Talanta 119 (2014) 553–563

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Chemometrics-assisted simultaneous voltammetric determination of ascorbic acid, uric acid, dopamine and nitrite: Application of non-bilinear voltammetric data for exploiting first-order advantage

Mohammad-Bagher Gholivand [a,*], Ali R. Jalalvand [a,b], Hector C. Goicoechea [b], Thomas Skov [c]

[a] Faculty of Chemistry, Razi University, Kermanshah 671496734, Iran
[b] Laboratorio de Desarrollo Analítico y Quimiometría (LADAQ), Cátedra de Química Analítica I, Universidad Nacional del Litoral, Ciudad Universitaria, CC 242, S3000ZAA Santa Fe, Argentina
[c] Quality and Technology group, Department of Food Science, Faculty of Life Sciences, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg, Denmark

ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form
7 November 2013
Accepted 8 November 2013
Available online 27 November 2013

Keywords:
Ascorbic acid
Uric acid
Dopamine
Nitrite
Simultaneous determination
Linear and non-linear multivariate calibration models

ABSTRACT

For the first time, several multivariate calibration (MVC) models including partial least squares-1 (PLS-1), continuum power regression (CPR), multiple linear regression-successive projections algorithm (MLR-SPA), robust continuum regression (RCR), partial robust M-regression (PRM), polynomial-PLS (PLY-PLS), spline-PLS (SPL-PLS), radial basis function-PLS (RBF-PLS), least squares-support vector machines (LS-SVM), wavelet transform-artificial neural network (WT-ANN), discrete wavelet transform-ANN (DWT-ANN), and back propagation-ANN (BP-ANN) have been constructed on the basis of non-bilinear first order square wave voltammetric (SWV) data for the simultaneous determination of ascorbic acid (AA), uric acid (UA), dopamine (DP) and nitrite (NT) at a glassy carbon electrode (GCE) to identify which technique offers the best predictions. The compositions of the calibration mixtures were selected according to a simplex lattice design (SLD) and validated with an external set of analytes' mixtures. An asymmetric least squares splines regression (AsLSSR) algorithm was applied for correcting the baselines. A correlation optimized warping (COW) algorithm was used to data alignment and lack of bilinearity was tackled by potential shift correction. The effects of several pre-processing techniques such as genetic algorithm (GA), orthogonal signal correction (OSC), mean centering (MC), robust median centering (RMC), wavelet denoising (WD), and Savitsky–Golay smoothing (SGS) on the predictive ability of the mentioned MVC models were examined. The best preprocessing technique was found for each model. According to the results obtained, the RBF-PLS was recommended to simultaneously assay the concentrations of AA, UA, DP and NT in human serum samples.

1. Introduction

Dopamine (DP), ascorbic acid (AA), uric acid (UA) and nitrite (NT) usually coexist in biological matrixes, and they were considered as crucial molecules for physiological processes in human metabolism. For instance, DP is one of the important natural catecholamine neurotransmitters for message transmission in the central nervous system, which plays a critical role in the function of central nervous, hormonal, and cardiovascular systems. Abnormal levels of DP will lead to Huntington's disease and neurodegenerative disorders, such as Alzheimer's and Parkinson's [1–3]. AA is another important component in human diet, and it plays a vital role in neurochemistry, bioelectrochemistry and clinical diagnostics applications [4]. More importantly, it has been used for prevention and treatment of scurvy, mental illness and cancer [5]. UA is a primary end product of purine metabolism.

Abbreviations: MVC, multivariate calibration; PLS-1, partial least squares-1; CPR, continuum power regression; MLR, multiple linear regression; SPA, successive projections algorithm; RCR, robust continuum regression; PRM, partial robust M-regression; PLY-PLS, polynomial-partial least squares; SPL-PLS, spline-partial least squares; RBF-PLS, radial basis function-partial least squares; LS-SVM, least squares-support vector machines; WT-ANN, wavelet transform-artificial neural network; DWT-ANN, discrete wavelet transform-artificial neural network; BP-ANN, back propagation-artificial neural network; SWV, square wave voltammetry; AA, ascorbic acid; UA, uric acid; DP, dopamine; NT, nitrite; GCE, glassy carbon electrode; SLD, simplex lattice design; AsLSSR, asymmetric least squares splines regression; COW, correlation optimized warping; GA, genetic algorithm; OSC, orthogonal signal correction; MC, mean centering; RMC, robust median centering; WD, wavelet denoising; SGS, Savitsky–Golay smoothing; LOO-CV, leave one out cross-validation; LVs, latent variables; rPCA, robust principal component analysis, MLP, multilayer perceptron; PDC, percentage of data contamination; RMSECV, root mean squared errors of cross-validation; RMSEP, root mean square errors of prediction; REP, relative error of prediction; Q^2, the square correlation coefficient of cross-validation; PRESS, prediction residual error sum of squares

* Corresponding author. Tel.: +98 8314274557; fax: +98 8314274559.
E-mail address: mbgholivand@yahoo.com (M.-B. Gholivand).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.11.028

Abnormal concentration levels of UA will lead to some diseases, such as gout and hyperuricaemia [6]. In recent years, many papers reported that NO could act as a neurotransmitter or a neuromodulator in the central nervous system. Although the physiological results of NO for DP release in the striatum are controversial, it is undisputed that NO can be oxidized to NT in biological circumstance as fast as in a few seconds [7–9]. Therefore, simultaneous determination of AA, DP, UA and NT is important for investigating their physiological functions and diagnosing diseases.

