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MATLAB in electrochemistry: A review

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Abstract: MATLAB (MATrix LABoratory) is a multi-paradigm numerical computing environment and fourth-generation programming language. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including C, C++, Java, Fortran and Python. Electrochemistry is a branch of chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice versa. MATLAB has obtained a wide range of applications in different fields of science and electrochemists are also using it for solving their problems which help them to obtain more quantitative and qualitative information about systems under their studies. In this review, we are going to cast a look on different applications of MATLAB in electrochemistry and for each section, a number of selected articles published in the literature will be discussed and finally, the results will be summarized and concluded.

Dear Editor,

Hereby, I confirm submission of a manuscript entitled “**MATLAB in Electrochemistry: A review**” to Talanta and I would like you to consider it for publication. This is a review article and is not currently submitted to any other Journal, and will not be submitted elsewhere before a decision is made by this Journal.

Sincerely Yours,

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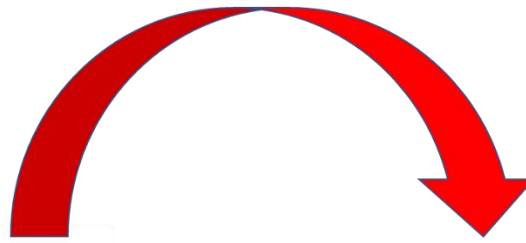
***Novelty Statement**

According to the experience of our research group we have provided an interesting and through review article which reflects the applications of a well-known software namely MATLAB in electrochemical projects. This review is very useful for expanding applications of MATLAB in electrochemistry.

*Highlights (for review)

- ✓ Required information to understand the review was collected.
- ✓ Chemometrics links MATLAB with electrochemistry.
- ✓ Applications of MATLAB in electrochemistry has been classified.
- ✓ According to the number of selected papers applications of MATLAB were introduced.
- ✓ The results were summarized and concluded.

MATLAB



MATLAB in Electrochemistry: A review

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Abstract

MATLAB (MATrix LABoratory) is a multi-paradigm numerical computing environment and fourth-generation programming language. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages, including C, C⁺⁺, Java, Fortran and Python. Electrochemistry is a branch of chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice versa. MATLAB has obtained a wide range of applications in different fields of science and electrochemists are also using it for solving their problems which help them to obtain more quantitative and qualitative information about systems under their studies. In this review, we are going to cast a look on different applications of MATLAB in electrochemistry and for each section, a number of selected articles published in the literature will be discussed and finally, the results will be summarized and concluded.

Keywords: MATLAB; Electrochemistry; Quantitative and qualitative information; Solving of problem.

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1. Required information

1.1. MATLAB

1.1.1. What is MATLAB?

MATLAB, an acronym for MATrix LABoratory, is a product of The MathWorks, Inc. of Natick, MA [1]. The MATLAB is a high-performance and powerful language for technical computing. It integrates computation, visualization, and programming in an easy-to-use environment where problems and solutions are expressed in familiar mathematical notation. Typical uses are included: math and computation, algorithm development, modeling, simulation and prototyping, data analysis, exploration and visualization, scientific and engineering graphics and application development such graphical user interface building.

The MATLAB is an interactive system whose basic data element is an array that does not require dimensioning. This allows the user to solve many technical computing problems, especially those with matrix and vector formulations, in a fraction of the time it would take to write a program in a scalar noninteractive language such as C or Fortran. The MATLAB was originally written to provide easy access to matrix software developed by the LINPACK and EISPACK projects. Today, MATLAB uses software developed by the LAPACK and ARPACK projects, which together represent the state-of-the-art in software for matrix computation. The MATLAB has evolved over a period of years with input from many users. In university environments, it is the standard instructional tool for introductory and advanced courses in mathematics, engineering, and science.

1.1.2. MATLAB environment

MATLAB a multi-panel window appears containing Command Window, Workspace, Current Directory, and Command History panels, among others. This, along with windows for the Editor/Debugger, Array Editor, Help Browser, etc., that can be invoked as needed, is the MATLAB environment [2].

1.1.3. The M-files

MATLAB allows writing two kinds of program files including scripts and functions. Script files are program files with .m extension. In these files, the user can write a series of commands which wants to execute together.

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2 Scripts do not accept inputs and do not return any outputs. They operate on data in the workspace. Functions files
3
4 are also program files with .m extension. Functions can accept inputs and return outputs. Internal variables are
5
6 local to the function. The user can use the MATLAB editor or any other text editor to create your .m files.
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9 *1.1.4. Toolboxes of MATLAB*

10 MATLAB features a family of application-specific solutions called toolboxes. Very important to most users of
11
12 MATLAB, toolboxes allow the user to learn and apply specialized technology. Toolboxes are comprehensive
13
14 collections of MATLAB functions (M-files) that extend the MATLAB environment to solve particular classes of
15
16 problems. Areas in which toolboxes are available include signal processing, control systems, neural networks,
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18 fuzzy logic, wavelets, simulation, and many others. But, in this review article, we are going to focus on those
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20 toolboxes which had been frequently used in electrochemical projects.
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25 *1.1.5. The most frequently used toolboxes of MATLAB in electrochemical projects*

26 *1.1.5.1. PLS toolbox*

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28 PLS Toolbox is a collection of essential and advanced chemometric routines that work within the MATLAB
29
30 computational environment [3]. It contains the tools required by chemical engineers, analytical chemists and
31
32 other scientists to explore their data and build predictive models. PLS Toolbox gets its name from the Partial
33
34 Least Squares (PLS) regression method, which has become the standard calibration method in many chemical
35
36 applications. Although PLS Toolbox has grown far beyond just PLS, the name has been retained for the sake of
37
38 continuity. Originally released in 1991, the routines in PLS Toolbox grew out of the authors' research and
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40 applications and were refined for publication [3]. All of these routines were originally coded so that their
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42 usefulness for modeling and monitoring dynamic systems could be confirmed. Indeed, the techniques were found
43
44 to be quite useful and it seemed that publication of the routines as a software package was the logical next step.
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48 The routines shared the basic theme of multivariate analysis, multivariate calibration and multivariate statistical
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50 process control. Over the years, the application areas have expanded along with the tool set. Particular emphasis
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52 has been placed on routines for use in analytical chemistry, especially spectroscopy, and on the development of
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54 multi-way tools for analysis of 3-way and higher arrays [3].
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4 *1.1.5.2. Image processing toolbox*
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6 An image may be defined as a two-dimensional function, $f(x, y)$, where x and y are spatial (plane) coordinates,
7
8 and the amplitude of f at any pair of coordinates (x, y) is called the intensity or gray level of the image at that
9
10 point. When x , y , and the amplitude values of f are all finite, discrete quantities, we call the image a digital image
11
12 [4]. The field of digital image processing refers to processing digital images by means of a digital computer. The
13
14 MATLAB has an image processing toolbox which provides a comprehensive set of reference-standard algorithms
15
16 for image processing, analysis, visualization, and algorithm development. The image processing toolbox enables
17
18 the user to perform image segmentation, image enhancement, noise reduction, geometric transformations, image
19
20 registration, and 3D image processing.
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26 *1.1.5.3. Neural network toolbox*
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28 Neural networks are composed of simple elements operating in parallel. These elements are inspired by
29
30 biological nervous systems [5]. As in nature, the connections between elements largely determine the network
31
32 function. A neural network is trained to perform a particular function by adjusting the values of the connections
33
34 (weights) between elements. Typically, neural networks are adjusted, or trained, so that a particular input leads to
35
36 a specific target output. Neural networks have been trained to perform complex functions in various fields,
37
38 including pattern recognition, identification, classification, speech, vision, and control systems.
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43 Neural networks can also be trained to solve problems that are difficult for conventional computers or
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45 human beings. The neural network toolbox emphasizes the use of neural network paradigms that build up to—or
46
47 are themselves used in engineering, financial, and other practical applications [5].
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50 *1.1.5.4. Toolbox for multivariate calibration techniques (TOMCAT)*
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52 Daszykowski et al. developed a user-friendly graphical interface (GUI) for robust calibration with a collection of
53
54 m-files, called TOMCAT (TOolbox for Multivariate Calibration Techniques) [6]. The GUI allows a user to apply
55
56 the implemented methods in an easy way and it gives a straightforward possibility to visualize the obtained
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58 results. Several useful features such as interactive numbering of the displayed objects on a plot, viewing the
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1 content of the data, easy transfer of the data between the toolbox and the MATLAB workspace and vice versa,
2
3 are also implemented. Among the implemented methods there are Principal Component Analysis (PCA) and its
4
5 robust variant, Partial Least Squares, Continuum Power Regression, Partial Robust M-Regression, Robust
6
7 Continuum Regression and Radial Basis Functions Partial Least Squares.
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10 11 *1.1.5.5. The N-way toolbox*

12 Andersson et al. introduced a free toolbox for MATLAB for the analysis of multi-way data called “The N-way
13
14 Toolbox for MATLAB” [7]. The N-way Toolbox for MATLAB is a collection of functions and algorithms for
15
16 modelling multi-way data sets by a range of multilinear models. Several types of models are covered; canonical
17
18 decomposition-parallel factor analysis (CANDECOMP-PARAFAC), multilinear partial least-squares regression
19
20 (PLSR), generalised rank annihilation method (GRAM), direct trilinear decom- position (DTLD), and the class of
21
22 Tucker models. Selected types of optional constraints have been built into the least-squares error minimization
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24 algorithms for CANDECOMP-PARAFAC and Tucker models; nonnegativity, unimodality, and orthogonality.
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26 Different constraints may be set up for the different modes. In addition to these constraints, the structure of the
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28 Tucker models can be forced to allow only selected factor interactions. Furthermore, three methods for core
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30 simplification by orthogonal rotations have been implemented. Most of the algorithms in the toolbox can handle
31
32 any number of modes ($N \geq 2$) in data.
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40 *1.1.5.6. MVC1 Toolbox*

41 Multivariate calibration 1 (MVC1) is a MATLAB toolbox for implementing several different first-order
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43 calibration methodologies including net analyte preprocessing followed by classical least squares (NAP/CLS) [8],
44
45 partial least squares-1 (PLS-1) [9], principal component regression (PCR) [9], orthogonal signal correction
46
47 followed by PLS (OSC/PLS) [10], net analyte preprocessing followed by PLS (NAP/PLS) [11], direct orthogonal
48
49 signal correction followed by PLS (DOOSC/PLS) [12], OSC followed by CLS (OSC/CLS) [11], DOOSC followed
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51 by CLS (DOOSC/CLS) [13], multilinear regression (MLR) [14] and stepwise multilinear regression
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53 (STEPW/MLR) [14] through easily managed graphical user interfaces which was developed by Olivieri et al.
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55 [15]. The toolbox accepts different input data formats (either arranged as matrices or vectors contained in raw
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1 data files or in already existing MATLAB variables) and incorporates many preprocessing algorithms in order to
2 improve prediction capabilities. The development and validation of each model and its subsequent application to
3 unknown samples are straightforward. Prediction results are produced along analytical figures of merit and
4 standard errors calculated by uncertainty propagation. Moreover, the toolbox allows one to manually select
5 working sensor regions, or to automatically find which region provides the minimum error. It also generates
6 many different plots regarding model performance, including outliers detection, facilitating both model
7 evaluation and interpretation.
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19 *1.1.5.7. MVC2 Toolbox*

21 Multivariate Calibration 2 (MVC2) is an integrated chemometric toolbox for MATLAB which was developed by
22 Olivieri et al. [16] in order to manage several different second-order multivariate calibration algorithms in an
23 easy-to-use graphical interface environment. The toolbox can be applied to any type of data which are structured
24 in matrix form for each sample, allowing for the efficient extraction of information concerning certain properties
25 or analytes of interest from the multi-component space. The toolbox is a sequel of the already described MVC1
26 toolbox and the MULTIVAR Visual Basic program [17], both developed for handling first-order multivariate
27 calibration methods. The calibration techniques included in the MVC2 toolbox can be divided in two relevant
28 groups, namely those based on: 1) trilinear decomposition (TLD) or 2) residual bilinearization (RBL). The former
29 group include parallel factor analysis (PARAFAC) [18], alternating trilinear decomposition (ATLD) [19],
30 alternating penalty TLD (APTLD) [20], and self-weighted ATLD (SWATLD) [21]. For a review of the
31 properties and applicability of the different algorithms, see ref. [22,23]. The second group of methods, based on
32 residual bilinearization, comprise: 1) bilinear least-squares followed by RBL (BLLS/RBL) [24,25], 2) unfolded
33 partial least-squares/RBL (U-PLS/RBL) [26,27], 3) multidimensional partial least-squares/RBL (N-PLS/RBL)
34 [28,29], and unfolded principal component analysis/RBL (U-PCA/RBL) [30]. The latter methodology has been
35 devised in order to produce suitably preprocessed data from non-linear instrumental data, for further analysis
36 using artificial neural networks [31,32]. Calculations and graphical outputs are conveniently managed in MVC2
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1 through GUI shells. The software does not require a highly experienced user, but a basic knowledge on the
2 underlying methods is advisable in order to successfully interpret the results.
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9 *1.1.5.8. MVC3 Toolbox*

10 Multivariate calibration 3 (MVC3) is a sequel of the already described MVC1 and MVC2 toolboxes which was
11 developed by Olivieri et al. [33] to manage several different third-order multivariate calibration algorithms in an
12 easy-to-use GUI environment. The third-order multivariate calibration techniques included in MVC3 can be
13 divided in two relevant groups, namely those based on: (1) quadrilinear decomposition (QLD) or (2) residual
14 trilinearization (RTL). The former group includes parallel factor analysis (PARAFAC) [34], alternating penalty
15 QLD (APQLD) [35] and alternating weighted residual constraint QLD (AWRCQLD) [36]. The second group of
16 methods, based on residual trilinearization, comprise: 1) trilinear least-squares followed by RTL (TLLS/RTL)
17 [37], 2) unfolded partial least-squares/RTL (U-PLS/RTL) [37], 3) multidimensional partial least-squares/RTL (N-
18 PLS/RTL) [38], and unfolded principal component analysis/RTL (U-PCA/RTL) [39]. The latter methodology has
19 been developed to produce test sample scores from nonlinear instrumental data, which are free from the
20 contribution of interferences, for further analysis using artificial neural networks [39]. Calculations and graphical
21 outputs are conveniently managed in MVC3 through GUI shells. The software does not require a highly
22 experienced user, but a basic knowledge on the underlying methods is advisable in order to successfully interpret
23 the results.
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44 *1.1.5.9. Successive projections algorithm toolbox*

45 The research group of Araujo developed a MATLAB GUI for the successive projections algorithm (SPA) which
46 is a variable selection technique aimed at reducing collinearity problems in multiple linear regression (MLR)
47 modelling [40]. The interface also offers the possibility of pre-processing the data using Savitzky-Golay
48 smoothing/differentiation and/or wavelet denoising. Sample selection routines for dividing the samples into
49 calibration and validation sets are also implemented. At the end, prediction statistics (PRESS, RMSEP, SDV,
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BIAS and correlation coefficient) are calculated to evaluate the performance of the resulting MLR model. All these operations can be carried out by the user without the need for MATLAB programming skills.

