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Three-Dimensional Voltammetry: A Chemometrical Analysis of Electrochemical Data for Determination of Dopamine in the Presence of Unexpected Interference by a Biosensor Based on Gold Nanoparticles

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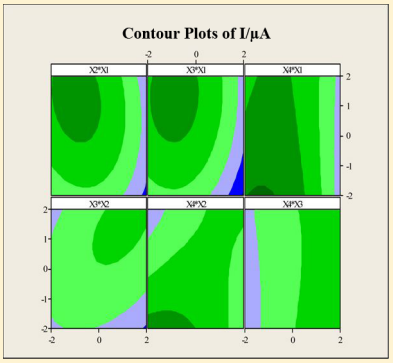
Supporting Information

ABSTRACT: Multivariate curve resolution by alternating least-squares (MCR-ALS) was used for voltammetric determination of dopamine (DA) in the presence of epinephrine (EP) at a gold nanoparticles chemically modified carbon paste electrode (AuNPs/CPE). Scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) techniques were applied for characterization of the nanostructure modified electrode. Central composite rotatable design (CCRD) was employed to generate an experimental program to offer data to model the effects of different parameters on voltammetric responses. Response surface methodology (RSM) was applied to show the individual and interactive effects of chemical and instrumental variables at five levels, combined according to CCRD. For determination of DA in the presence of unexpected interference, three-way data were achieved from various pulse heights in differential pulse voltammetry (DPV) technique. This type of data construction, analyzed by MCR-ALS, makes it possible to exploit the so-called "second-order advantage". The second-order advantage provided unbiased results even in the presence of electroactive interferences with highly overlapped peaks. Also, an algorithm was applied to correct the detected potential shift in the voltammetric data. The voltammograms of the samples were then deposited in an augmented data matrix (column-wise) and subsequently analyzed by MCR-ALS. The effect of rotational ambiguity associated with a particular MCR-ALS solution under a set of constraints was also studied. The proposed method could be applied for the determination of DA and EP in the presence of each other in a wide concentration range of 0.1−205.0 μM, and the detection limit of DA has been found to be 35.5 nM. Finally, the technique has been used for the reliable analysis of DA in real samples.



Electroanalytical techniques are subject to the same quality assurance criteria and common method preferences, such as rich signal information content, not being time-consuming, not requiring sample preparation, versatility, and lower costs than other analytical subdisciplines such as spectroscopy methods. Generally, over the last 20 years, with rapid growth in electronics, the improvement of instrumentation has been considerable, especially in the case of electrochemistry. Such improvement has allowed faster measurement and well-organized storage of data, and has presented growing opportunities for the application of multivariate methods, i.e., chemometrics in the context of analytical chemistry, for quick data analysis. Among the most relevant multivariate techniques, second-order multivariate algorithms play an important role in numerous analytical fields.[1,2] When developing an electrochemical technique, using chemometric methods may supply a valuable resource for accurate analyte quantification when the absolute separation is not accomplished, or unexpected components are present in the sample being analyzed. Chemometrics will be useful when second-order data are recorded, for instance, applying a fast scanning fluorescence detector (FSFD), a diode array detector (DAD), or an electrochemical system.[3−7] A fascinating basic property that second-order data possess is the so-called "second-order advantage",[8] which in principle allows quantification of analytes in samples with unexpected components that are potential interferences.[9] Among the important numbers of algorithms that have been applied in order to get the second-order advantage, multivariate curve resolution by alternating least-squares (MCR-ALS)[10] is demonstrated to be a capable method for resolution and quantification of complex mixtures.[11] MCR-ALS has been employed to analyze different data sets that can be expressed by a bilinear model related to processes and mixtures such as industrial processes, chemical reactions, spectroscopic measurements, chromatographic analysis, environmental data, and electrochemical multivariate responses.[12] The success and comprehensive use of MCR-ALS method is dependent to the possibility to work with multiway data structures.[13]

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The catecholamines (CAs), such as dopamine (3,4-dihydroxyphenyl ethylamine, DA) and epinephrine (Adrenaline, (1R)-1-(3,4-dihydroxyphenyl)-2-(methylamino) ethanol, EP) are key neurotransmitters in the mammalian central nervous system of mammals and human beings.[14] These compounds play important roles in the adjustment of physiological processes in living systems. Excessive abnormalities of CA levels in biological fluids are symptoms of some diseases, for example Parkinsonism.[15,16] CA compounds are also applied to treat bronchial asthma, anaphylactic shock, and organic heart disease.[17] To investigate their physiological function and aid diagnosis of some diseases, it is essential to expand methods for determination of DA in the presence of EP with high overlapping voltammograms.

