Symmetry and shape of voltammetric signals in the light of time-series classification based on qualitative space fragmentation

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ABSTRACT

For the first time, recently developed time-series classification based on qualitative space fragmentation (QSF) was applied to simple and complex voltammetric responses and their components in order to describe peak shape and symmetry. Symmetrical and asymmetrical reduction signals were obtained experimentally by square wave voltammetry (SWV) and differential pulse polarography (DPP) in model systems. It was found that, through the properties of color matrices, the method recognizes (a) symmetry of the peaks as well as some other details – not visible by the naked eye. Therefore, it could be useful to accept symmetry and shape of the electrode response as additional diagnostic criteria during studies of unknown processes, i.e. to introduce the mentioned treatment of voltammetric responses as a new branch of software packages for signal processing.

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1. Introduction

At the beginning of year 2009, a PhD thesis entitled *Time-series classification based on qualitative space fragmentation* was presented at the University of Zagreb [1]. The author described translation of quantitative data (of the considered time-series) into qualitative space, presented through qualitative matrices. This new approach to time-series analysis is closely related to the human way of data interpretation, based on data visualization and shape description [2]. The method seems potentially useful in different fields [2], including voltammetry.

Taking into account that each individual voltammogram can be seen as a time-series, because it reflects a measurement performed at a constant scan rate, application of the mentioned procedure to the recorded signal appears as a possible source of new information. The existing software packages for treatment of experimentally obtained signals usually give the values of peak height, peak potential, half-peak width and peak area. Therefore, a method that could "extract" some additional information is welcomed. Each experienced electroanalytical chemist knows that under the influence of reactant, ligand or electrolyte concentration, increased/decreased pH value or changed potential/timing parameters of the applied voltammetric technique initially symmetrical signal sometimes gradually changes its shape and more or less pronounced additional peak finally develops. For different stages of such a transformation, only "literary" description could be given but quantitative, semi-quantitative or even qualitative indicators are not available. In other words, a method that recognizes the shape and symmetry of the whole electrode response is needed. In this article, application of the qualitative space fragmentation (QSF) as a tool for recognition of such signal properties is described. It is expected to be useful in characterization of the peaks that reflect different electrode processes (while using a chosen voltammetric technique) or comparison of the signals obtained by different techniques for the same process, i.e. for recognition of the most sensitive technique when specific electrode reaction or phenomenon (adsorption, IR drop, catalysis etc.) is studied.

2. Experimental

All voltammetric measurements were performed using reagent grade chemicals and deionized water. The applied instrument was always µAutolab (Ecochemie, Utrecht, The Netherlands). Static mercury drop electrodes were of PAR 303 and 663 VA stand (Metrohm) types with platinum counter electrodes and Ag/AgCl reference electrodes. The latter were filled with saturated NaCl solution (PAR) or 3 mol/L KCl (Metrohm). In order to prevent formation of sparingly soluble $KClO_4$ in the frit, electrolyte bridge (as a part of the Metrohm reference electrode) was filled with 3 mol/L NaCl solution during measurements in perchlorate medium. Solution in the voltammetric cell was always deaerated with high purity nitrogen (for 15 min) before each new series of measurements. Room temperature was maintained at 25 ± 1 °C.

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3. Data treatment

Details of the original data treatment procedure (concerning time series expansion, coding, qualitative matrix construction and feature extraction) are given elsewhere [2]. From the practical point of view, somewhat different (i.e. simpler) approach seems more appropriate for the present purpose.