1.1.5.10. Least square support vector machine toolbox

Least square support vector machine (LS-SVM) is a state-of-the-art statistical algorithm and is capable of learning in high-dimensional feature space with fewer training variables or samples [41,42]. SVM has the capability of dealing with linear and nonlinear multivariate calibration and resolving these problems in a relatively fast way. Support vectors (SVs) were obtained by applying linear equations instead of quadratic programming problems. The details of LSSVM algorithm could be found in the literature [43,44].

1.1.5.11. Multivariate curve resolution-alternating least squares toolbox

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). Currently, the most popular and flexible MCR algorithm is undoubtedly multivariate curve resolution-alternating least squares (MCR-ALS), proposed by Tauler in 1995 [45]. The MCR-ALS has become a popular chemometric method used for the resolution of multiple component responses in unknown and unresolved mixtures [46]. 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 [46,47]. 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 [45,48,49] and/or data rank deficiencies [50,51]) and the diversity and flexible application of constraints to help and improve the resolution results.

1 The MCR-ALS was originally developed by Tauler for spectroscopic data (obeys Beer's law) and it was
2 shown to be a very powerful chemometric tool for spectroscopic studies. Later, the method was applied for
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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 [52]. 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 [53]. 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 [48,54], 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 [52,55] 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) [52,55]. 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 [53], that restricts pure signals to the expected peak shape by fitting it to a proper parametric equation, e.g. asymmetric logistic peak or

1
2 logistic power peak. Comparative studies with different voltammetric techniques [56] have shown that the best
3
4 results with MCR-ALS are obtained with peak-shaped signals (as compared with sigmoidal-shaped ones) with
5
6 practically equal baselines at both sides of the peaks. As mentioned before, the main premise of MCR-ALS is to
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8 follow the multicomponent Beer's law. Consequently, it can be used to analyze the bilinear data and applying it
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10 to resolve data requires the uniform presentation of data, i.e., all signals have to be adjusted to the same length
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12 and corresponding variables have to be placed into the proper columns of the data matrix. The signals obtained
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14 from voltammetric techniques often do not fulfill this requirement. This problem is seen as the potential shift in
15
16 electrochemical data. These facts cause a decrease in the linearity, which depends on the magnitude of the
17
18 potential shift. In many cases, large lack of fit (*lof*) values are obtained and impel the analyst to use a higher
19
20 number of components to explain the non-linearity.
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25 26 *1.1.5.12. MCR-BANDS toolbox*

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28 MCR-BANDS is a user friendly graphical interface and a command line MATLAB computer program for the
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30 evaluation of the extent of rotation ambiguities associated to MCR solutions [57]. The program allows for an
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32 easy check of the extent of rotation ambiguity remaining in MCR solutions in the investigation of a particular
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34 system and it also allows for the checking of the effect of applied constraints. In this way, conditions and
35
36 limitations to achieve optimal solutions in MCR are easily assessed.
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40 41 *1.1.5.13. shiftfit, pHfit, GPA, GPA2D, and ALPA toolboxes*

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43 The *shiftfit* corrects the data matrix from signal movements and for this purpose, it optimises by least squares the
44
45 potential shift of every pure voltammogram with respect to a reference position. To correct the potential shift,
46
47 there are three MATLAB functions including *peakmaker*, *shiftcalc* and *shiftfit*. *Peakmaker* is a function that
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49 generates a Gaussian peak as an initial estimation of the pure voltammograms. The *shiftcalc* function displaces
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51 every signal in every experimental voltammograms matrix for a given potential shift ΔE . The *shiftfit* function
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53 iteratively optimizes the values of ΔE to generate a matrix (I_{cor}) in which all signals remain at the fixed potentials
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55 stated in the pure voltammograms matrix (V_o) [58,59].
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2 The *pHfit* algorithm can solve more intricate systems like those encountered in voltammetric pH titrations
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4 by imposing a shape restriction to the movements of the signals as a function of potential, by means of adjustable
5
6 sigmoid or linear functions [60]. Both *shiftfit* and *pHfit* strategies could be used with any type of shape: the only
7
8 restriction is that the pure signals of all components must remain unchanged along the whole experiment except
9
10 for the height and the x-axis position, which are adjusted by the program. Nevertheless, losses of electrochemical
11
12 reversibility, which are among the most usual non-linearity sources in voltammetric data, can dramatically affect
13
14 the performance of both *shiftfit* and *pHfit* algorithms. The reason for that is the progressive broadening (and even
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16 the changes in peak symmetry) which take place as the electrochemical process becomes more irreversible. The
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18 mentioned algorithms could compensate the potential shift of pure signals whose shape remains unchanged, but
19
20 they cannot cope with signals continuously changing their width and symmetry.
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26 After *shiftfit* and *pHfit*, the Gaussian Peak Adjustment (GPA) algorithm based on a new strategy,
27
28 parametric signal fitting (PSF), was proposed for the chemometric analysis of voltammetric data when the pure
29
30 signals do not maintain a constant shape [61]. This is based on the fitting of parametric functions to reproduce the
31
32 shape of the signals. As a first approach, two Gaussian functions are fitted, one at each side of the signal, and the
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34 parameters are least-squares optimised. Such parameters determine not only the height and position of the signals
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36 (as in the algorithms above), but also the width at both sides of the maximum. It is important to note that, unlike
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38 *shiftfit* and *pHfit*, the use of Gaussian functions restrict the GPA exclusively to peak-shaped signals. Moreover, it
39
40 must be remarked that, despite fitting of Gaussian peaks has been already used in some situations such as the
41
42 resolution of UV-vis spectra, in such approaches the symmetric character of the Gaussian function prevents an
43
44 appropriate treatment of asymmetric signals. In the proposed method, the use of two separated Gaussian
45
46 functions at both sides of the maximum (sharing the same height and position but different widths) is a new and
47
48 simple solution for the fitting of asymmetric peaks. Fig. 1 summarizes the main steps of the fitting procedure.
49
50
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54
55

56 Figure 1

57
58 A new method, GPA2D, was developed as a significant improvement of the GPA which includes, for the
59
60 first time, transversal constraints to increase the consistency of the resolution along the different signals of a
61
62
63
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65

1
2 voltammetric dataset [62]. The aim of GPA2D is to extract a physicochemical sense to the evolution of the
3
4 signals and their shifts along the experimental axis. The imposition of the transversal constraints makes this
5
6 method more powerful for the analysis of voltammetric data, especially if they are non-bilinear. Fig. 2 shows the
7
8 main structure of the operation program, which is based on a common GPA procedure with two alternative
9
10 intermediate paths depending on the kind of transversal constraint to be applied (signal shift evolution or
11
12 equilibrium).

Figure 2

13
14
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17
18 The asymmetric logistic peak adjustment (ALPA) was developed as a new function for the PSF of highly
19
20 asymmetric electrochemical signals in non-bilinear datasets or in the presence of irreversible electrochemical
21
22 processes [63]. Fig. 3 summarizes the main steps of the fitting procedure.

Figure 3

1.1.5.14. Correlation optimized warping (COW)

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24
25
26
27 The correlation optimized warping (COW) algorithm is also based on a piece-wise linear correction function and
28
29 it is continuous and made up of segments whose slope is allowed to take a limited number of discrete values
30
31 determined by the length ℓ of the interval in which the voltammograms are divided and the maximum number of
32
33 scan points, s , by which the length of each interval is allowed to change [64,65]. When the slope of a segment of
34
35 the correction function $f(t_y)$ is not one, the corresponding intervals in sample and target contain a different
36
37 number of points and linear interpolation is used so that the interval in the sample is compressed or expanded to
38
39 the same length as the corresponding interval in the target. The optimized cost function is the sum of the
40
41 Pearson's correlation coefficient for all segments after interpolation and Dynamic Programming is used to attain
42
43 the global maximum given the constraints. Typically, a maximum allowed correction is set to further reduce the
44
45 feasible region for $f(t_y)$. One known problem of the standard COW method is that, close to the endpoints, the
46
47 maximum correction allowed by the slope constraints is reduced. While it is possible to modify the algorithm to
48
49 account for this, a computationally more intensive but equally effective solution is to attach zeroes at both ends of
50
51 the signals so that the necessary flexibility is guaranteed (namely $w_{\max} \ell s^{-1}$ zeroes should be attached at each end).

1
2 It is worth mentioning, that, while COW also allows for custom intervals, here its commonest format is used in
3
4 which sample and target are divided in segments of equal length.
5

6 7 *1.1.5.15. Interval correlation optimised shifting (icoshift)* 8

9 The interval correlation optimised shifting (icoshift) programme allows for different ways of aligning signals
10
11 primarily due to different NMR alignment procedures [66]. The most relevant to voltammetry uses a piece-wise
12
13 linear correction function based on an insertion/deletion (I/D) model [65]. In this method, one or more intervals
14
15 are defined, either manually or automatically, on the potential axis and the segments in the sample to be aligned
16
17 are shifted in order to maximize their cross-correlation with the corresponding segment of the target. The local
18
19 maximum cross correlation upon shift is calculated using a Fast Fourier Transform (FFT) computation engine in
20
21 which the optimal correction for all the samples is computed together and it is possible to fill in the inserted part
22
23 using missing values [65]. Compared with other FFT based alignment methods (e.g., peak alignment by FFT
24
25 (PAFFT) and recursive alignment by FFT (RAFFT)), endpoint contamination during the calculation of cross
26
27 correlation (aliasing) is avoided by padding the segments with a number of zeroes corresponding to the maximum
28
29 allowed correction w_{\max} and improved efficiency is obtained by treating all the samples at once [65]. The icoshift
30
31 only implements simple segmentation strategies, e.g., one can define a number of segments of equal length, but
32
33 accepts interval definitions provided by the user, as is the case here. icoshift uses a greedy algorithm for the
34
35 optimization [65], which means that the intervals are optimized separately, without accounting for any global
36
37 effects. Note that, like other alignment methods but unlike COW, the icoshift optimization criterion is not well
38
39 defined mathematically unless missing values are used for the insertion, because the cross-correlation function is
40
41 not calculated after the correction is applied and the segment boundary point replicated. With respect to w_{\max} , it is
42
43 possible to let icoshift automatically increase it, for each interval separately, if the optimal shift for any of the
44
45 signals is found to be exactly on the boundary of the interim w_{\max} value. The iterative procedure starts at 5% of
46
47 the segment length and increases by an additional 5% at each iteration, up to 50% of the segment length. The
48
49 icoshift programme has the built-in option of automatically picking the signal with the largest area under the
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1
2 curve as a target for each interval. This option was tested against the more standard approach of using as a single
3
4 target either the average voltammogram or a representative sample with average potential shift.
5

6 7 *1.2. Electrochemistry*

8
9 Electrochemistry is a branch of chemistry concerned with the interrelation of electrical and chemical effects. A
10
11 large part of this field deals with the study of chemical changes caused by the passage of an electric current and
12
13 the production of electrical energy by chemical reactions [67]. In fact, the field of electrochemistry encompasses
14
15 a huge array of different phenomena (e.g., electrophoresis and corrosion), devices (electrochromic displays,
16
17 electroanalytical sensors, batteries, and fuel cells), and technologies (the electroplating of metals and the large-
18
19 scale production of aluminum and chlorine). Electroanalytical methods are a class of electrochemical techniques
20
21 in analytical chemistry which study an analyte by measuring the potential or current in an electrochemical
22
23 cell containing the analyte [68-71]. In general, it is well-known that electrochemical analysis has benefited from
24
25 the electronics revolution in at least two important ways (i) the development of neater, faster, more simple and
26
27 arguably, competitively affordable instrumentation, and (ii) the potential for rapid analysis. In addition,
28
29 electrochemistry is a very versatile science offering the analyst a wide range of methods for analysis, e.g.,
30
31 coulometry, potentiometry, polarography and voltammetry, many of which are often available on the same
32
33 instrument, and together provide optimum analytical solutions over a wide concentration range generally from
34
35 ppb to mg L^{-1} levels.
36
37

38 39 40 41 42 *1.3. Chemometrics*

43
44 Chemometrics is a chemical discipline that uses mathematics, statistics, and formal logic: (a) to design or to
45
46 select optimal experimental procedures; (b) to provide maximum relevant chemical information by analyzing
47
48 chemical data; and, (c) to obtain knowledge about chemical systems [72]. Chemometric analysis has gained
49
50 widespread acceptance over the past two decades, responding to the need to study increasingly complex samples
51
52 by improving existing analytical protocols. There is intensive research devoted to the development and the testing
53
54 of multivariate algorithms applied to progressively more difficult chemical scenarios [73-76].
55
56

57 58 59 *1.4. Nomenclature for data, sample constituents and calibration*

60 61 *1.4.1. Data*

1
2 *1.4.1.1. Zeroth-order data*

3
4 Zeroth order corresponds to instruments producing a single response per sample (a zeroth-order tensor), such as
5
6 the current at a single potential or the reading of an Autolab instrument [77]. When zeroth-order data for a group
7
8 of samples are joined into a single, a vector is produced. Hence, zeroth-order data are also known as one-way
9
10 data. Fig. 4 shows the natural progression from zeroth-order data as the simplest data to higher-order data.