Current methods to determine DA and EP are fluorescence,[18] high-performance liquid chromatography,[19] capillary electrophoresis,[20] flow injection,[21] and electrochemistry.[22] Because DA at conventional electrodes created weak electrochemical signals,[23] chemically modified electrodes (CMEs) became valuable electrochemical detection methods with good selectivity, sensitivity, and stability. Numerous materials, such as nanoparticles,[24] organic redox mediators,[25] and self-assembled monolayer,[26] have been used as modifiers to construct highly sensitive and selective DA biosensors. Among these materials, colloidal gold nanoparticles (AuNPs) have been usually applied in analytical research fields due to their significant specific surface area and excellent biocompatibility, besides their unique electrical and optical properties.[27] Furthermore, DA and EP show peaks with high overlapping in differential pulse voltammetry (DPV) technique. Therefore, voltammetric determination of DA in the presence of EP assisted with MCR-ALS gives additional information allowing their better resolution.

In this work we present the first application of MCR-ALS for investigation of the overlapping voltammetric signals of the DA and EP. For achieving that aim, a gold nanoparticles chemically modified carbon paste electrode (AuNPs/CPE) was constructed and the performance characteristics for increasing sensitivity of DA determination were investigated. Also, for investigating simultaneous effect of all variables on DPV response of DA, optimization studies were conducted. One of the experimental design methods to reach this purpose is central composite rotatable design (CCRD) of response surface methodology (RSM). This method is an efficient and adaptable methodological tool to determine optimum levels of all effective parameters on analytical responses.[28] The CCRD offers as much information as a three factorial design, and requires many fewer experiments than full factorial design.[29] In addition, linear, interaction, and quadratic effects of all parameters were modeled to develop predictive models for the tested parameters using RSM and to optimize the levels of processing that maximize the analytical responses of DA. After potential shift correction procedure, sample voltammograms were arranged in augmented data matrices in order to get the second-order advantage. The MCR-BANDS method[30] is also used to estimate the amount of rotation ambiguity associated with the resolved pure spectral and concentration profiles under the constraints imposed during their estimation. Finally, the proposed method was used to determine DA in the presence of EP in biological samples in Britton–Robinson (B–R) buffer solution.

EXPERIMENTAL SECTION

Materials. DA, EP, hydrogen tetrachloroaurate ($HAuCl_4$), sodium citrate, pure fine graphite powder, paraffin oil (ρ = 0.88 g cm^{-3}) and other reagents were of analytical-reagent grade and supplied by Merck. B–R buffer solutions (total concentration 0.2 M) were prepared with CH_3COOH, H_3PO4, H_3BO_3 and a saturated solution of sodium hydroxide with different pH values, and were applied as supporting electrolyte. Deionized water was used in all experiments.

Instrumentation and Software. All voltammetric measurements and electrochemical impedance spectroscopy (EIS) experiments were implemented in an electroanalyzer system, SAMA 500 (Islamic Republic of Iran) and Autolab potentiostat/galvanostat PGSTAT 35 (Eco Chemie Utrecht, Netherlands), attached to a computer with data acquisition SAMA and NOVA 1.6 softwares, respectively. A conventional three-electrode system was applied with a bare or modified CPE (2 mm diameter), an Ag/AgCl/KCl(sat.) (Metrohm, Switzerland), and a Pt wire (Metrohm, Switzerland) as a counter electrode. Scanning electron microscopy (SEM) micrographs were performed using a KYKY-EM3200. A 691 pH meter (Metrohm, Switzerland) was applied to adjust the pH of the supporting electrolyte. Deionized water was produced from an ultra pure water system type smart-2-pure, TKA (Germany). The UV–vis absorption of the gold nanoparticles was recorded using UV–vis spectrophotometer (PerkinElmer Lambda2S). All electrochemical measurements were performed at 25.0 ± 0.5 °C.

MINITAB (Minitab Inc.) Release 16.0 statistical package was used for design and analysis of the CCRD experiments. MCR-ALS procedures were carried out through several programs implemented in MATLAB 2010.[31] Correlation optimized warping (COW) was implemented with MATLAB to correct the shifts or misalignments in voltammograms.[32]

AuNPs Preparation. AuNPs were synthesized in accordance with the Frens method[33] by adding 1.0% (w/v) sodium citrate solution (0.5 mL) to 0.01% (w/v) $HAuCl_4$ (50.0 mL). The two solutions were heated to 60 °C. The final mixture of red color was kept at the boiling point for 15 min. The solution was stored in a dark-colored glass bottle at 4 °C.

