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Automatic baseline correction in voltammetry

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ABSTRACT

Problem of the effective baseline correction method in voltammetry remains important. Therefore, this work presents an automatic effective algorithm, uncomplicated in implementation and convenient in usage. The idea of the presented strategy is iterative fitting the whole voltammogram by the polynomial, without prior separation of the peaks. The points of the generated curve are used as threshold values in the temporary modification of the signal.

With the use of simulated signals we demonstrated operation of the algorithm and optimized its parameters. Further, in voltammetric determination of Pb(II) traces (5.0 and 25.0 $ng \cdot mL^{-1}$) in two certified reference materials, the obtained percent of recovery was 101.8-106.6 and correlation coefficient not lower than 0.998.

1. Introduction

Background is a typical low-frequency undesired component of the signals recorded in voltammetric experiments. The shape and the level of such residual current is related to the type of the working electrode, composition of the sample and supporting electrolyte, concentration of oxygen dissolved in solution, presence of interfering substances like surfactants or other impurities, as well as ambient conditions in the series of experiments. Usually reproducibility of the residual current is low.

In our works, optionally as a synonym of 'background' we use the term 'baseline'. Such substitution is possible because in voltammetry, in typically applied differential methods with double sampling, the influence of apparatus drift on the result is very low. Time variations of the electrochemical analyzers electronic circuits do not generate any essential hardware distortions in the baseline of the registered signal. Therefore the term 'baseline' may be attributed solely to experimental conditions.

Problem of the effective baseline correction method in voltammetry remains important. Additionally, the task of automatic background simulation is still unresolved, because shape of the residual current under a peak is unknown. The solution is even more complicated as the real height of the signal is also unknown. Accessibility of non-parametric procedures which enable effective background removal, may result in significant progress in application of voltammetry as a routine method of chemical analysis. The optimal baseline fitting method should be either non-parametric or be dependent only on a few easy to optimize parameters. The parametric methods are often time consuming in selection of the adequate variant.

Generally, two strategies may be applied in voltammetry in resolving of the considered problem. The first relies on subtraction of the experimentally recorded background, the second (most often used) utilizes numerical procedures simulating the baseline which is then removed as an undesired component of the recorded data. The first approach is applied when the solution components responsible for the background signal might be determined. Often the sample matrix, rather than the supporting electrolyte, has significant influence on the baseline being the source of disturbances. However, separation of matrix from the sample is, in principle, not applied in voltammetry. Therefore, numerical strategies play an important role in the baseline correction. Background-subtraction can digitally minimize or remove the background current. However, such approach is also not free of drawbacks. The applied algorithms require selection of some operation parameters and manual indication of the points on the curve which are further the base of background approximation. Additionally, during registration of signals for increasing concentrations of the analyte (as in the calibration process), the baseline shape often changes. Therefore, the important step is decision whether it is necessary to simulate background signal for each curve separately, or otherwise–one for the whole set.

The most often applied, effective procedure relies on approximation of the baseline by polynomials. In this case manual control of its operation is obligate. Moreover, because the most frequently used polynomials are of lower degree, the simulated curve does not fit the base of the peak in the whole potential window. Polynomial fitting does not operate optimally for low signal-to-noise ratios and when baselines are complex [1]. This problem may be solved by the application of splines. However, here the next operation

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parameter should be optimized–distance between the knots of the spline function [2–4]. Selection of the points for fitting may be resolved by repeated application of the discrete wavelet transformation [4]. Decrease of the curve resolution supports this important step. Usage of the genetic algorithm [5] also helps to limit manual control of the baseline correction process but implementation of such approach is relatively complex and this strategy is not available in the typical numerical software packages. The novel, fully automated background correction method, which internally validates its results, was presented in [6]. But this algorithm requires a set of voltammograms recorded for calibration with different sensitivities what was obtained by registrations of the signals for increasing accumulation times.

The baseline subtraction, when the methods of mathematical resolution of the overlapping signals are applied, was considered in [7]. The authors proposed correction of only the linear component of the baseline, assuming that the nonlinear component is constant in significant part of the voltammograms. The technique of estimation and compensation of systematic error based on modelling of series of voltammetric curves by empirical functions was developed in [8], and used for compensation of systematic error of baseline subtraction in the stripping voltammetry.

In this work we proposed an automatic iterative procedure of baseline correction in voltammetry. With the use of the simulated signals we have demonstrated operation of the algorithm and optimized its parameters. Further, in determination of Pb(II) traces using the silver annular band working electrode, we presented usefulness, efficiency and convenience of the proposed method.