11
12
13 **Figure 4**

14
15 *1.4.1.2. First-order data*

16 First-order data for a given sample are arranged as a vector or first-order tensor (Fig. 4), such as a voltammogram
17
18 or chronoamperogram [77]. When first-order data for a group of samples are joined into a single, a matrix is
19
20 produced. Hence, first-order data are also known as two-way data.

21
22
23
24 *1.4.1.3. Second-order data*

25 A data matrix for a single sample are considered to be second-order (Fig. 4) [77]. They can be recorded in two
26
27 ways: (1) using a single instrument (e.g., such as an Autolab registering current-potential matrices at different
28
29 pulse heights or pulse times); or, (2) coupling two “hyphenated” first-order instruments such as gas
30
31 chromatography-mass spectrometry. When second-order data for a group of samples are joined into a single,
32
33 three-dimensional array, the resulting object is known as three-way array. Hence, second-order data are also
34
35 known as three-way data.

36
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40 *1.4.1.4. Third-order data*

41 Introducing an extra dimension in the data leads to higher-order data, in which case the mathematical object
42
43 obtained by grouping third-order data for several samples into the fourth dimension is known as a four-way array
44
45 [77].

46
47
48
49 *1.4.1.5. Linearity and non-linearity of the data*

50 There is much confusion about the terms linear and linearity. Suppose a model is needed for relating x_i (the
51
52 predictor) to y_i (the predictand), where i indexes the objects and runs from 1 to I . Such a model is linear in the
53
54 parameters and in the variables if it can be written as [78]:

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56
57
58
59
$$y_i = b_0 + b_1x_i + e_i; \quad i = 1, \dots, I \quad (1)$$

1
2 which is the usual linear regression model with an intercept (b_0) and an error term (ε_i). An example of a model
3
4 linear in the parameters but non-linear in x is:

$$5 \quad y_i = b_0 + b_1 x_i + b_2 x_i^2 + e_i; \quad i = 1, \dots, I \quad (2)$$

6
7
8
9 It is useful to distinguish these two types of linearity. If in the chemical sciences the term ‘linearity’ is
10 loosely used, then often linearity in the parameters is meant. Hence, models in Eqs. (1) and (2) are linear in the
11 parameters, because when x is fixed, y is a linear function of the parameters b_0 , b_1 (and b_2).
12
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15
16 Non-linearity is a relationship which cannot be explained as a linear combination of its variable inputs. In
17 other words, the outcome does not change in proportion to a change in any of the inputs.
18
19

20
21 Prior to selecting a linear or non-linear regression to fit the data for building a calibration model, it is
22 important to know whether the signal varies linearly with analyte concentration or not. In next sections, different
23 types of linearity a non-linearity will be discussed.
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25
26

27 28 *1.4.1.5.1. Bilinearity versus non-bilinearity*

29 Bilinearity is a property assumed by multivariate linear calibration algorithms. This requires that a data matrix
30 can be expressed as a sum of single component (analyte) data matrices, where each of them decomposes into the
31 product of two vectors containing the concentrations and currents [79]. However, in many analytical situations,
32 slight deviations from these assumptions have to be considered, such as, for example, in the presence of
33 interactions between different individual components. In general, non-linearity of the signals results in the
34 observation of strong signal shifts, peak broadening or non-proportional increase of the peak height. Any of these
35 effects strongly hinder the direct application of bilinear data models. Such problems become more complicated
36 when signals generated by successive analytes or interferences overlap [79].
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50 *1.4.1.5.2. Trilinear data*

51 When second-order data are processed for a set of samples, it is important whether the three-dimensional array
52 built with these data complies or not with the so-called trilinearity condition. The latter establishes that the three-
53 way data array built with a set of second-order signals can be modeled through the following expression:
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$$X_{ijk} = \sum_{n=1}^N a_{in} b_{jn} c_{kn} + E_{ijk} \quad (3)$$

where N is the total number of chemical constituents generating the measured signal, a_{in} is the relative concentration or score of component n in the i -th sample, and b_{jn} and c_{kn} are the intensities in the instrumental channels (or data dimensions) j and k , respectively. The values of E_{ijk} are the elements of the three-dimensional array \mathbf{E} , representing the residual error, and having the same dimensions as \mathbf{X} . The column vector a_n is collected in the scores matrix \mathbf{A} , while vectors \mathbf{b}_n and \mathbf{c}_n are collected in the loading matrices \mathbf{B} and \mathbf{C} (usually \mathbf{b}_n and \mathbf{c}_n are normalized to unit length). The above principle can be formulated in a less mathematical way. A three-dimensional array will be trilinear provided the following requirements are verified: (1) the signal is linearly related to the analyte concentration; (2) the signal for a given sample is bilinear; and, (3) the component profiles are constant across the different samples. The first point simply means that the maximum signal, measured for a pure component at selected values of the sensors in each of the two data dimensions, is directly proportional to the component concentration. The second requirement implies that a single component data matrix can be decomposed into the product of two vectors, each containing the component profile in one of the two data dimensions. Finally, the third requirement implies that the shape of the profiles in all dimensions for a given component must be the same, with intensity variations being due only to different concentrations in different samples [80].

1.4.1.5.3. Non-trilinear data

To evaluate the linearity of a three-way data array should first consider its basic ingredients, i.e., the individual data matrices and whether they are bilinear or not. In case they are bilinear, a further subdivision can be made on the existence and number of trilinearity-breaking modes: (1) when one of the data modes is non-reproducible and breaks the trilinearity, the data are not trilinear, but can be unfolded into a bilinear augmented matrix, and (2) when both data modes are trilinearity breaking, the data are not trilinear and cannot be unfolded into a bilinear augmented matrix. To distinguish these two latter non-trilinear data types, we propose to call them non-trilinear Type 1 and non-trilinear Type 2, respectively. Finally, in case the individual matrices are non-bilinear, we have a fourth data type, which we may call non-trilinear Type 3. There is no point in further dividing Type 3 data

1 according to the number of non-reproducible modes, since the former are neither trilinear nor unfoldable to an
2 augmented bilinear matrix [77,80]. Fig. 5 illustrates the classification of three-way data for a sample set.
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6
7 **Figure 5**

8 *1.4.1.5.4. Quadrilinear data*

9
10 Quadrilinearity of a four-way array can be defined by extension of Eq. (3), including an additional mode: the
11 sample mode. A four-way data array obtained by “joining” three-dimensional data arrays for a sample set is
12 quadrilinear if its elements can be thought to be obtained through:
13
14

$$15 \quad X_{ijkl} = \sum_{n=1}^N a_{in} b_{jn} c_{kn} d_{ln} + E_{ijkl} \quad (4)$$

16
17 where all symbols are as in Eq. (3), with d_{in} describing the changes in constituent concentrations along the sample
18 mode. A requirement for quadrilinearity of a data array for a sample set is that the three instrumental profiles for
19 each constituent are equal for all samples [77].
20
21

22 *1.4.1.5.5. Non-quadrilinear data*

23
24 Quadrilinearity may be lost if one or more modes behave as quadrilinearity-breaking, in the sense that constituent
25 profiles change from sample to sample along this mode. In the present case there might be one, two, or three
26 quadrilinearity-breaking modes. Hence, a pertinent classification of non-quadrilinear third-order/four-way data
27 would be in types 1, 2, and 3 respectively. On the other hand, intrinsically non-trilinear data for each sample for
28 reasons of mutual correlations among the phenomena in the different data modes will be classified as non-
29 quadrilinear of type 4 [77]. Fig. 6 illustrates a classification tree.
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31

32
33
34 **Figure 6**

35 *1.4.1.6. Generation of second- and third-order electrochemical data*

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37 Differential pulse voltammetry (DPV) is the most frequently used technique for generation of second- and third-
38 order electrochemical data. The second- or third-order data could be obtained via changing one or two of the
39 instrumental parameters of DPV [81]. The theory behind the proposed procedure will be briefly discussed. The
40 current signal intensity in DPV can be obtained using the following equations [82]:
41
42



$$\delta_i = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}(\tau-\tau')^{1/2}} \left[\frac{P_A(1-\sigma^2)}{(\sigma+P_A)(1+P_A\sigma)} \right] \quad (6)$$

$$P_A = \xi \exp \left[\frac{nF}{RT} \left(E + \frac{\Delta E}{2} - E^0 \right) \right] \quad (7)$$

$$\sigma = \exp \left(\frac{nF}{RT} \frac{\Delta E}{2} \right) \quad (8)$$

$$\xi = \left(\frac{D_O}{D_{Red}} \right)^{1/2} \quad (9)$$

where O and Red are species involved in the electrode reaction (Eq. (5)), n is the number of electrons involved in the electrode reaction, F is the faraday constant, A is the electrode area, D_O and D_{Red} are diffusion coefficients of O and Red species, respectively, C_O^* is the concentration of O species at the electrode surface, R is gas constant, T is temperature, ΔE , E and E^0 are pulse height, potential and formal potential of the electrode, respectively, τ and τ' are, pulse duration or pulse time and starting time of potential pulse, respectively. For a typical electrochemical reaction, a data vector can be obtained by sweeping the potential at constant ΔE and τ . Applying a different ΔE and sweeping potential at the constant τ , will produce different data vectors, i.e., sweeping the potential and applying different ΔE at a constant τ in DPV produces a non-bilinear second-order data. By the same way, third-order voltammetric data could be obtained by sweeping potentials at different pulse heights and pulse durations [83]. Literature survey revealed that change of ΔE can cause non-linearity in the recorded DPV data while change of τ doesn't cause any non-linearity [81,84]. Therefore, it is reasonable to have a non-bilinear (change in ΔE) and trilinear (change in τ) three-way data array for each sample and finally a non-quadrilinear (change in concentration for sample to sample) four-way data array.

1.4.2. Sample constituents

It is important to define categories of sample constituents, focusing on those generating a signal that overlaps with the analyte of interest, as they can be considered as potential interferents. A distinction should first be made between constituents present in the calibration and validation sets of samples, and those that are present in only the unknown sample. The former can be called ‘‘expected’’ constituents, because they are included in the

1 calibration and validation sets in order to ensure that they are sufficiently representative. However, truly
2 unknown samples may contain additional constituents: the “unexpected”. The expected constituents can be
3 further divided into “calibrated” (referring to those for which calibration concentrations are available (including
4 the analyte of interest)) and “uncalibrated” (referring to
5 constituents for which only a common subspace that contains them is accessible). Notice that potential
6 interferences will not always produce an interference, in the sense of generating a systematic error in the analyte
7 determination [85]. Whether the interference will be real or will remain as potential only depends on the type of
8 instrumental signals and on the calibration methodology.

21 *1.4.3. Calibration*

22 According to the international union of pure and applied chemistry (IUPAC), calibration is, in a general sense,
23 “an operation that relates an output quantity to an input quantity for a measuring system under given conditions”
24 [86,77]. The input quantities of our primary interest, i.e., in analytical calibration, are the concentrations of a
25 sample constituent of interest (the analyte), while the output quantities are analytical signals or responses
26 delivered by analytical instruments (a spectrometer, chromatograph, voltammetric equipment, etc.). Therefore, in
27 this review article calibration will mean the operation of relating instrumental signals to analyte concentrations.

38 *1.4.3.1. Univariate calibration*

39 A specific case of the general calibration process is the one relating the content of a single analyte in a sample to
40 a single value of an instrumental signal, and is called “univariate calibration”. In analytical chemistry, univariate
41 calibration employs a calibration curve as a general method for the determination of the concentration of a
42 constituent in an unknown sample [77].

49 *1.4.3.2. Multivariate calibration*

50 A more general calibration process involves the relationship between the concentrations of various constituents in
51 a test sample and multiple measured responses, i.e., multivariate instead of univariate [77,87]. In contrast to
52 univariate calibration, which works with a single instrumental response measured for each experimental sample,
53 multivariate calibration works with many different signals for each sample. Depending on the instrumental setup,
54 the delivered data for a single sample may have different degrees of complexity. The simplest multivariate data

1
2 are those produced in vector form, i.e., as a series of responses, which can be placed one on top of each other to
3
4 generate a mathematical object known as a column vector. This object is also referred as having a single “mode”
5
6 or “direction”. Multivariate calibration using vectorial data has given rise to a highly fruitful analytical field,
7
8 which today is routine in many industrial laboratories and process control units [88]. Multiple analytes can be
9
10 determined simultaneously in the presence of other, possibly unknown constituents, provided they have been
11
12 properly taken into account during the calibration phase [89,90].
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21 *1.4.3.3. Multi-way calibration*

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23 Multi-way calibration is based on many instrumental signals per sample, which can be meaningfully organized
24
25 into a certain mathematical object with more modes than a vector, for example, as a data table or matrix [77,78].
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28 The most important advantage of multi-way calibration is the fact that analytes can be determined in the presence
29
30 of unexpected constituents in test samples. It is called the “second-order advantage”.
31
32

33 Multi-way calibration has interesting advantages relative to other calibration methods. One is the increase
34
35 in sensitivity, because the measurement of redundant data tends to decrease the relative impact of the noise in the
36
37 signal. Selectivity does also increase, because each new instrumental mode, which is added to the data
38
39 contributes positively to the overall selectivity. Still another one is the possibility of obtaining qualitative
40
41 interpretation of chemical phenomena through the study of multi-way data, in a much better way than with
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43 univariate or first-order data.
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47 **1. Casting a look on applications of MATLAB in electrochemistry**

48 MATLAB is the most important program used by the chemometricians to solve their chemical problems.
49
50 MATLAB can be linked with electrochemistry by the chemometricians and those electrochemists who are
51
52 familiar with MATLAB-based chemometrical approaches. In electroanalytical projects, the sensor is usually
53
54 modified with different materials to enhance the selectivity and sensitivity of the developed method [91-103], but
55
56 the treatment involved is time-consuming and the associated cost is high. It is thus important to develop new
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1 methodologies. An attractive possibility is the coupling of chemometric approaches with electrochemical
2 methods. This possibility have caused a lot of applications for MATLAB in electrochemical projects and we are
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6
7 going to cast a look on them in next sections.

