



# Investigating the discrimination potential of linear and nonlinear spectral multivariate calibrations for analysis of phenolic compounds in their binary and ternary mixtures and calculation $pK_a$ values



Zolaikha Rasouli, Raouf Ghavami \*

Department of Chemistry, Faculty of Science, Kurdistan University, P. O. Box 416, Sanandaj, Iran

## ARTICLE INFO

### Article history:

Received 25 October 2015

Received in revised form 20 March 2016

Accepted 24 April 2016

Available online 27 April 2016

### Keywords:

Phenolic compounds

Multivariate calibration methods

Partial least square

Partial robust M-regression

Artificial neural networks

Multivariate curve resolution-alternating least squares (MCR-ALS)

## ABSTRACT

Vanillin (VA), vanillic acid (VAI) and syringaldehyde (SIA) are important food additives as flavor enhancers. The current study for the first time is devote to the application of partial least square (PLS-1), partial robust M-regression (PRM) and feed forward neural networks (FFNNs) as linear and nonlinear chemometric methods for the simultaneous detection of binary and ternary mixtures of VA, VAI and SIA using data extracted directly from UV-spectra with overlapped peaks of individual analytes. Under the optimum experimental conditions, for each compound a linear calibration was obtained in the concentration range of 0.61–20.99 [LOD = 0.12], 0.67–23.19 [LOD = 0.13] and 0.73–25.12 [LOD = 0.15]  $\mu\text{g mL}^{-1}$  for VA, VAI and SIA, respectively. Four calibration sets of standard samples were designed by combination of a full and fractional factorial designs with the use of the seven and three levels for each factor for binary and ternary mixtures, respectively. The results of this study reveal that both the methods of PLS-1 and PRM are similar in terms of predict ability each binary mixtures. The resolution of ternary mixture has been accomplished by FFNNs. Multivariate curve resolution-alternating least squares (MCR-ALS) was applied for the description of spectra from the acid-base titration systems each individual compound, i.e. the resolution of the complex overlapping spectra as well as to interpret the extracted spectral and concentration profiles of any pure chemical species identified. Evolving factor analysis (EFA) and singular value decomposition (SVD) were used to distinguish the number of chemical species. Subsequently, their corresponding dissociation constants were derived. Finally, FFNNs has been used to detection active compounds in real and spiked water samples.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Natural vanilla extract is a mixture of several hundred different compounds. Vanillin (VA) is one of main aromatic flavor compounds in natural vanilla derived from *Vanilla planifolia* [1]. VA is readily available from low cost synthetic procedures based on eugenol, guaiacol and from lignin-containing sulfite liquor, a byproduct of wood pulp processing in paper manufacture [2]. The flavor profile of vanilla contains >200 components, of which vanillic acid (VAI) and syringaldehyde (SIA) are other flavor compounds founded in vanilla. In addition to, VAI was identified as natural antioxidant [3]. Although, SIA is not detected in significant amounts in vanilla extract, is formed as lignin degradation products in oak barrels during coopering and is subsequently extracted into wine or spirits during barrel aging [4]. Chemical structures and formula of VA, VAI and SIA are as presented in Fig. S1 in the online version at <http://dx.doi.org/10.1016/j.saa.2016.04.044>. (Supplementary material). Although these compounds can enhance the scent of foods and beverages, they

are synthetic perfumes and food additives and usually are used to keep up the quality and promote their safety. In other words, it must be ensured that a product's label is accurate and not misleading. These findings have increased the interest for developing reliable sensitive quantitative methodologies for the determination of these flavor enhancers.

To the best of our knowledge, no analytical method has been reported for simultaneous determination of VA, VAI and SIA in binary and ternary multi-component mixtures in food samples or vanilla extracts, while several analytical methods have been published for determination of these compounds, whether alone or in combination with other flavor compounds, such as, high-performance liquid chromatography (HPLC) [5–8], capillary electrophoresis (CE) [9–12], gas chromatography–mass spectrometry (GC–MS) [13], nuclear magnetic resonance spectroscopy [14] electrochemical methods [15,16] have been reported. Spectrophotometric methods, replacing wet chemical analytical procedures, can be used for the quantification of different classes of phenolic compounds due to its simplicity, low cost, shorter analysis time, non-destructive nature, and small amount of sample, accuracy, and reliability when associated with chemometric approaches [17]. The modern spectral techniques usually produce abundant data for the analyzed sample. Hence,

\* Corresponding author at: Department of Chemistry, Faculty of Science, University of Kurdistan, P.O. Box 416, Iran.

E-mail addresses: [r.ghavami@uok.ac.ir](mailto:r.ghavami@uok.ac.ir), [rghavami2000@yahoo.com](mailto:rghavami2000@yahoo.com) (R. Ghavami).

it is very crucial to use multivariate calibration algorithms to develop relationship between spectral data and analyzed sample. The main advantage of multi-component analysis by using multivariate calibration is the speed of the determination for the components in mixtures and avoiding the need for prior separation, that is, otherwise necessary owing to the overlapping of the absorption spectra [18,19]. The most commonly used linear methods are classical least squares (CLS), principal component regression (PCR) and partial least squares regression (PLSR) [20–22]. The partial robust M-regression (PRM) is an efficient chemometrics approach for the detection of outlier data in chemical analysis. The presence of outlier data can have a significant effect on the determination of sensitivity, linear range or capability of detection amongst others [23,24]. But the problem which restricted the application of linear methods in multi-component determination is the intrinsic non-linearity is observed in the system. The artificial neural networks (ANNs) typically the multi-layer feed forward neural networks (FFNNs) or multi-layer perceptron, with the back-propagation learning algorithm are very efficient chemometrics approaches as modelling tool to provide non-linear relations [25–27]. This is mainly due to the increases in computing power, which makes it possible to perform calculations on a personal computer that previously required a very powerful mainframe. In addition to, these methods are quite appealing since they are inspired by biological phenomena [28].