Fabrication of CPE and AuNPs/CPE Composite. Unmodified CPE was prepared by adding 0.5 g of graphite powder to 0.2 mL of paraffin with a mortar and pestle. The modified electrode was prepared in a similar fashion, except that the graphite powder was mixed with a desired weight of AuNPs (0.057, 0.086, 0.115, 0.143, and 0.172 mg) to get different electrodes. Then, both bare and modified pastes were packed into the end cavity of the electrode body. Electrical contact to the paste was instituted by a copper wire thorough flank. A clean electrode surface was achieved by squeezing more out.

Experimental Design. The experimental design methods that generally have been used for modeling and process analysis are the full factorial, fractional factorial, and central composite designs. A full factorial design needs at multilevel many more tests than a fractional factorial design.[34] A practical alternative to the factorial design is the central composite design (CCD), first presented by Box and Wilson[31] and advanced upon by Box and Hunter.[35] The CCD provides almost as much information as a multilevel factorial, but needs much fewer tests than a full factorial design.[36]

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The present work performed the CCRD method for analyzing voltammetric data. The CCRD includes of 2^n factorial points with 2n axial points and N_c central points. For four factors, a CCRD, including 16 factorial points, 8 axial points, and 3 replicates at the center points were used. For estimation of the experimental error and the reproducibility of the data the center points were applied. The independent factors are coded to the (−1, +1) interval, whereas the low and high levels are coded as −2 and +2, respectively. The axial points are placed at distance α from the center and render the design rotatable. In the present study, α value was fixed at ±2.

The studied factors were pH (X_1), AuNPs amount (X_2), scan rate (X_3), and step potential (X_4). The mathematical relationship of the response (Y) on the four significant independent factors X_1, X_2, X_3, and X_4 can be estimated by eq 1

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k-1} \sum_{j=2}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_{ii} X_i^2 + e \quad (1)$$

where Y is the analytical response, b_0 is the model's intercept (constant), b_i is the linear coefficients, b_{ii} is the squared coefficients, and b_{ij} is the interaction coefficients.

A four-factor, five-level CCRD leading to 27 runs was employed for the optimization of the effective parameters on voltammetric current of DA in the presence of EP. The experiments were designed and analyzed by the MINITAB (Minitab Inc.) Release 16.0 statistical package. The ranges and the levels of the variables are presented in Table 1.

Table 1. Coded and Actual Levels of the Variables

	levels				
original variable	−2	−1	0	+1	+2
pH: X_1	4.0	5.0	6.0	7.0	8.0
AuNPs amount (mg): X_2	0.057	0.086	0.115	0.143	0.172
scan rate (V s^{-1}): X_3	0.03	0.06	0.09	0.11	0.14
step potential (V): X_4	0.001	0.003	0.005	0.007	0.009

RESULTS AND DISCUSSION

Characterization of AuNPs. A UV−vis spectrometer was used to record UV−vis absorption spectrum. The fresh AuNPs solution was applied as the sample for UV−vis experiment in the presence of deionized water as a blank for background correction. The UV−vis measurements (Figure S1 in the Supporting Information (SI)) represented a maximum absorption at 528 nm which indicated the average diameter of AuNPs in the colloidal solution was 25 ± 5 nm.[37]

In addition to UV−vis measurement, SEM was applied for more characterization of AuNPs. The SEM micrograph presented in Figure 1 shows the particles are practically spherical in shape and monodisperse.

Response Surface Methodology Studies. The RSM introduces a statistical modeling method applied for multiple regression analysis by quantitative data achieved from suitably designed experiments to resolve multivariable equations simultaneously.[38] RSM is employed to determine the optimal DPV response for DA in the presence of EP. 3D response surfaces (Figure 2) and 2D contour plots (Figure S2 in the SI) apply as plots that exhibit the voltammetric response as a function of two parameters. The results presented in Figures 2 and S2 (SI) show voltammetric peak current of DA in the presence of EP as a function of pH (X_1), AuNPs amount (X_2), scan rate (X_3), and step potential (X_4). Also, in Table 2 the optimum value for each parameter has been shown.

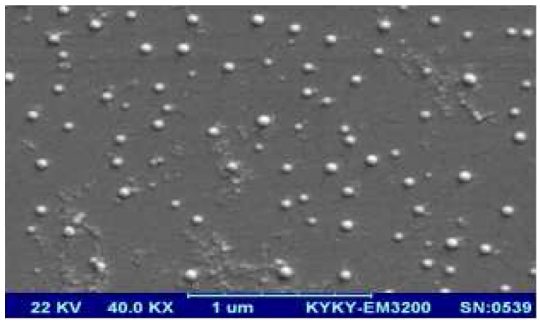

Figure 1. SEM micrograph of gold nanoparticles.