9 *2.1. Improving the signal quality*

10 *2.1.1. Enhancing the sensitivity of electroanalytical methods*

11 In electroanalytical methods, many efforts have been made over the last several decades to enhance the
12 sensitivity as a key parameter by improving the electrochemical signals [104-106].The double layer charging
13 current, which is generated with the change of potential on the working electrode surface, causes interference
14 with the accurate measurement of the faradaic current and restricts the detection limit [107,108]. Since the
15 analytical signal is usually generated by changing the potential in most electrochemical techniques, it is inevitable
16 to include the charging current in the measured signal of an electroanalytical system. Therefore, elimination of
17 the charging current has been an important goal in electrochemical analysis. Applications of chemometrics
18 methods such as MCR-ALS [109,110], iterative target transformation factor analysis (ITTFA) [111], and ATLD
19 and PARAFAC [112,113] for resolving net faradaic current contribution from total current have been reported.
20 Safavi et al. have reported a work in which by using MCR-ALS as a powerful chemometrics method, a
21 straightforward method has been introduced for resolving faradaic current from the two types of charging
22 currents (step charging current and induced charging current) [109]. Cyclic voltammograms of a solution of 2.0
23 mM $\text{Co}(\text{phen})_3\text{Cl}_2$ and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in 0.1 M KCl at different scan rates are shown in Fig. 7. Figs. 8 and 9 show
24 the application of the MCR-ALS to resolve different current types. As it is obvious from Figs. 8a and 9a , the net
25 faradaic current cyclic voltammograms are very similar to the corresponding voltammograms of the raw data
26 which are shown in Fig. 7. But, the values of current are about much larger than the corresponding values of raw
27 data. This is because the induced charging current has negative contribution in total current and thus it suppress
28 the observed faradaic current. Therefore, the pure faradaic component shows higher sensitivity rather than the
29 raw cyclic voltammograms. Shao and Hemmateenejad who have the most important works on application of
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1 chemometrics to increase the sensitivity of electrochemical approaches have also performed more projects [110-
2 113].
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6 Figure 7

7 Figure 8

8 Figure 9

9 2.1.2. Data treatment

10 2.1.2.1. Baseline correction

11 A variety of instruments deliver signals that consist of a series of more or less isolated peaks. The physical or
12 chemical information is in the positions and the heights of the peaks. Ideally the baseline should be flat, but this
13 is seldom the case. In practice slow, but strong, fluctuations are seen, which are known as background, drift, or
14 baseline. Therefore, baseline correction has been considered as a critical step for enhancing the signals and
15 reducing the complexity of the analytical data [65,114]. Considering this aim, Eilers et al. have introduced an
16 algorithm for baseline elimination based on asymmetric least squares splines regression (AsLSSR) approach
17 [115]. This algorithm is the most frequently used algorithm for baseline correction in electrochemical projects
18 [65,83,116-118].
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32 2.1.2.2. Potential shift correction

33 Linearity is a property that is estimated by multivariate linear calibration algorithms. However, in many
34 electroanalytical situations, slight deviations from linearity could be observed such as in the presence of
35 interactions between different individual components. In general, nonlinearity of the signals results in the
36 observation of strong signal shifts, peak broadening, or nonproportional increase in the peak height. Any of these
37 effects strongly hinder the
38 direct application of linear data models. Such problems become more complicated when signals generated by
39 successive analytes or interferences overlap. Therefore, the alignment of voltammograms is an important
40 chemometric activity, which should be conducted before the application of multilinear data processing
41 algorithms. The basis of these techniques involves digitally moving (and/or stretching or compressing) a
42 voltammogram until it matches a reference one, with certain objective functions indicating the quality of the
43 match (correlation coefficient, residual fit, similarity index, etc.). Some of the main differences among them are
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2 as follows: (1) whether alignment is performed using the continuous signal or individually detected peaks, (2)
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4 whether or not signal intensity is used, and (3) whether or not scale changes are corrected. The most important
5
6 alignment methods that have been employed for aligning the voltammograms are COW, icoshift, GPA, GPA2D,
7
8 ALPA, shiftfit and pHfit [58-63,65,83,116,117,119,120].
9

10
11 The work reported in Ref. [83] is interesting in which the raw DPV data (Fig. 10A) has been baseline
12 corrected by AsLSSR (Fig. 10B) and then, the observed shift in the data has been corrected by the alignment of
13
14 the data with help of COW as an efficient chemometric tool (Fig. 10C).
15
16
17
18

19 Figure 10

20 1.2. Data exploration and sample classification

21
22 There are some chemometric methods which are able to provide a way to visualize variation within large
23
24 multivariate data sets as an end in itself or as a preprocessing step to discriminate information before building a
25
26 classification model [121]. The PCA is the main tool for this purpose, and it can be implemented through a
27
28 number of multivariate algorithms [121]. Some applications of chemometric methods to build classification
29
30 models for screening different types of electrochemical data have been reported in the literature [122-150].
31
32
33

34 1.3. Complexation

35
36 Electrochemical methods can provide detailed information on processes taking place in solution because
37
38 complexation or exchanging interactions can be gradually studied by changing the concentration of one
39
40 component with respect to another. Polarographic and voltammetric techniques have been widely used to study
41
42 the interactions between metal ions and a diversity of ligands [151-160]. These techniques can yield information
43
44 about the physicochemical properties of the metal complexes. A major drawback of these techniques is the
45
46 limited sensitivity which hinders the study at the low concentrations existing in natural media and anodic
47
48 stripping voltammetry (ASV) seems to be a solution to this problem, but adsorption and especially the
49
50 irreversible character of the reduction of metal complexes which does not produce the corresponding oxidation
51
52 signals during the stripping step hinder its application [158]. Stripping chronopotentiometry (SCP) techniques
53
54 appear as an alternative to voltammetry because it has been empirically proved to be less sensitive to the presence
55
56 of important quantities of organic matter [161-167].
57
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1 MCR-ALS as a soft modeling method plays a key role in metal-ligand complexation studies and for many
2 systems high quality results were obtained by electrochemical data analyzed by MCR-ALS [158-160,167-172].
3
4 In an interesting work published by Chekmeneva *et al.* a novel electrochemical method based on DPV at a
5 rotating Au-disk electrode was proposed to study binding of Hg^{2+} with several ligands by applying a previous
6 deposition potential which allowed the adsorption of Hg^{2+} ions and/or their complexes on Au surface, followed
7 by a cathodic potential scan [173]. The classical DPV scheme, without any preconcentration step, did not yield
8 reproducible and reliable results. In order to reach additional information on the complexation processes, the
9 MCR-ALS was used for data processing and interpretation, which permitted to obtain both the dynamic picture
10 of complexation and stoichiometries of formed species. Fig. 11 shows the normalized individual voltammograms
11 (a) and concentration profiles (b) obtained from MCR-ALS, with a lack of fit of 7.08%. The constraints of non-
12 negativity, signal shape and selectivity were applied. Seven components were necessary for satisfactory
13 completion of the data. The components I and II are related to Hg^{2+} reduction while the peak at 0.1 V does to the
14 reduction of Hg^{2+} adsorbed on the electrode surface. The nature of component III appears to be very interesting.
15 This type of signal is always observed with thiols at Hg electrodes, and it is of great importance because serves
16 for determination of thiols. The component V, which develops before the Cys/Hg ratio of 1 and achieves the
17 maximum at ratios close to 1, seems to be related to a 1:1 Hg(Cys) complex. The component IV rises just after
18 the profile of component V begins to descend (Fig. 11b). Moreover, it appears from the displacement of the peak
19 described by component V towards more positive potential. They proposed that this could be due to the
20 reorganization from one of the 1:1 complexes to another one, when increasing Cys concentration. Thereby, the
21 signal displacement of component IV is observed and this peak persists until the end of the titration. The
22 components VI and VII correspond to the signals appearing at very negative potentials. The component VI
23 stabilizes at the Cys/Hg ratio of 1, and it can be related to a 1:1 Hg-Cys complex. Component VII achieves
24 almost constant value at the ratio of 2, and thus it is attributed to a stable 1:2 complex. Due to very negative
25 potentials and the shape of these signals, they are related with reported phenomenon of cathodic reductive
26 desorption of thiol-containing molecules from the Au-disk electrode.

A great variety of complexation systems have also been investigated by different electroanalytical techniques and MCR-ALS [174-185].

1.4. *Small molecule-biomacromolecule interactions*

In general, there are many examples of complex reactions for which it is not only important to analyze the reactants but also the products. However, it can be quite difficult to analyze a multi-component reaction system, especially if one or more of the reaction species are complex. Typical illustrations of such systems are the interactions of small molecules with biomacromolecules such as DNA, human serum albumin (HSA) and bovine serum albumin (BSA), and it is often desirable to estimate simultaneously, the amounts of the small molecule, the biomacromolecule and their complex product. Such analytical tasks can be quite challenging, and composite profiles of the reactants and products are collected from instrumental analyses. Thus, the application of the common methods of data interpretation is often limited. However, chemometrics methods such as MCR-ALS, have provided a potential solution to resolve the analytical profile complexities. It is also possible, with the use of the expanded matrix methods [186], to combine data matrices of analyte profiles derived from different analytical methods [187]. In general, the results of such approaches have indicated that the increased information in the expanded matrix improves data analysis and subsequent interpretation of the results.

There are several reports on application of chemometric methods for resolving interactions of small molecules with biological macromolecules such as HSA, BSA and DNA [101,102,188-192]. In these studies, an augmented data matrix has been built by the combination of different spectroscopic and voltammetric data and then, the augmented data matrix has been resolved by MCR-ALS. The outputs of MCR-ALS had new information about small molecule-biomacromolecule interactions which helped the authors to better justify the interactions.

2.5. *Concentrations determination and calibration*

Calibration model building based on coupling of chemometric methods with electrochemical data for concentration determination includes first-, second- and third-order multivariate calibrations where the

1
2 electrochemical data are processed by different algorithms and in this section, we are going to cast look on the
3
4 works reported in the literature.
5

6 *2.5.1. First-order multivariate calibration*

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8 The first-order multivariate calibration approach considers a series of experiments, e.g., the experimental data as
9
10 a whole, without explicitly treating the individual signals, voltammogram by voltammogram [121]. For the most
11
12 usual case of voltammetry, the fundamental starting point is the arrangement of the data as a matrix of currents \mathbf{I}
13
14 ($n\mathbf{R}$, $n\mathbf{C}$), where $n\mathbf{R}$ indicates the number of rows as the number of recorded voltammograms (of different
15
16 samples, or of the same system but at some different conditions of any relevant variable), and $n\mathbf{C}$ indicates the
17
18 number of columns, for example, potentials scanned during the current measurements [121]. The basic goal of
19
20 the different multivariate analysis methods is to decompose mathematically the experimental current data matrix
21
22 \mathbf{I} into a product of two matrices (or vectors, depending on the case) containing the information of concentrations
23
24 (\mathbf{C}) and of the individual voltammograms (\mathbf{V}). This decomposition is based on the assumption that the measured
25
26 instrumental responses are bilinear and can be expressed as $\mathbf{I}=\mathbf{CV}+\mathbf{X}$, where \mathbf{X} is a residual matrix containing the
27
28 variance not explained by \mathbf{C} and \mathbf{V} . The most popular first-algorithms which have been applied to
29
30 electroanalytical data are including MLR, principal components regression (PCR), classical least squares (CLS),
31
32 PLS, non-linear PLS and inverse least squares (ILS).
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41 There are too many works which have been reported in the literature in which first-order electrochemical
42
43 data have been used to build first-order multivariate calibration models. These works have been performed for
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45 food analyses [193-208], pharmaceutical and pesticide residues analyses [209-223] and environmental pollutant
46
47 analyses [224-245]. Developing novel and efficient analytical methods based on coupling of first-order
48
49 multivariate calibration with electrochemical data is very important from analytical point of view because such
50
51 analyses are usually performed by UV-visible spectrophotometry, atomic absorption spectroscopy, inductively
52
53 coupled plasma-mass spectrometry, X-ray fluorescence analysis, gas and liquid chromatography, near infra-red
54
55 spectroscopy and mass spectrometry. However, these methods are accurate but are limited by time and cost while
56
57 electrochemical methods such as voltammetry and polarography, are readily available for quantitative analyses.
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61

1
2 In most cases, the responses from such analyses overlap but these complex signals can be often resolved by the
3
4 application of chemometrics.
5

6 *2.5.2. Multiway calibration*

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8 Multi-way calibration increases the sensitivity due to the measurement of redundant data which decreases the
9
10 relative impact of the noise in the data and selectivity is also increased because each new instrumental mode
11
12 contributes positively to the overall selectivity [246,247]. Furthermore, multi-way calibration enables the
13
14 analytical chemist to obtain more qualitative information about the chemical phenomena than with univariate or
15
16 first-order data. Several techniques such as fluorescence excitation-emission [248], high performance liquid
17
18 chromatography with diode array detection (HPLC-DAD) [249], liquid chromatography-attenuated total
19
20 reflectance-Fourier transform infrared spectroscopy (LC-ATR-FTIR) [250], liquid chromatography-DAD-mass
21
22 spectrometry (LC-DAD-MS) [251], flow injection analysis-DAD (FIA-DAD) [252], DAD-kinetics [253] and
23
24 pH-DAD [254] have been used to obtain second-order data. Although these techniques are accurate and reliable
25
26 but suffer from several disadvantages such as high-cost and complexity of their instruments. Therefore, new
27
28 techniques are highly required for the inexpensive quantification of analytes in complex matrices. Among the
29
30 available analytical methods, electrochemical methods with low-cost instruments and applicability to
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32 miniaturization are a good choice for accurate, fast and reliable determination of the analyte(s) of interest in
33
34 interfering media. In this section, we are going to cast a look on applications of multi-way calibration in
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36 electrochemical analyses.
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45 The use of multiway calibration in electrochemical analysis is still in its infancy and for many years, its
46
47 application to electroanalytical data had been quite scarce as compared to the case of first-order multivariate
48
49 calibration. There are some research groups which have been working on coupling of multiway calibration with
50
51 electrochemical data and have performed interesting works [81,83,118,120, 255-265].
52
53
54