2. Theory

To fulfill requirements of the fully automatic baseline correction strategy in voltammetry, which additionally will be uncomplicated in mathematical sense and in implementation, the proposed approach utilizes the iterative algorithm previously used in chromatography [9,10]. Polynomials are used for approximation, but unlike to the methods used so far, the data used for calculation herein are not selected manually. The basic idea of the presented strategy is fitting of the generated background utilizing the whole voltammogram, without preceding separation of the peaks. In the proposed procedure points of the generated curve are used as threshold values in temporary modification of the discrete signal. The values which are greater than the threshold (like the points belonging to the peak) are substituted by this cut-off value. Other points in the curve are not modified. In this way the modified signal, which mostly consists of the background (while the peaks regions are successively flattened by the threshold values), is created. Finally, using such transformed signal, the baseline is generated and subtracted from the recorded voltammogram, giving peaks with a flat, horizontal base. The algorithm operates iteratively, until it fulfills the final conditions.

Operation of the iterative algorithm of the baseline approximation may be presented in the following steps:

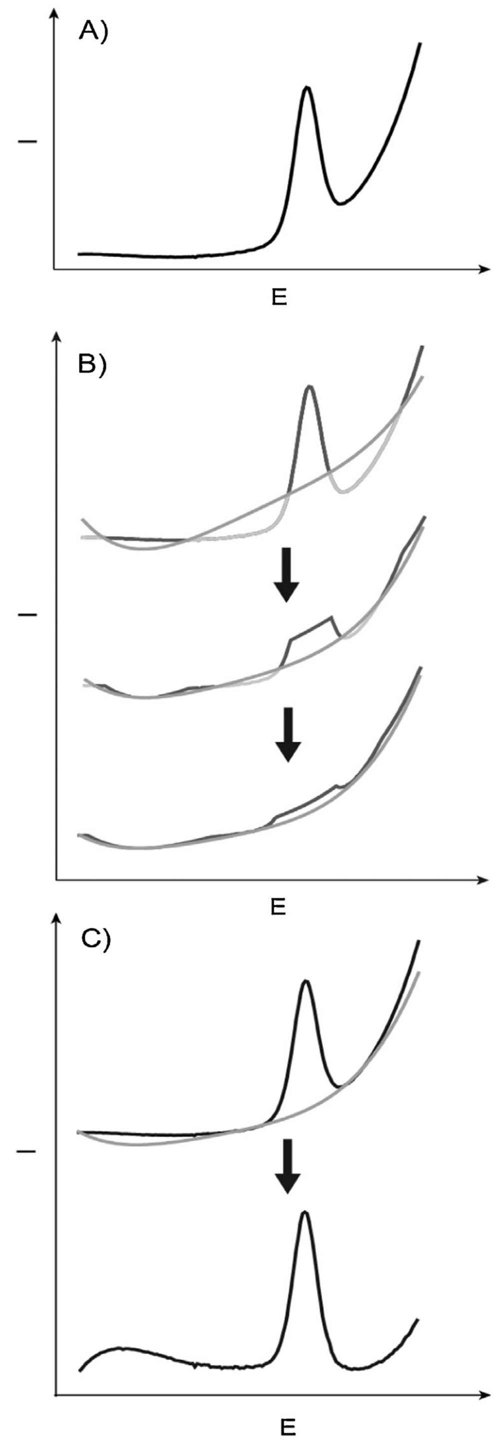

Fig. 1. Main steps of the proposed automatic algorithm of baseline correction: (A) input voltammogram, (B) iterative modification of the signal by cutting-off the values which are greater than threshold, (C) input voltammogram with fitted baseline and subtracted baseline.

1. The procedure operates on the recorded or simulated voltammogram. In the case of the set of curves measured for calibration or in the case of repetitions, each signal should be processed separately.
2. The whole voltammetric signal (Fig. 1A) is approximated by the polynomial. Individual points of the calculated curve are the threshold values for further estimation of the baseline. The points of the voltammogram which are greater than the threshold are substituted by this value. The obtained modified signal is iteratively processed in the following steps of the procedure.
3. The operation defined in p. 2 is repeated usually a few or a dozen times. The obtained curves successively fit the baseline. Part of the curve which belongs to the peak is being cut-off by the threshold values which are changed in every iteration of the algorithm (Fig. 1B).
4. Finally, the transformed signal has a flattened shape. It may be used in generation of the baseline (Fig. 1C), which is further subtracted from the input voltammogram.