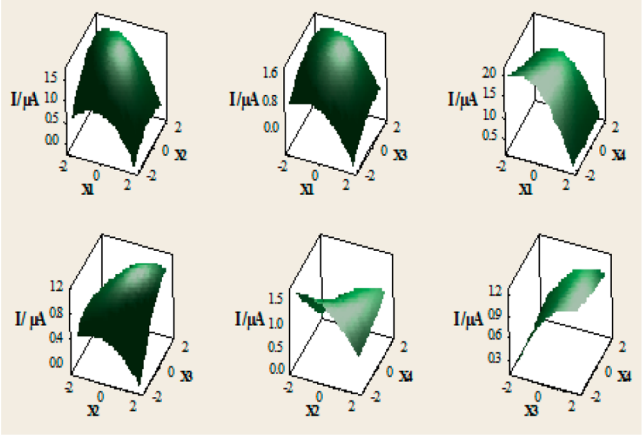

Figure 2. 3D response surface plots of the effects of pH (X_1), AuNPs amount (X_2), scan rate (X_3), step potential (X_4), and their interaction on DPV response of DA in the presence of EP.

Table 2. Optimized Parameters for the Determination of DA in the Presence of EP, Measured by DPV

variable	coded optimized values	actual optimized values
pH	−1.0303	4.90
AuNPs amount (mg)	−1.4747	0.0723
scan rate (V s^{-1})	0.3838	0.094
step potential (V)	−2.0000	0.001

Characterization of AuNPs/CPE by SEM. For characterization of surface morphology of AuNPs/CPE a scanning electron microscope was employed. Figure 3 shows the SEM micrographs of bare CPE and modified AuNPs/CPE. These results indicate that the CPE surface becomes available to electrochemical probes with the modification of AuNPs. According to Figure 3B, the nanometer-sized colloidal gold particles were distributed uniformly. The prepared AuNPs were evenly distributed and created individual elements at the surface of the modified electrode.

Characterization of AuNPs/CPE by EIS. Electrochemical impedance spectroscopy (EIS) has been considered as an effective technique for the impedance investigation of the different electrodes surfaces. The EIS measurements were operated at open-circuit with amplitude of 5.0 mV and a frequency range from 0.1 to 10 000 Hz for both the bare CPE and AuNPs/CPE in 0.2 M B-R buffer solution (pH = 7.0) including 5.0×10^{-3} M $[Fe(CN)_6]^{3-/4-}$. A semicircle bulk

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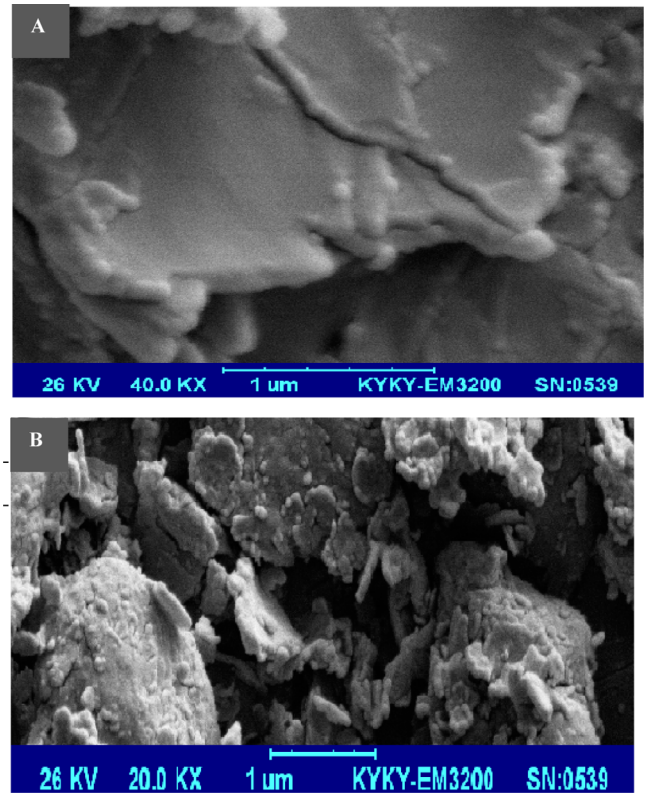

Figure 3. Typical SEM of (A) unmodified CPE and (B) modified AuNPs/CPE.

impedance at the high frequency region and Warburg impedance (Z_w) at the low frequency is shown in Figure 4.