Multivariate curve resolution-alternating least squares (MCR-ALS) is a soft-modelling method which has been shown to be a powerful tool for exploiting first-order advantage by spectroscopic means [29] besides advantageous for quantification [30]. One of the outstanding characteristics of this the resolution method (or in generally soft modelling methods) is that there is no need of any previous knowledge, either chemical or mathematical, to analyze the system under investigation.

The current paper is divided as follows: Section II introduces experiments including procedures for preparation of synthesis and real samples. In Section 3 initially the chemical parameters affecting for each of systems were studied, then the simultaneous determination VA, VAI and SIA in the binary and ternary mixtures will be described in details in synthesis and real samples. Section 4 presents the application MCR-ALS to drive the dissociation constants. Section 5 summarizes concluding remarks.

## 2. Experimental

### 2.1. Instrumentation and software

The absorbance measurements were carried out on an analyticjena E250 spectrophotometer equipped with a thermostat Lauda Ecoline Staredition RE 104 and 1-cm quartz cells. The spectra of analytes were recorded from 200 nm to 400 nm with 2 nm slit width and wavelength-scanning speed 2800 nm/min and absorbance values were transferred to Pentium (IV) personal computer for further analysis. All experiments were performed at  $25.0 \pm 0.5$  °C. The pH measurements were carried out using Metrohm 713 model pH meter (with precision of  $\pm 1$  mv) furnished with a combined glass-saturated calomel electrode. All computations involved in the design FFNN and PLS-1 were performed using Matlab 7.1 (Math works). PRM and rPCA algorithms analysis was carried out in MATLAB using m-files written by Walczak and Massart [31]. The MCR-ALS program and a series of functions for exploratory analysis are available at the multivariate curve resolution web page: <http://www.ub.es/gesq/mcr/mcr.htm>.

### 2.2. Chemical reagents and stock solutions

All reagents and solvents were of analytical reagent grade (Sigma-Aldrich and Merck) and used without further purifications. Stock solutions of VA, VAI and SIA (0.1 M) were prepared individually by dissolving each of the compounds in 95% ethanol. Doubly distilled deionized water was used throughout. Working solutions was prepared daily by

proper dilution from the stock solutions. Other chemicals such as hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydrogen phosphate ( $K_2HPO_4$ ), potassium dihydrogen phosphate ( $KH_2PO_4$ ), and phosphoric acid ( $H_3PO_4$ ) were used for pH adjustments and constructing buffer solutions. A phosphate buffered saline (PBS) 0.1 M, was prepared using phosphate salts.

### 2.3. Analytical procedures

#### 2.3.1. Binary and ternary standard solutions

Nine sets of standard solutions including four sets of calibration (three sets for the binary mixtures and one set for the ternary mixture), four sets of prediction (three sets for the binary mixtures and one set for the ternary mixture) and one set of validation (only for the ternary mixture) were prepared. Thus, different aliquots of VA, VAI and SIA from their corresponding working solutions for each of set were transferred simultaneously into a series of 5.0 mL volumetric flasks. Then, 2.50 mL from pH = 2.00 buffer solution was added and diluted to the mark with doubly distilled water. Concentrations of each analyte in all data sets were within the linear dynamic range of that analyte. The electronic absorption spectrum of each solution was measured over the wavelength range of 200–400 nm at 1.0 nm intervals with respect to a blank solution, and all these data were recorded and used for analyze.

#### 2.3.2. Acid-base titrations

Spectrophotometric pH-metric titrations of VA, VAI and SIA were performed in aqueous solutions; the known volumes of VA, VAI and SIA with constant analytical concentrations individually were titrated with HCl or NaOH. In the case of each pH, the absorbance spectrum of the resulting solution was recorded in the region of 200–400 nm. A total number of 33 pH readings and absorption spectra were collected for each of compounds, providing three matrices each of with dimensions of ( $33 \times 201$ ).

#### 2.3.3. Procedure for real samples

The solid samples including chocolate (1 and 2) and biscuit (3) were purchased from a local market in Sanandaj. The amounts 30.0 g of biscuit and 18.0 g for each of the chocolate samples (chocolate samples were of wafer type coated with cocoa) firstly using the spatula, were divided to very small pieces and then to assistance porcelain mortar were transformed to fine powder. Then, the powdered samples were transferred into 250 and 100 mL Erlenmeyer flasks, respectively. This was followed by adding 100 and 50 mL (for each of chocolate samples) of ethanol (99%), respectively. The samples were sonicated for 1 h and suitable aliquots of each sample were centrifuged at 1000 rpm for 10 min. The filtered solutions were used for analysis under optimum experimental conditions.

## 3. Results and discussion

### 3.1. Spectral behavior

The development of analytical methods for the determination of VA, VAI and SIA in binary and ternary mixtures without preliminary separation was of interest. Fig. 1 shows the absorption spectra over 200–400 nm of VA, VAI and SIA individually and at binary and ternary mixtures under optimized experimental conditions in a buffer solution of pH 2.00. As can be seen, the exhibited spectra have overlapped seriously bands in their absorbing regions. Thus, quantitative estimations of these phenolic compounds in the presence of each other (simultaneous analysis of binary or ternary mixtures) are difficult when conventional, derivative and derivative ratio spectrophotometric techniques used. For this reason we propose, linear and non-linear multivariate calibration methods for simultaneous determination of these compounds in the mixtures with different composition.

Download English Version:

<https://daneshyari.com/en/article/1228685>

Download Persian Version:

<https://daneshyari.com/article/1228685>

[Daneshyari.com](https://daneshyari.com)