55 All the works published in the literature have been focused on the coupling of three-way calibration with
56
57 second-order electrochemical data in which second-order advantage has been exploited for simultaneous
58
59 determination of some analytes in the presence of uncalibrated interference. But, there is only one work which is
60
61

1 related to coupling of four-way calibration with third-order electrochemical data [83]. In this work, a four-way
2 multivariate calibration approach based on the combination of differential pulse voltammetric (DPV) data and
3 four-way algorithms is described for the first time. To achieve this goal, the DPV response of each sample was
4 recorded thirty-six times. Six current-potential matrices were recorded at six different pulse durations. Each
5 matrix consists of six vectors which have been recorded at six different pulse heights. The three-way data array
6 obtained for the calibration set and for each of the test samples were joined into a single four-way data array. The
7 recorded four-way data array was nonlinear, thus, the non-linearities were tackled by potential shift correction
8 using COW and subsequently was analyzed with U-PLS/RTL and N-PLS/RTL as third-order multivariate
9 calibration algorithms. A comprehensive and systematic strategy for comparing the performance of the two
10 algorithms was presented in this work, in particular with a view of practical applications. This comparison was
11 developed to identify which algorithm offers the best predictions for the simultaneous determination of levodopa,
12 carbidopa, methyldopa, acetaminophen, tramadol, lidocaine, tolperisone, ofloxacin, levofloxacin, and norfloxacin
13 in the presence of benserazide, dopamine, and ciprofloxacin as uncalibrated interferences using a multi-walled
14 carbon nanotubes modified glassy carbon electrode (GCE). This study demonstrated the more superiority of U-
15 PLS/RTL to resolve the complex systems. The results of applying U-PLS/RTL for the simultaneous
16 determination of the studied analytes in human serum samples as experimental cases were also encouraging.

2.6. *Developing sensors and biosensors based on digital image processing*

23 Metallic nanoparticles (NPs) due to having high catalytic activity and catalytic selectivity are extensively used in
24 fabrication of electrochemical sensors and biosensors. Their sizes are commonly linked directly to their catalytic
25 activity, with different crystal nucleation and growth processes giving rise to different particle size distributions
26 (PSDs). Therefore, estimation of PSD is an important parameter which must be statistically meaningful. Digital
27 image processing (DIP) is an important which can be applied to determine PSD. Therefore, DIP can be used in
28 fabrication of electrochemical sensors and biosensors. In a work published by Hezard *et al.*, a GCE modified by
29 Au NPs has been developed to Hg(II) trace analysis [266]. In this work, six GCEs have been modified by
30 electrodeposition of Au NPs using cyclic voltammetry under applying different numbers of cyclic scans

1
2 (N=1,2,4,8,12 and 16) and then, the images of the surfaces of the GCEs have been captured by field emission gun
3
4 scanning electron microscopy (FEG-SEM). They have written a MATLAB code which can be applied to the
5
6 FEG-SEM images for determination of NPs density and average diameter. Their results showed that the best
7
8 performance has been observed for the GCE modified by 4 cyclic scan (the small-sized particles with high
9
10 density). Finally, this modified GCE has been applied to the determination of Hg(II) with a linearity range from
11
12 0.64 to 4.00 nM and a limit of detection of 0.42 nM.
13
14

15
16 Gholivand et al. have published a work on application of DIP in fabrication of a biotin biosensor [95]. In
17
18 this work, nine GCEs modified by a room-temperature ionic liquid (RTIL)-chitin (Ch) composite film
19
20 (PdFeNi/ChRTIL) were further modified by electrodeposition of PdFeNi trimetallic alloy NPs with help of cyclic
21
22 voltammetry under applying different numbers of cyclic scans (N=1,2,4,8,12,16,20,24 and 28). Then, the SEM
23
24 images were captured from the surface of the modified electrodes which are showing in Fig. 12. Then, the images
25
26 were analysed by a MATLAB code to obtain PSDs which are showing in Fig. 13. As can be seen, the best results
27
28 were obtained for eight electrodeposition cyclic scans, where small-sized particles (19.54 ± 6.27 nm) with high
29
30 density (682 particles μm^{-2}) were obtained. Finally, the PdFeNi/ChRTIL/GCE was satisfactorily applied to the
31
32 determination of biotin in infant milk powder, liver, and egg yolk samples.
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39 Figure 12

40 Figure 13

41 2. Conclusions

42
43 The information collected in this review article confirmed that MATLAB is a powerful software which has a lot
44
45 of applications in electrochemistry and electrochemists have used it for their qualitative and quantitative
46
47 purposes. The works published in the literature showed that MATLAB could improve the quality of the
48
49 electrochemical projects. MATLAB allows the electrochemists to write new algorithms which can help them to
50
51 obtain more information about the systems under their study which can not be obtained by direct analysis of the
52
53 electrochemical data. MATLAB has many toolboxes which have outstanding applications in different areas of
54
55 electrochemistry such as complexation studies, separation of the faradic current contribution from total current to
56
57 enhance the sensitivity of the electroanalytical
58
59
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1 techniques, calibration and concentration determination, small molecule-biomacromolecule interactions,
2
3
4 improving the signal quality, data exploration and sample classification and digital image processing. The newest
5
6 application of MATLAB in electrochemistry is using its digital image processing toolbox to explore the sensor
7
8 surface to obtain a desirable and optimal surface for developing electrochemical sensors and biosensors. On the
9
10 whole, this review was written from both electrochemical and chemometrical points of view with the aim of
11
12 providing useful information for the electrochemists and to promote the use of MATLAB in electrochemistry.
13
14

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18
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41 **Caption to figures:**

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43 **Fig. 1.** Flowchart of the GPA [61].

44 **Fig. 2.** Flowchart of the GPA2D [62].

45 **Fig. 3.** Flowchart of the ALPA [63].

46 **Fig. 4.** Hierarchy of data illustrating the nomenclatures based on the concept of “Order” and “Ways”. Top: data
47 for a single sample. Bottom: data for a set of samples [77].

48 **Fig. 5.** Classification tree for three-way data for a set of samples, according to whether the individual data
49 matrices are bilinear or not, and to the number of trilinearity-breaking modes [77].

50 **Fig. 6.** Classification tree for four-way data for a set of samples, according to whether the individual three
51 dimensional arrays data are trilinear or not, and to the number of quadrilinearity-breaking modes [77].

52 **Fig. 7.** Cyclic voltammograms of (a) 2.0 mM Co(phen)₃Cl₂ and (b) 1.0 mM Ru(NH₃)₃Cl₃ in 0.1 M KCl at
53 different scan rates [109].

54 **Fig. 8.** MCR-ALS derived cyclic voltammograms of (a) net faradaic, (b) step charging (c) induced charging and
55 (d) total current contribution for 2.0 mM Co(phen)₃Cl₂ in 0.1 M KCl at different scan rates [109].

56 **Fig. 9.** MCR-ALS derived cyclic voltammograms of (a) net faradaic, (b) step charging (c) induced charging and
57 (d) total current contribution for 1.0 mM Ru(NH₃)₆Cl₃ in 0.1 M KCl at different scan rates [109].
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2 **Fig. 10.** Differential pulse voltammetric data corresponding to the calibration set. (A) Raw data. After
3 preprocessing: (B) baseline correction and (C) alignment with COW [83].

4 **Fig. 11.** Normalized individual voltammograms (a) and concentration profiles (b) obtained from MCR-ALS
5 optimization by applying the non-negativity, signal shape and selectivity constraints [173].

6 **Fig. 12.** SEM images of PdFeNi/ChRTIL/GCEs prepared by CV from a 0.2 mol L⁻¹ KCl solution containing
7 0.5×10⁻³ mol L⁻¹ PdCl₂, 0.5×10⁻³ mol L⁻¹ NiCl₂ and 0.5×10⁻³ mol L⁻¹ FeCl₃. Number of cyclic scans (*N*): (A) 1,
8 (B) 2, (C) 4, (D) 8, (E) 12, (F) 16, (G) 20, (H) 24, and (I) 28 [95].

9 **Fig. 13.** Histograms of PSDs measured by DIP from the images presented in Fig. 12A-I [95].
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Figure 1

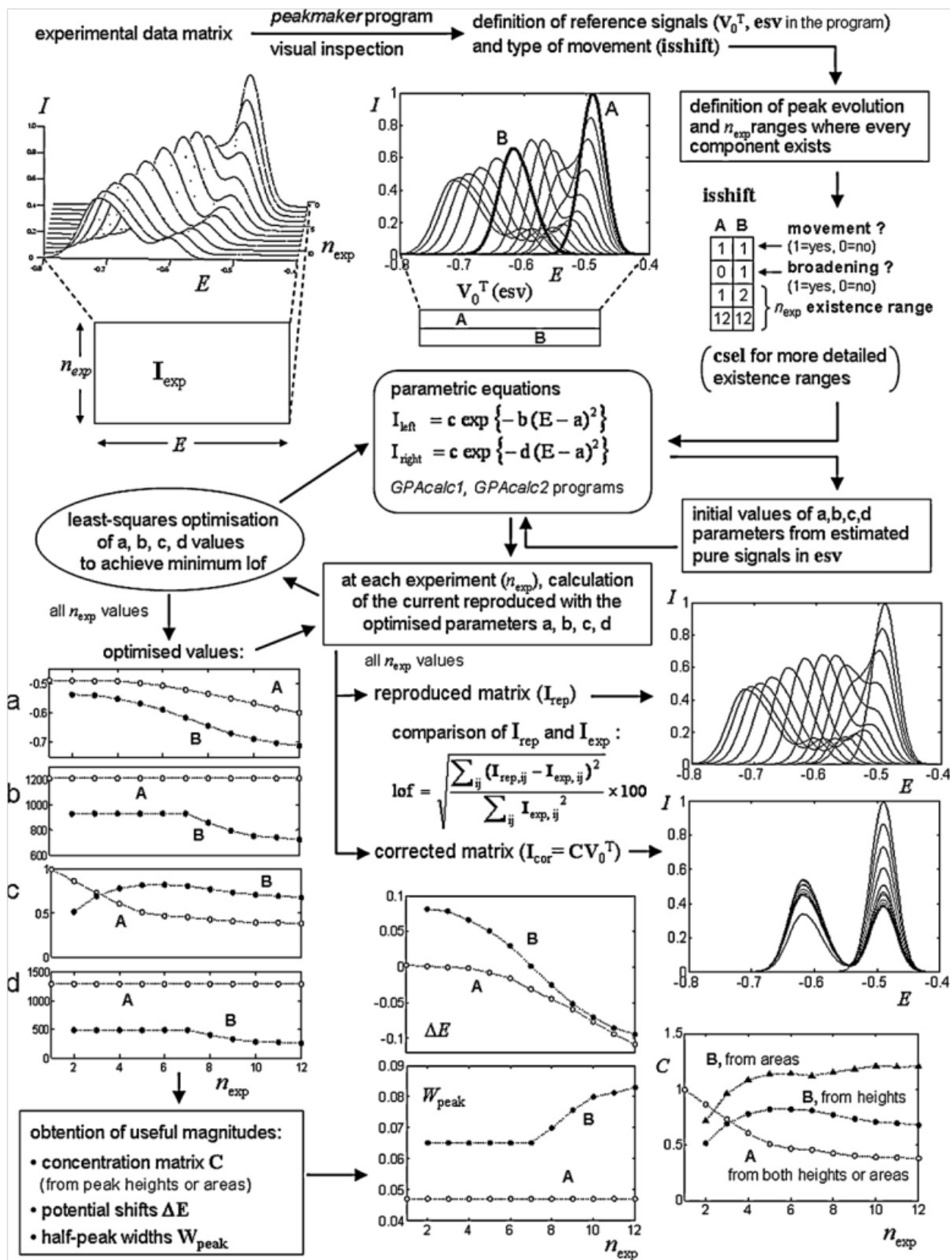


Fig. 1.