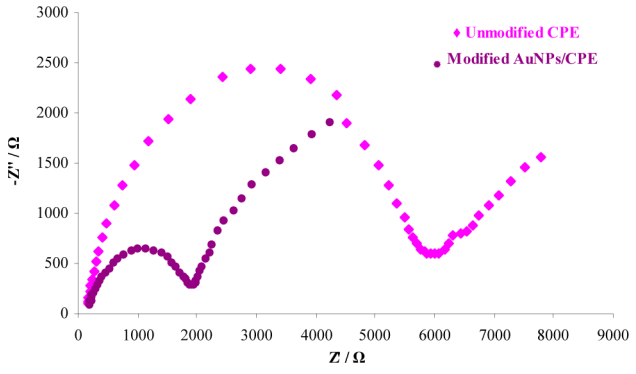

Figure 4. Electrochemical impedance spectra of CPE and AuNPs/CPE at open-circuit voltage.

The semicircle is interrelated to the charge-transfer resistance process (R_{ct}), and the oblique line that defines a region of semi-infinite diffusion of analytes in the electrodes corresponds to the Warburg impedance.[36] As can be observed in Figure 4, it is concluded that the R_{ct} of the modified electrode is smaller than that of the unmodified electrode. These values correspond with 5.58 and 1.63 kΩ for the unmodified CPE and AuNPs/CPE, respectively. Therefore, by modification of CPE with AuNPs, the bulk resistance decreases. This result suggests that the electron transfer is easier at the surface of modified AuNPs/CPE.

Effect of AuNPs on the Behavior of Electrode. Cyclic voltammograms recorded for a solution containing 50.0 μM DA and 50.0 μM EP in 0.2 M B-R buffer of pH 4.9 at the bare CPE and AuNPs/CPE are presented in Figure 5. As can be

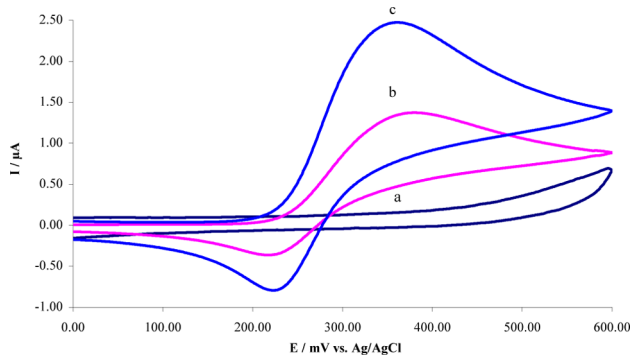

Figure 5. (a) Cyclic voltammogram of AuNPs/CPE in 0.2 M B-R buffer solution (pH = 4.9), and (b) and (c) cyclic voltammogram of CPE and AuNPs/CPE, respectively, taken from 50.0 μM DA in the presence of 50.0 μM EP solution.

observed, the electro-oxidation of DA in the presence of EP at the CPE is slow so that a wide anodic voltammogram with an oxidation peak potential of about 379.0 mV is resulted. On the other hand, at the surface of AuNPs/CPE, a well-defined oxidation voltammogram with an improvement in the peak current and a peak potential of 358.0 mV is achieved. Such enhancement of current illustrates that by lowering the anodic overpotential of the electrode process, the kinetics of electron transfer for DA in the presence of EP improves at the surface of AuNPs/CPE. Therefore, a synergic effect on electroacatalytic oxidation of DA in the presence of EP is created by AuNPs.

Determination of DA in the Presence of EP by MCR-ALS. *Generation of Nonbilinear Second-Order Data.* For voltammetric determination of DA in the presence of EP, first it is necessary to record their voltammograms. Thus, DPV technique was performed in optimized condition. But DA and EP showed highly overlapping peaks in DPV (Figure 6).

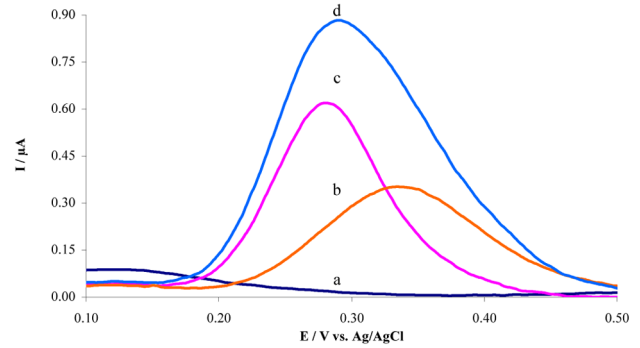

Figure 6. Differential pulse voltammograms obtained at AuNPs/CPE for (a) 0.2 M B-R buffer solution (pH = 4.9), (b) a 50.0 μM EP solution, (c) a 50.0 μM DA solution, and (d) a mixture containing 50.0 μM DA and 50.0 μM EP under the optimized condition.

