were investigated, separately. In this manner, the effect of concentration variations on three kinds of currents for both oxidation and reduction processes can be explored by analysis of chronoamperograms of Co(phen)$_3$Cl$_2$ and Ru(NH$_3$)$_6$Cl$_3$ species, respectively. So, two series of solutions containing the corresponding standard probe with different concentrations were prepared. For each solution, with a specific concentration of analyte, a data matrix was provided as described elsewhere [3] (the chronoamperograms of each step potential collected in the rows). In the next section, the details of the used methodology which applied for analysis of Co(phen)$_3$Cl$_2$ will be explained and then the results obtained for Ru(NH$_3$)$_6$Cl$_3$ will be presented and discussed.

3.1. Co(phen)$_3$Cl$_2$ probe

At first, the calibration data sets for oxidation process of Co(phen)$_3$Cl$_2$ were analyzed. So, the current data matrices of **D$_0$**, **D$_1$**, **D$_2$**, … and **D$_{13}$** for solutions of Co(phen)$_3$Cl$_2$ with different concentrations of 0.00, 2.00×10^{-6}, 4.00×10^{-6}, 9.00×10^{-6}, 1.40×10^{-5}, 4.00×10^{-5}, 9.99×10^{-5}, 2.99×10^{-4}, 9.90×10^{-4}, 1.48×10^{-3}, 3.85×10^{-3},