Figure 2

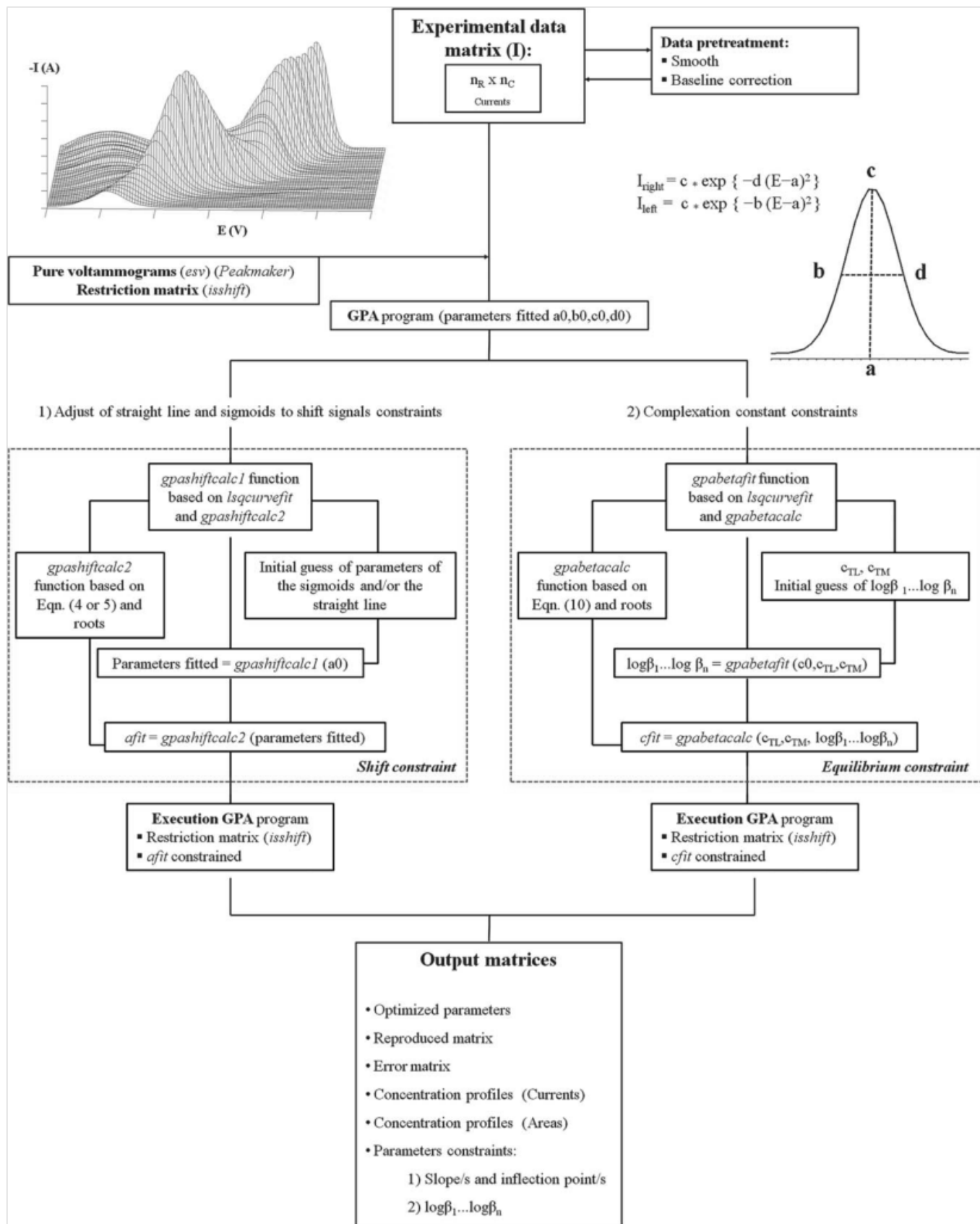


Fig. 2.

Figure 3

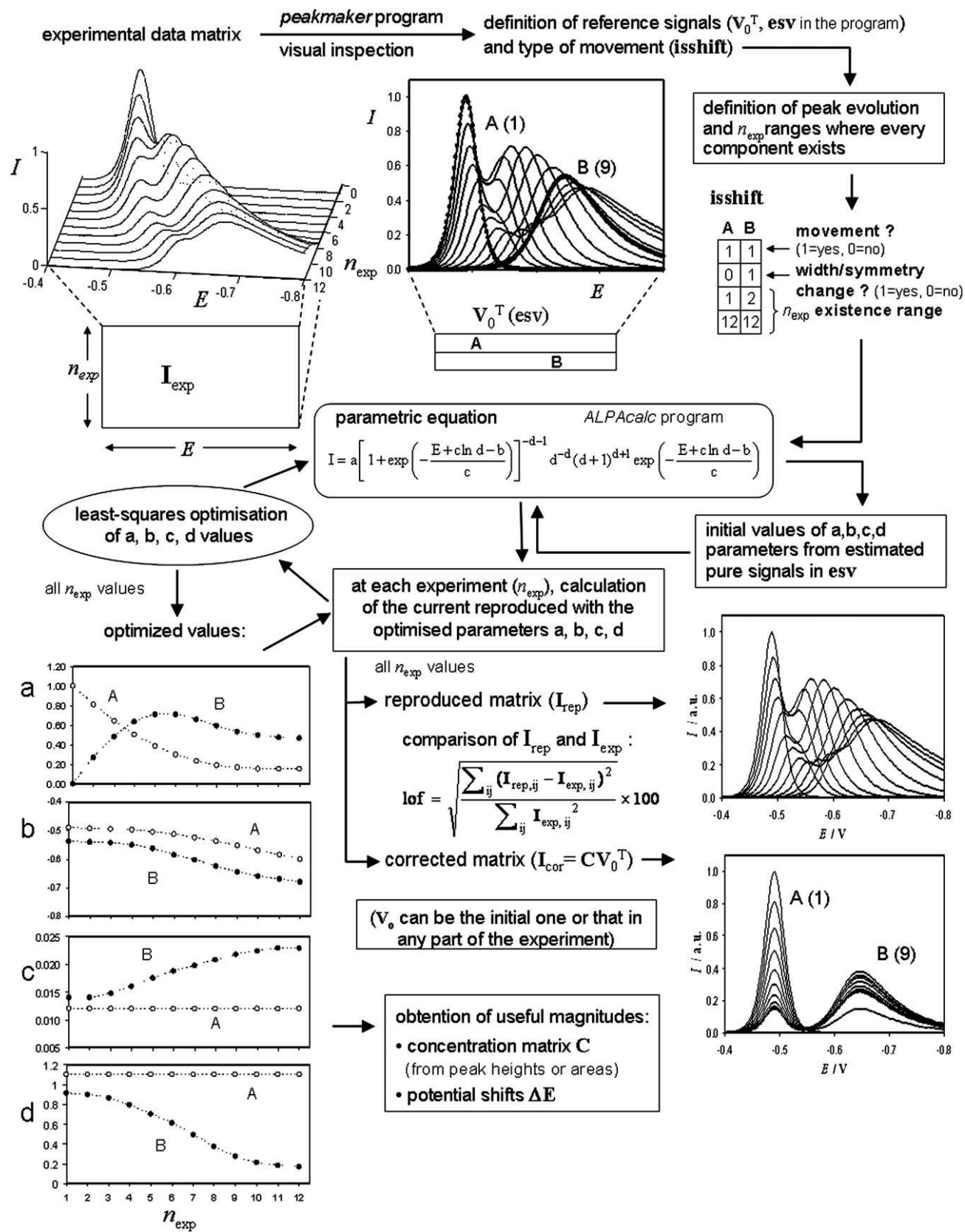


Fig. 3.

Figure 4

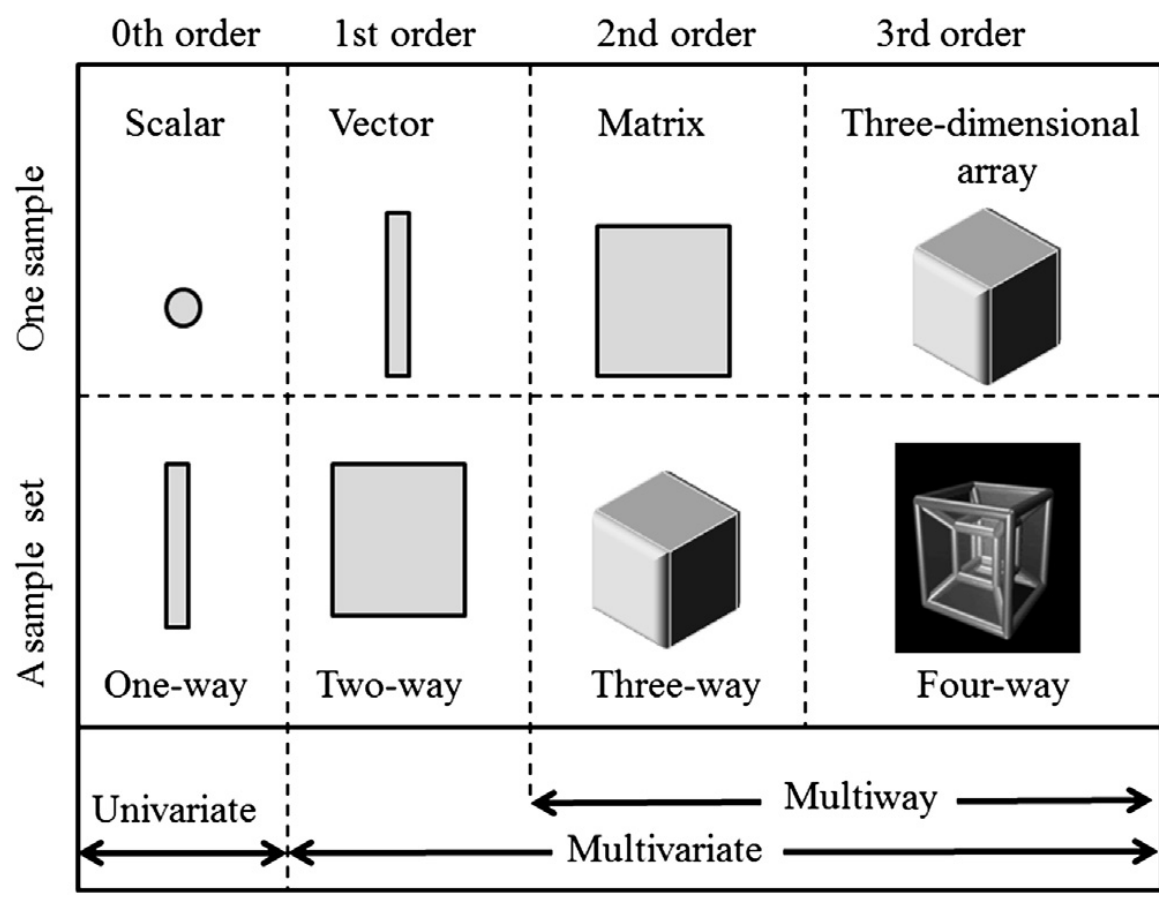


Fig. 4.

Figure 5

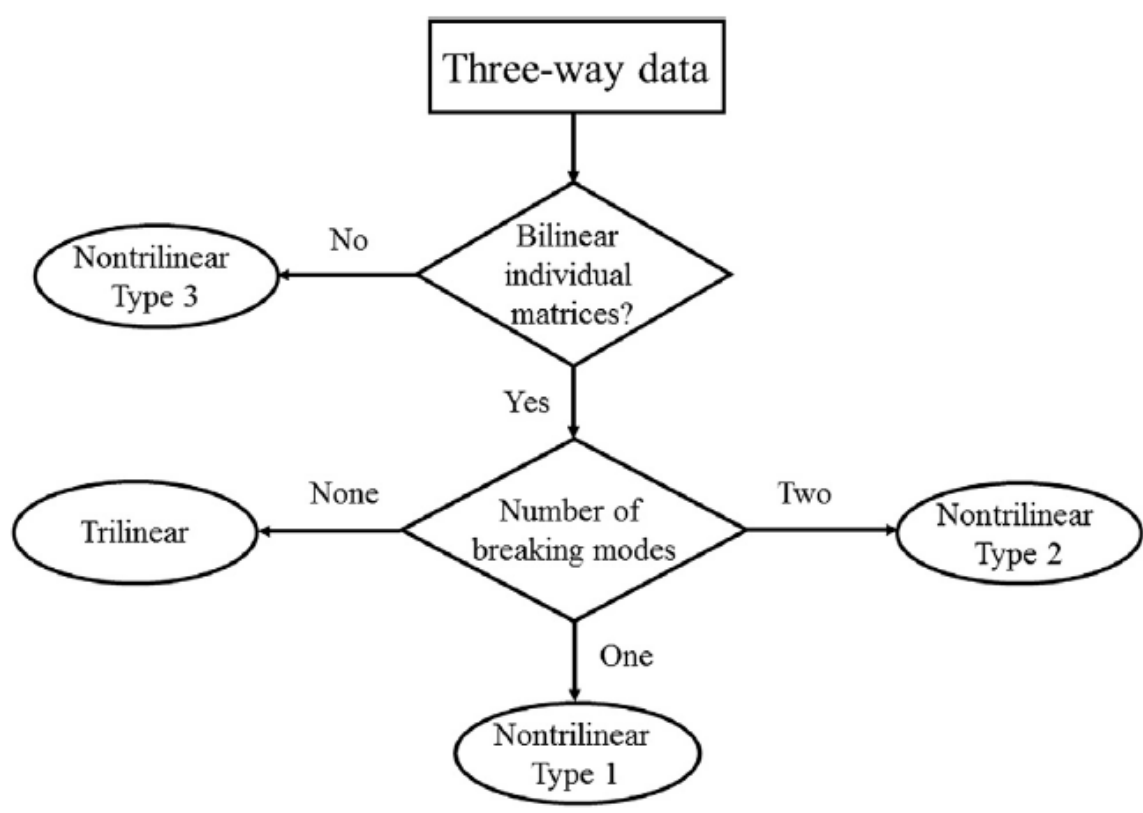


Fig. 5.

Figure 6

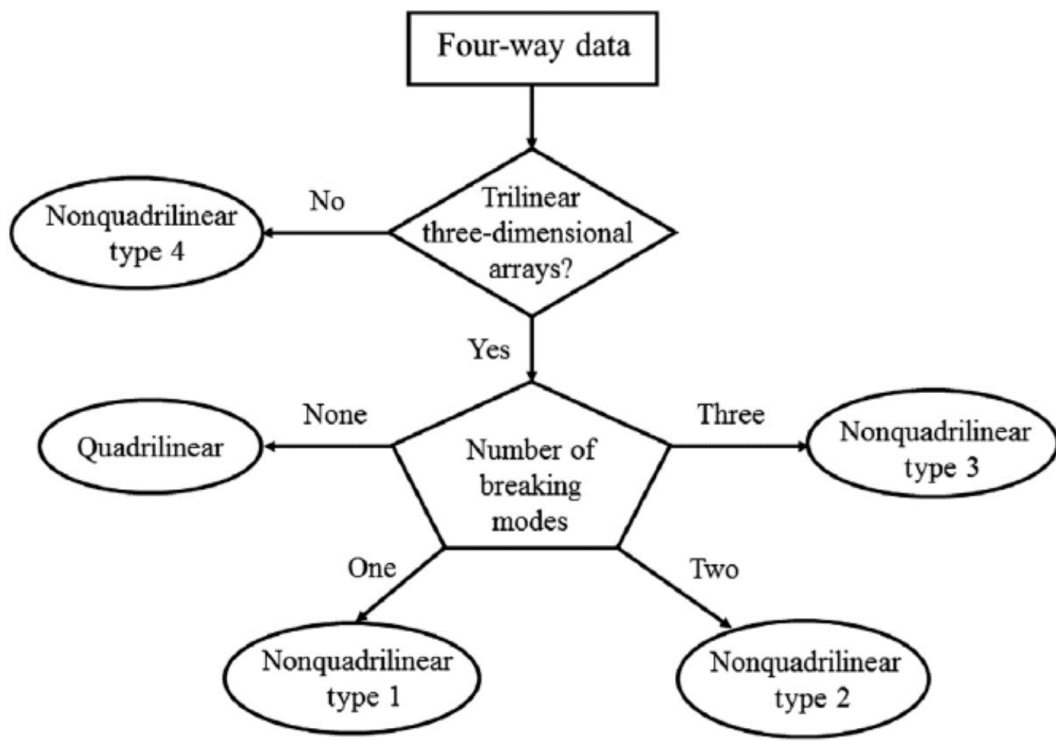


Fig. 6.