Therefore, it seemed that determination of DA in the presence of EP only by voltammetric techniques was not possible. On the other hand, it was needed to resolve these signals. For achieving this aim, MCR-ALS method by creating electrochemical second-order data was used. The purpose of second-order data-treatment process is to convert the raw matrix into the product of two matrices. One matrix describes concen-

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tration profiles and the additional matrix describes spectra profiles of all the components in the studied system. In this work, electrochemical second-order data were created via changes in pulse height (ΔE) as an instrumental variable of DPV technique.

The theory of the proposed method will be explained. The current intensity in DPV technique for an electrochemical reaction is obtained by eqs 2−5[39]

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

$$P_A = \xi\exp\left[\frac{nF}{RT}\left(E + \frac{\Delta E}{2} - E^{0'}\right)\right] \quad (3)$$

$$\sigma = \exp\left(\frac{nF}{RT}\frac{\Delta E}{2}\right) \quad (4)$$

$$\xi = (D_O/D_R)^{1/2} \quad (5)$$

where n is the number of electrons of process, F describes the Faraday constant, A explains the electrode area, D_O is the diffusion coefficient, $C_O{}^*$ is the bulk concentration of electroactive species, τ' is the first current sampling that is taken immediately before the pulse, τ is the second current sampling that is obtained later in the pulse, and ΔE describes the pulse height.

For a typical electrochemical reaction, by a different ΔE and scanning potential at the constant τ, various data vectors will be obtained. On the other hand, in DPV technique using various pulse heights (ΔEs) at constant pulse duration with scanning the potential generates a nonbilinear second-order data.[40] Figure 7A shows electrochemical second-order data for a typical mixture inclouding 30.0 μM of DA and 30.0 μM of EP (as interference) at various pulse heights of 10.0−60.0 mV with a 10.0-mV interval in the optimized conditions.

Potential Shift Correction. For voltammetric determination of DA in the presence of EP, ten mixtures containing different concentrations of DA and EP in 0.2 M B-R buffer (pH = 4.9) were selected. These concentration levels are presented in Table 3. DPV peaks of the each mixture were recorded in different pulse heights of 10.0−60.0 mV with a 10.0-mV interval at optimized conditions. But as can be seen in Figure 7A, by changing pulse height, the voltammograms shifted. Comparable results also were observed for other mixtures. Then, for a concentration estimation of DA in the presence of unexpected electroactive interference, MCR-ALS method was carried out on a column-wise augmented data matrix achieved from ten calibration sets of DA and EP. Subsequently, non-negativity and unimodality for concentration and voltammogram profiles constraints were applied. But because of potential shift, a LoF of 4.7% was obtained by MCR-ALS. Therefore, a correction in potential shift can be useful before MCR-ALS procedure.

In the present study, to correct the shifts, COW was applied as an alignment method. COW justifies two peaks by means of piecewise linear stretching and compression of the peak to justify. At first, the profile to justify and the reference profile are split into a user-specified number of sections (N). Then, each section in the profile is warped to justify, beginning from the first section. The length of this section is shortened or stretched by shifting the position of its end point by a limited number of points (from −s to s), expressed by the slack parameter (s).