Whereas zeroth-order univariate calibration cannot detect sample components producing an interfering signal, first-order MVC, which operates using a vector of data per sample, may compensate for these potential interferents, provided they are included in the calibration set, a property known as the "first-order advantage". The MVC methods are increasingly used to extract relevant information from different types of absorptive spectral and electrochemical data to predict analyte concentrations or properties of complex samples [10–12]. Several tools have been reported in the literature for processing these data [13], and the most important linear calibration method is PLS [14]. One problem which restricted the application of chemometrics in electroanalytical chemistry is the non-linearity of electrochemical data [15]. Several strategies have been used for the calibration of non-linear data systems. They are: data pretreatment (such as data alignment); the use of linear methods (for slight nonlinearities only); the use of local modeling; the addition of extra variables; the use of non-linear calibration techniques [16–18]. Among these strategies, non-linear calibration techniques are able to build robust calibration models.

In this work, we are going to compare the performance of classical linear (PLS-1, CPR, and MLR), robust linear (PRM, and RCR), and non-linear (PLY-PLS, SPL-PLS, RBF-PLS, LS-SVM, WT-ANN, DWT-ANN, and BP-ANN) MVC models for predicting the concentration of AA, UA, DP and NT in a synthetic sample with a complex matrix to choose the best MVC model for determining the concentration of the mentioned analytes in human serum samples which have a very complex matrix. Literature survey revealed that no attempt has been made till date to the simultaneous voltammetric determination of AA, UA, DP and NT with the aid of Chemometrics.

2. Experimental

2.1. Chemicals and solutions

The AA, UA, and DP were purchased from Sigma-Aldrich Chemie, Steinheim, Germany. Sodium nitrite was obtained from Riedel-de Haën (Sigma-Aldrich Chemie, Steinheim, Germany). Sodium dihydrogen phosphate (NaH_2PO_4), and disodium hydrogen phosphate (Na_2HPO_4) were obtained from Merck. All other materials were used of the highest quality available and purchased from regular sources. The human serum samples used in this study were obtained from a Medical Diagnostic Laboratory in Kermanshah, Iran. Phosphate buffered solution (PBS, 0.1 M, pH2) was prepared using NaH_2PO_4, and Na_2HPO_4 and titrated with H_3PO_4 to pH2. All working and sample solutions were analyzed in the PBS. All solutions were prepared with double-distilled water (ddH_2O). Pure nitrogen was passed through all the experimental solutions.

Stock standard solutions (0.01 M) of the analytes were prepared daily by exact weighing and dissolving their solid powder in a PBS (0.1 M, pH2). Working solutions were prepared immediately before their use by taking appropriate aliquots of each stock standard solution and diluting with PBS to the desired concentrations.

2.2. Apparatus and softwares

Electrochemical experiments were performed using a μ-Autolab TYPE III, Eco Chemie BV, Netherlands, and driven by the NOVA software (Version 1.8). A conventional three-electrode cell was used with a saturated Ag/AgCl as reference electrode, a Pt wire as counter electrode and a GCE as working electrode. The pH values were measured using a JENWAY-3345 pH-meter equipped with a combined glass electrode. The recorded experimental data was smoothed, when necessary, and converted to matrices by means of several homemade mfiles. Baseline correction was performed using AsLSSR [19], and signal alignment was performed using correlation optimized warping (COW) [20] employing MATLAB software (Version 7.14 from MathWorks, Inc.) [21]. PLS-1, PLY-PLS, SPL-PLS, GA, MC, and OSC analyzes were performed using PLS-Toolbox (Version 3.5, Eigenvector Research Inc., USA [22]). All ANN modellings were implemented employing MATLAB. Computations based on CPR, PRM, RCR, rPCA, and RBF-PLS were performed in MATLAB environment using a series of m-files written by Walczak et al. [23,24]. Computations based on SGS, SPA, and MLR were performed in MATLAB environment using a series of m-files written by Paiva et al. [25]. All calculations were run on a DELL XPS laptop (L502X) with Intel Core i7-2630QM 2.0 GHz, 8 GB of RAM and Windows 7-64 as its operating system.

2.3. Model optimization

To truly compare the different MVC models, the efficiency of the best possible model should be found. Because of the dependence of the calibration model efficiency on its parameters, the following parameters were varied (optimized):

- *PLS-1*: number of latent variables (LVs).
- *CPR*: number of LVs, and power.
- *MLR*: number of LVs.
- *PRM*: number of LVs, and percentage of data contamination (PDC).
- *RCR*: number of LVs, PDC, and delta parameter (δ).
- *PLY-PLS*: number of LVs and degree of polynomial (D).
- *SPL-PLS*: number of LVs, number of knots (K), and D.
- *RBF-PLS*: number of LVs, and sigma parameter (σ).
- *LS-SVM*: number of LVs, regularization parameter (γ), and kernel-related parameter (σ^2, here, RBF kernel function was selected).
- *ANNs*: Number of input neurons (IN), number of hidden neurons (HN), number of output neurons (ON), and transfer functions of the hidden and output layers.

2.4. Model efficiency estimation

Whether a model can be applied to analysis of human serum samples or not, model validation is possibly the most important step in the model building sequence. In order to evaluate the performance of the previously mentioned MVC models, each model was validated for the prediction of the validation set, evaluating root mean squared errors of cross-validation (RMSECV), cross-validated correlation coefficient (Q^2), root mean square errors of prediction (RMSEP), and relative error of prediction (REP).

$$\mathrm{RMSECV} = \sqrt{\frac{1}{m}\sum_{1}^{m}\left(y_{pred} - y_{act}\right)^2} \quad (1)$$

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{1}^{n}\left(y_{pred} - y_{act}\right)^2}{n}} \quad (2)$$