Figure 7

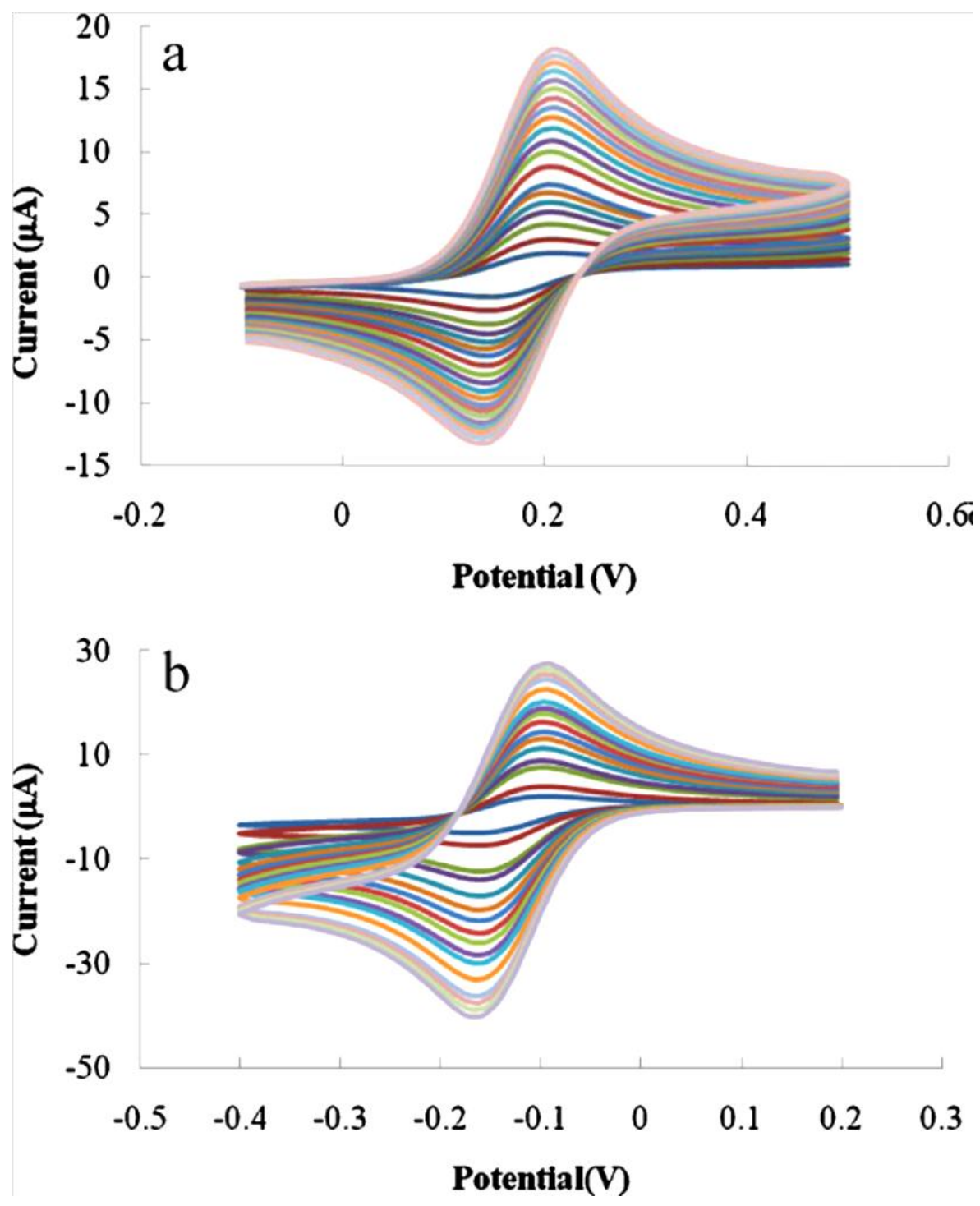


Fig. 7.

Figure 8

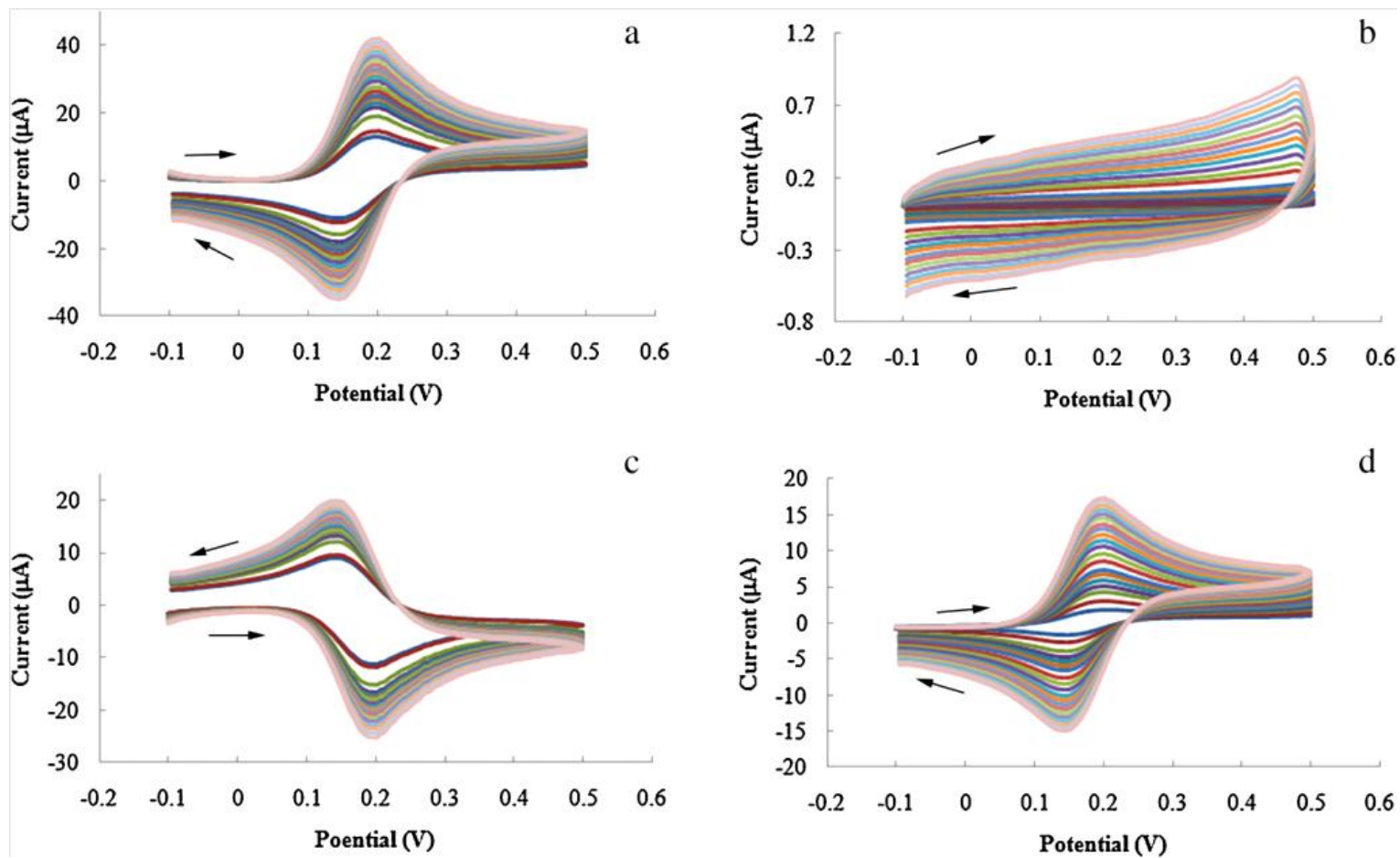


Fig. 8.

Figure 9

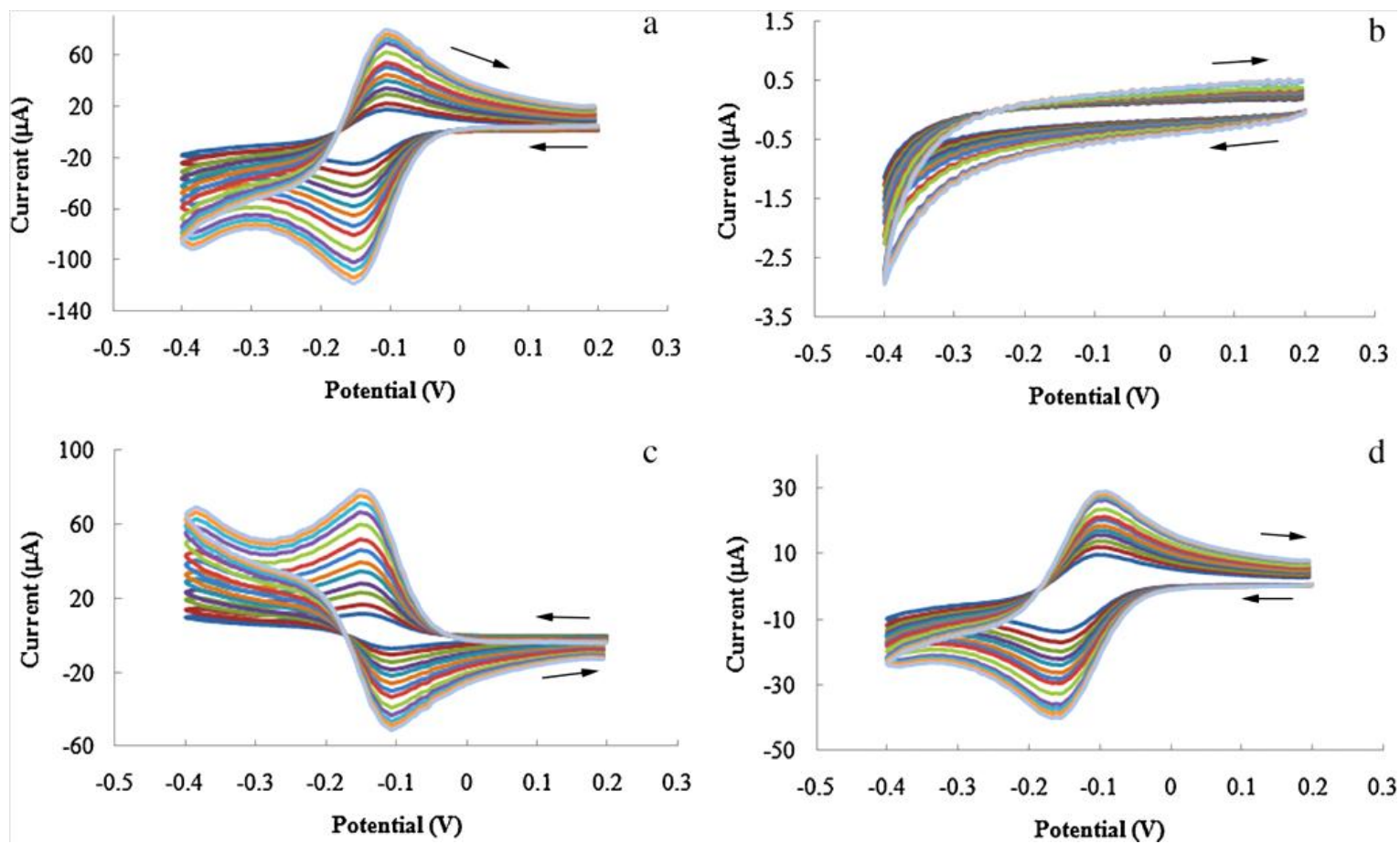


Fig. 9.