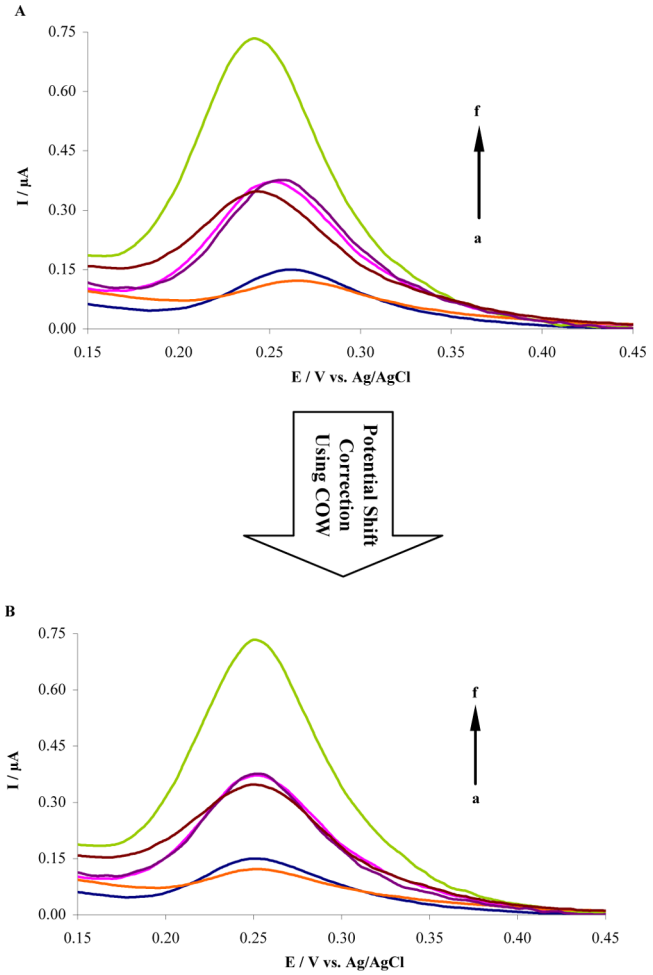

Figure 7. (A) Voltammetric second-order data achieved from a mixture containing 30.0 μM DA and 30.0 μM EP at AuNPs/CPE in the optimized conditions (a−f correspond to 10.0, 20.0, 30.0, 40.0, 50.0, and 60.0 mV of pulse heights, respectively). (B) Effect of COW on voltammograms of (A).

Table 3. Selected Concentration Levels of DA and EP

DA concentration (μM)	EP concentration (μM)
o.1	0.8
5.0	5.0
15.0	15.0
30.0	30.0
50.0	60.0
70.0	80.0
90.0	100.0
110.0	120.0
150.0	170.0
205.0	230.0

The achieved shortened and stretched sections for this section are subsequently linearly interpolated to the length of the corresponding section in the reference profile. The correlation coefficients between the interpolated segment and the corresponding reference segment for each possible end point of this section (from −s to s), are calculated and stored together with the position of the section end points. Subsequently, one transfers to the second section which is begun at the different end points of the first section and which end point is also shifted from −s to s points for each end point

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of the first section. Then the shortened and stretched segments are linearly interpolated to the length of reference section two and the correlation coefficients are again calculated.[41]

The COW was carried out for potential shift correction on a column-wise augmented data matrix that included ten calibration sets of DA and EP. Subsequently, MCR-ALS was carried out on the reconstructed augmented data and LoF is decreased to 4.0%, which was better than the achieved amount in the absence of applying COW algorithm. Figure 7B shows the effect of correction in potential shift by COW on voltammograms of Figure 7A. After potential shift correction on the voltammograms of concerned electroactive components, MCR-ALS was carried out on corrected column-wise augmented data achieved from ten standards of the analyte of interest and interference. The decomposed voltammograms DA in the presence of EP that were used in calibration curve are shown in Figure 8.

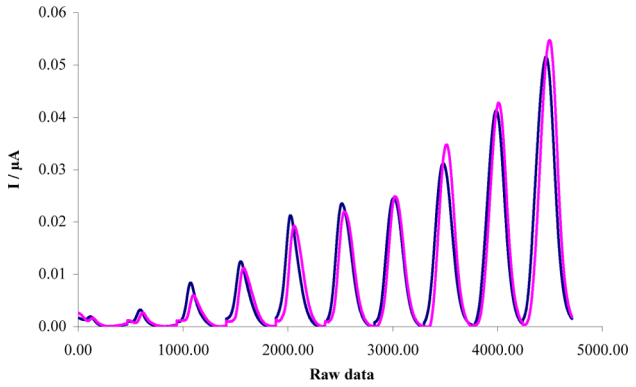

Figure 8. Decomposed voltammograms of DA in the presence of EP created by MCR-ALS after COW.

Performance of the System for DA Measurement in the Presence of Unexpected Interference. In the previous section, MCR-ALS resolved concentration profiles were achieved in the analysis of the analyte (DA) in the presence of unexpected interference (EP) and presented in Figure 8. As a consequence of that, the area under the concentration profile is considered as proportional to analyte concentration, and subsequently the required pseudo-univariate graph is formed.[42]

The AuNPs/CPE was applied for the assessment of the analytical utility of the proposed method as a means of trace amounts of DA. On the other hand, the DPV assisted by MCR-ALS method using modified electrode was utilized as a method featuring very low detection limit, high sensitivity, and good selectivity in 0.2 M B-R buffer solution. The dependencies of the peak area on DA concentration are represented by the regression equation I (μA) = 0.0493 C (μM) + 0.2982. The peak area demonstrates a linear variation with the concentrations of DA in the range of 0.1−205.0 μM. The slope of the calibration curve in this range is 0.0493 μA μM^{-1} and the correlation coefficient (R^2) is 0.9974. The detection limit for the determination of DA in the presence of EP using the proposed method, taken as the concentration that creates a signal equivalent to three times the standard deviation of the blank signal, was calculated to be 35.5 nM.