In Fig. 1, a bell-shaped curve, composed of 19 points and similar to a voltammetric peak is presented. The exact values of its x, y pairs are given in the supplement (Table 1S). At the start, from each individual y-value, all consecutive y-values are subtracted. This means that (in the present example) $y2$, $y3$, $y4$, ... and $y19$ values will be subtracted from $y1$; $y3$, $y4$, $y5$, ... and $y19$ values will be subtracted from $y2$ and so forth. Finally, only $y19$ value will be subtracted from $y18$. Presentation of the whole "process" is, for the model curve from Fig. 1, given in the supplement (Tables 1S–3S). The first row (of Table 3S) contains the differences obtained by subtractions from $y1$, and generally in nth row the differences obtained by subtractions from yn are given. By numbering the columns (from 2 to 19 in the present case) it can be read not only from which y value the subtraction is performed, but also which y values are subtracted. The resulting differences are positive,
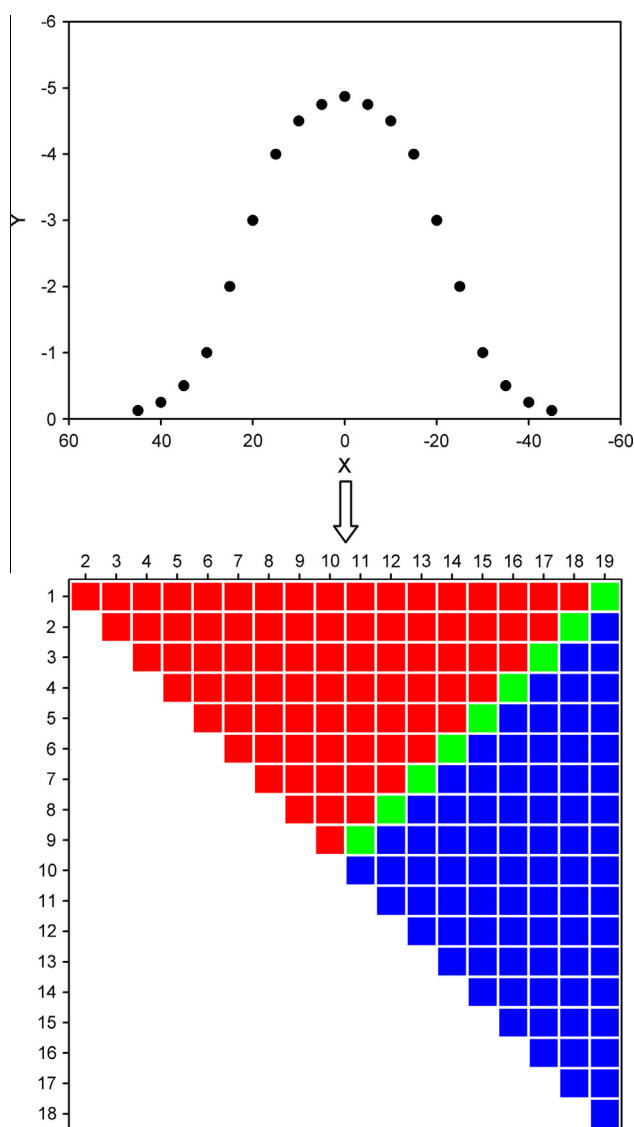

Fig. 1. A symmetrical bell-shaped curve and its colored matrix.

Table 1
Qualitative matrix for any number of data points.

Δ_{12}	Δ_{13}	–	–	$\Delta_{1(n-1)}$	Δ_{1n}
	Δ_{23}	Δ_{24}	–	–	Δ_{2n}
			–	–	–
				–	–
				$\Delta_{(n-2)(n-1)}$	$\Delta_{(n-2)n}$
					$\Delta_{(n-1)n}$

$\Delta_{ij} = y_i - y_j$.

negative or equal to zero. The whole presentation, however, cannot be analyzed without difficulties. After transformation of its positive, negative and zero values to red, blue and green cells, respectively, everything becomes clearer.[1] The resulting color matrix is given as a part of Fig. 1. In order to make the "construction" of a qualitative matrix really clear, it is schematically presented in Table 1 for any number of points.

4. Results and discussion

4.1. Simple symmetrical and asymmetrical signals

The curve in Fig. 1 is perfectly symmetrical and similar to a voltammetric reduction signal. Its symbolic color matrix is built from two identical but differently oriented triangles (each consisting of 81 cells). The first of them is red and reflects the region in which y-values become more negative, i.e. reduction current increases. The second is blue and reflects increasing y-values (i.e. decreasing reduction current) whereas green cells appear as a border line between the two areas. The peak position (E_p) is defined by the first cell of the changed (i.e. blue) color that appears on the "hypotenuse" of the color matrix while going from left to right. In the described example, the first blue cell is located in the tenth row where the peak position and the peak height (0.000, −4.870) are originally defined (Table 1S within supplement).

According to the mentioned observations, each symmetrical voltammetric peak, that reflects a simple reduction process, should give a symbolic matrix of the type presented in Fig. 1, although based on significantly more points. In practice, however, a zero difference between two points usually cannot be obtained because measured currents are often given in nine digits. The impression is that under real conditions the green border line between red and blue areas should disappear with the corresponding cells being "divided" between the other two colors.

Square-wave peaks of reversible reduction processes are generally described as symmetric [3]. An experiment, performed with UO_2^{2+} in perchlorate medium, i.e. in a system that gives a solution soluble reduction product (UO_2^+) [4], really results in only four zero values along the straight line between red and blue segments. By inspection of the numerical values (within presentation of Table 3S type) from which the cells on the borderline originate, it could be noticed that many of them are very small (about 10^{-10} A), i.e. virtually negligible in comparison with the peak current of 1.5 μA. Therefore, each value absolutely lower than 1.5 nA was arbitrarily taken as zero. In such a manner, the number of green cells was increased (from 4 to 37, i.e. from 5.4% to 50%) along the studied straight line but not within other parts of the matrix (Fig. 2). Consequently, the final presentation was very similar to the color matrix from Fig. 1. Results of the same type were obtained with SWV reduction peaks of Pb^{2+} and Cd^{2+} in acidified perchlorate solutions, i.e. in the systems with amalgam forming reduction products.

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[1] For interpretation of color in Figs. 1–6, the reader is referred to the web version of this article.