Figure 10

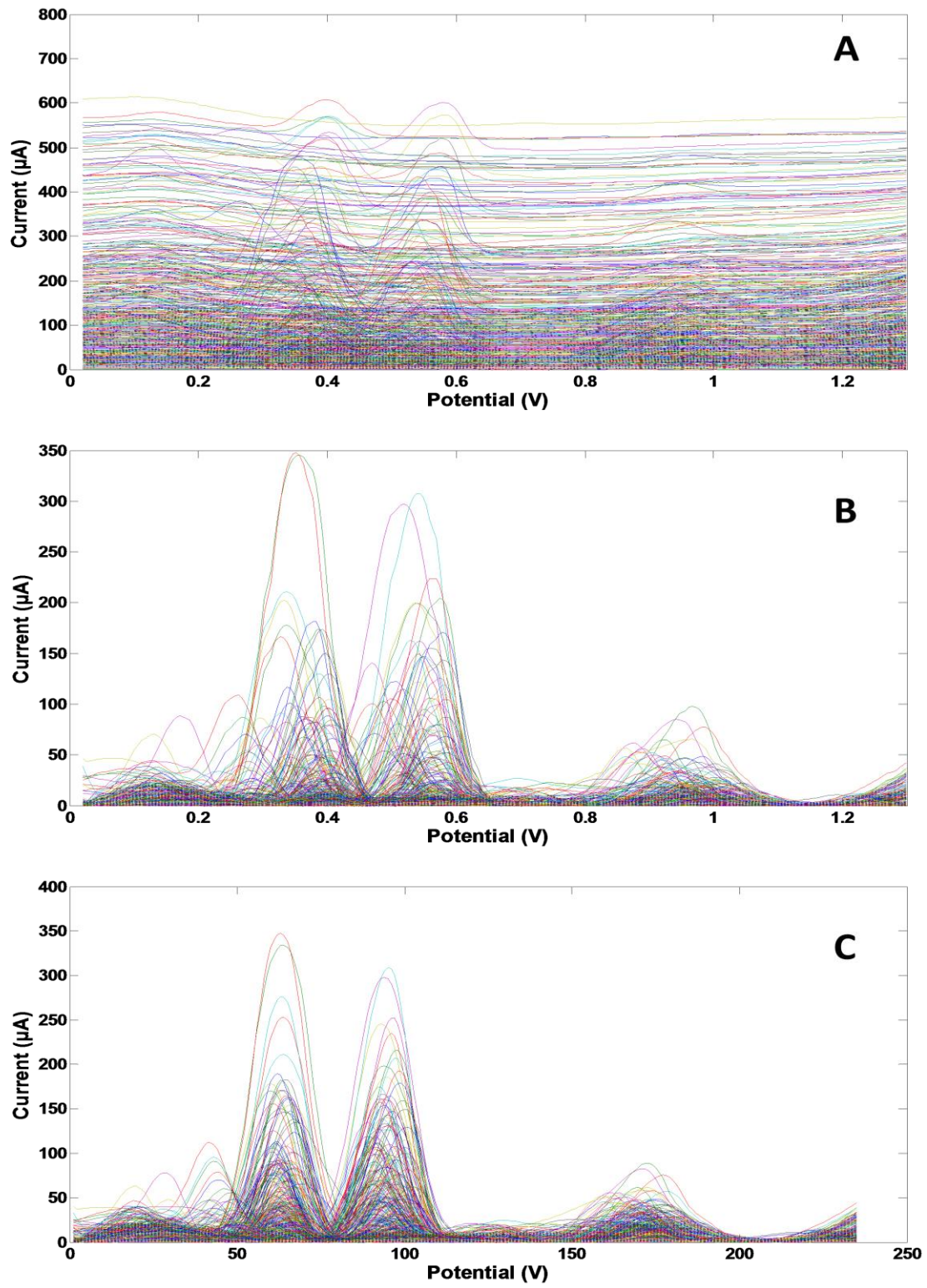


Fig. 10.

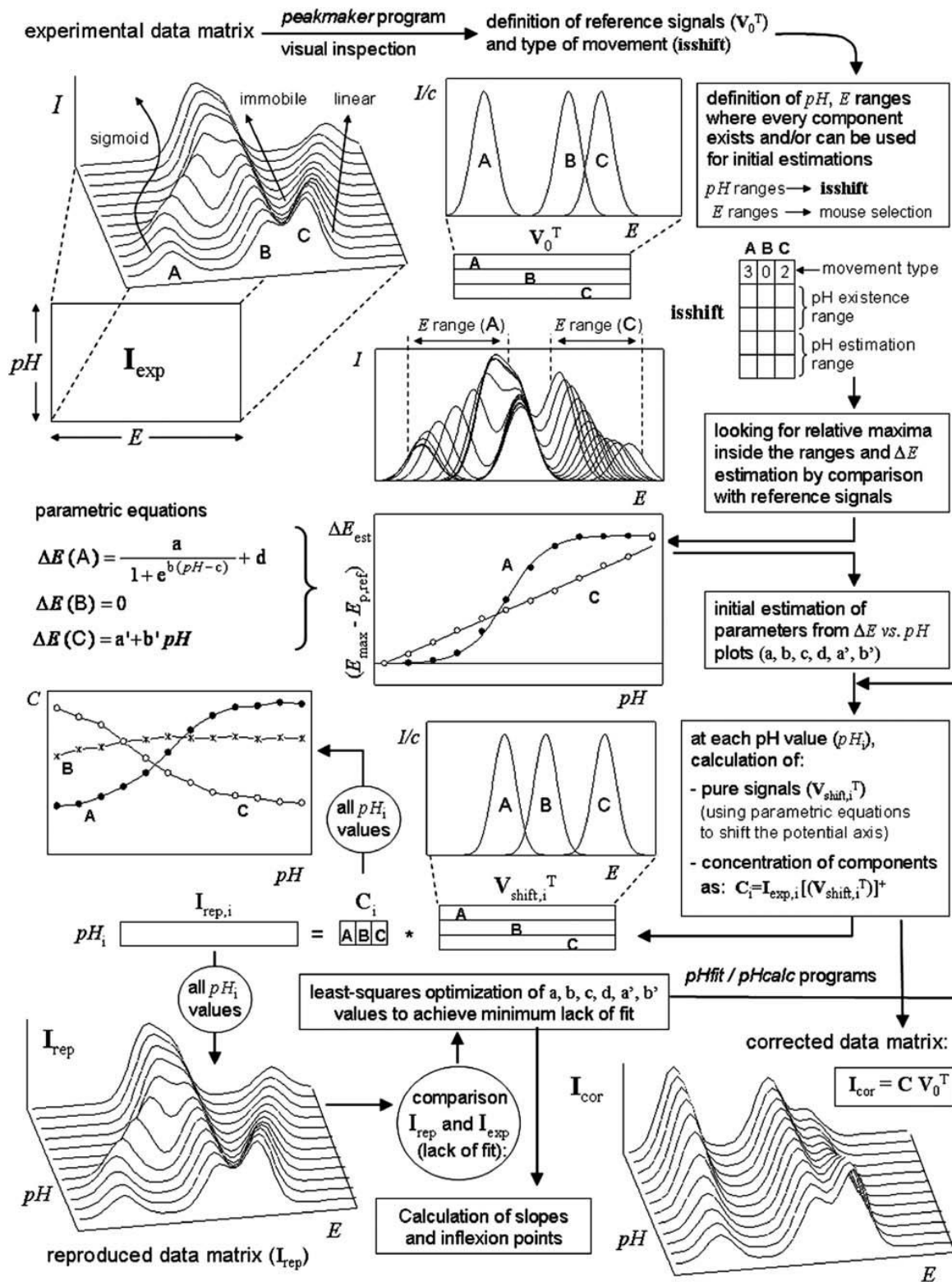


Fig. 11.

Figure 12

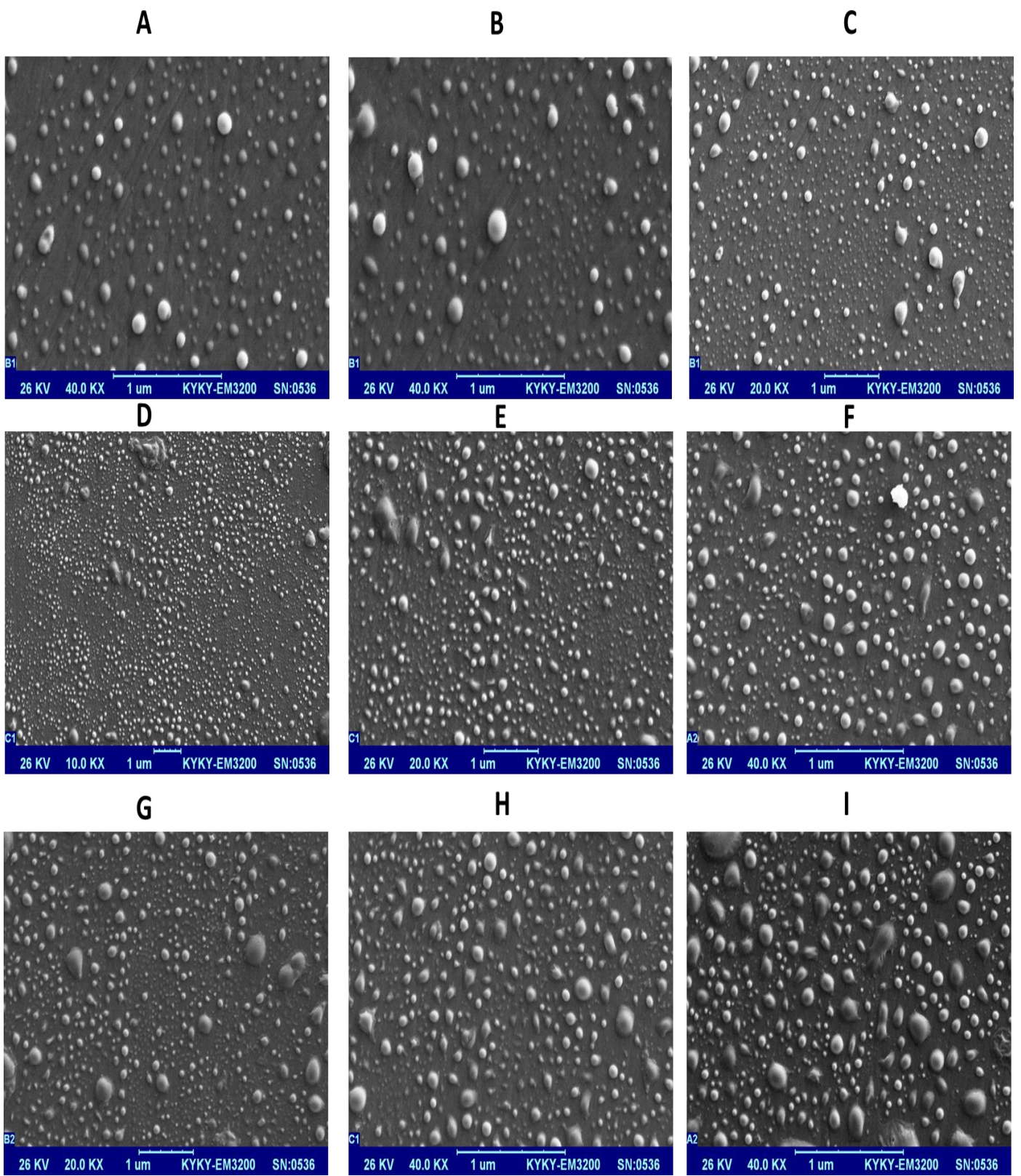


Fig. 12.

Figure 13

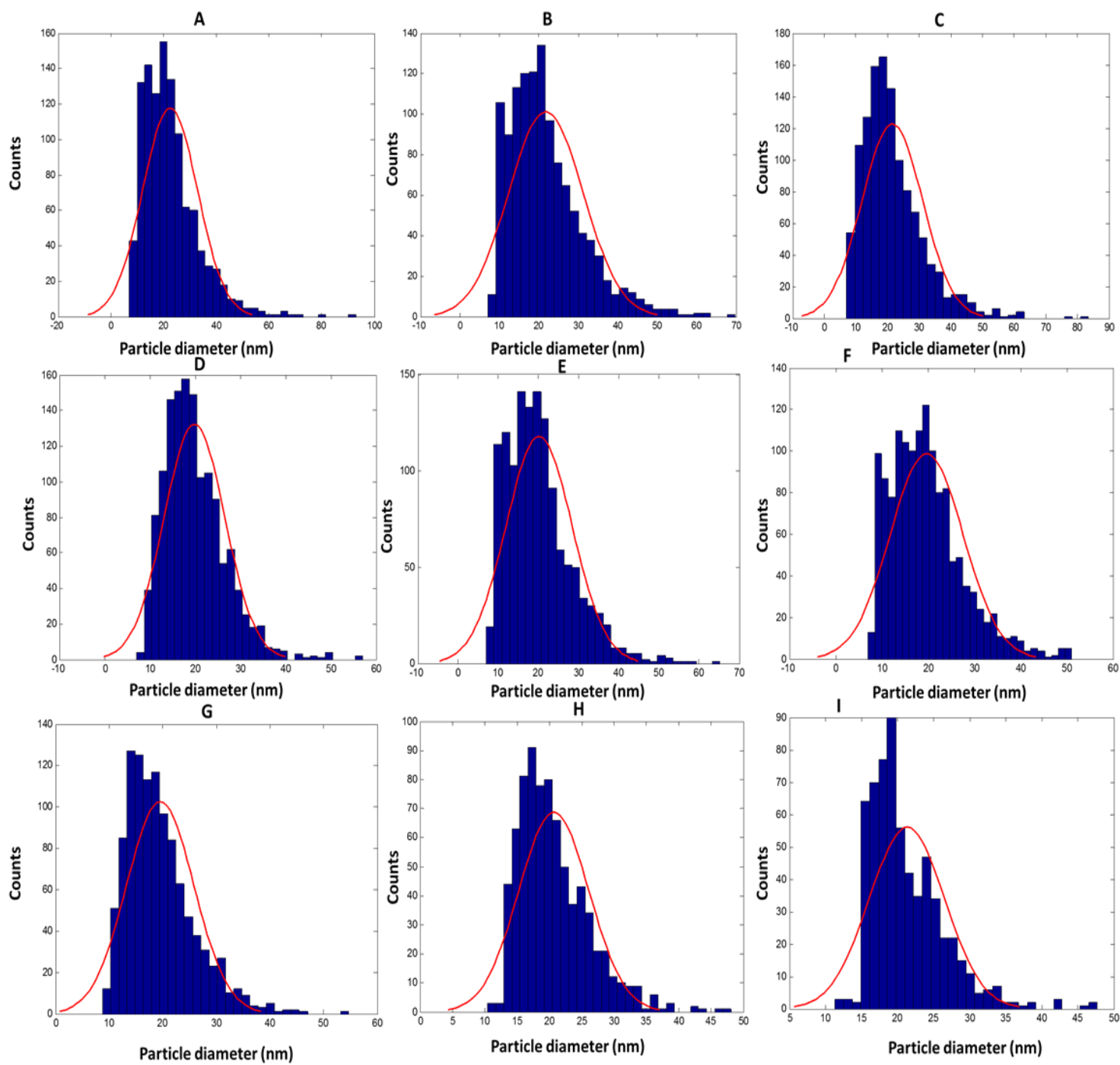


Fig. 13.

Checklist

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