Analytical Performance Characteristics. To evaluate the feasibility of the proposed method, the recovery of DA in the presence of EP was determined in human blood serum samples. All samples were diluted with 0.2 M B-R buffer solution (pH = 4.9) and then appropriate amounts of these diluted samples were transferred to the electrochemical cell. Mixtures including various amounts of DA and EP were then added to the electrochemical cell in the presence of 0.2 M B-R buffer solution (pH = 4.9). DPV peaks for the prepared samples in optimized conditions and different pulse heights (10.0−60.0 mV with 10.0 mV increment) at the AuNPs/CPE were recorded. The recovery rates of the spiked sample were achieved between 94.80% and 110.53%, showing that the blood serum samples matrix does not interfere with the detection procedures (Table 4). Also to validate the recovery results, amperometry technique was performed for determination of DA in human blood serum samples. The diluted serum sample with B-R buffer solution (pH = 4.9), was spiked with various concentrations of DA and its amperogram in accordance with standard addition method was obtained by the modified electrode. The AuNPs/CPE shows agreeable recoveries in two techniques; proposed and amperometry techniques (Table 5).

Table 4. Determination of DA Levels in the Presence of EP in Real Samples (Human Blood Serum) Using DPV and MCR-ALS Method at the AuNPs/CPE

sample	added (μM)	found (μM)	recovery (%)
DA			
1	40.00	42.71 (±1.15)	106.78
2	45.00	49.74 (±2.43)	110.53
3	55.00	52.14 (±1.69)	94.80

Table 5. Determination of DA Levels in Real Samples (Human Blood Serum) Using Amperometry Technique at the Surface of AuNPs/CPE

sample	added (μM)	found (μM)	recovery (%)
DA			
1	1.10	1.00 (±1.83)	90.91
2	4.50	5.00 (±1.47)	111.11
3	9.50	10.00 (±2.11)	105.26

MCR-BANDS Analysis to Study Ambiguities. Bilinear models usually suffer from the existence of intensity and rotational ambiguity. On the other hand, the concentration profiles and pure component spectra achieved by MCR-ALS usually are not unique, but they pertain to a group of equally probable solutions. In this research, the MCR-BANDS method was used to evaluate the rotational ambiguity created in the obtained results of MCR-ALS.[30] The program can be estimate the rotational ambiguity in a straightforward way.[43] In fact, for estimating the elucidation of MCR analysis, characterizing the ambiguity is necessary. First, MCR-BANDS were used with constraints of spectra normalization and non-negativity of spectra and concentrations. Generally the rotational ambiguity ranged from 0.9618 to 0.9859 (Table 6), which can be

Table 6. Rotational Ambiguity for DA Quantitation, Estimated Using MCR-BANDS Program

	without unimodality constraints		with unimodality constraints	
augmented matrix	upper-level concentration	lower-level concentration	upper-level concentration	lower-level concentration
	0.9859	0.9618	0.9942	0.9919

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considered as rather large. Consequently, applying the same settings, but by inserting a unimodality constraint, the rotational ambiguity as evaluated by the MCR-BANDS strategy was considerably reduced for the system (Table 6). From the obtained results, it can be concluded that resolving of this system under the most possible constraints can provide the most accurate and reliable quantitative results.

CONCLUSIONS

As a conclusion, it can be observed that combining the high sensitivity of DPV data with MCR-ALS analysis can provide useful information on quantification of a component in the presence of unexpected interferences with overlapping peaks. In the present study, a chemometric methodology is proposed for the analysis of voltammetric data in the sensitive determination of DA in the presence of EP at the surface of AuNPs/CPE. Characterization of the modified electrode was investigated using SEM, EIS, and CV techniques. Using AuNPs leads to improvement of the electrochemical signals for this determination. Different variables affecting the DPV responses of DA in the presence of EP were optimized using CCRD. The electrochemical second-order advantage was obtained by changing pulse height in DPV technique. COW was used for alignment of the data sets. To check the amount of rotational ambiguity combined with particular MCR solution, MCR-BANDS program was applied. Using the proposed method, a dynamic range of 0.1−205.0 μM and a detection limit of 35.5 nM is obtained for DA in the presence of EP. Additionally, satisfactory results were obtained in the determination of DA in the presence of EP in spiked human blood plasma samples.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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