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Simultaneously detection of calcium and magnesium in various samples by calmagite and chemometrics data processing



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ABSTRACT

The current study describes results of the application of radial basis function-partial least squares (RBF-PLS), partial robust M-regression (PRM), singular value decomposition (SVD), evolving factor analysis (EFA), multivariate curve resolution with alternating least squares (MCR-ALS) and rank annihilation factor analysis (RAFA) methods for the purposes of simultaneous determination of trace amounts calcium (Ca^{2+}) and magnesium (Mg^{2+}) and exploratory analysis based on their colored complexes formation with 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (calmagite) as chromomeric reagent. The complex formation Ca^{2+} and Mg^{2+} with calmagite was investigated under pH 10.20. The performance of RBF-PLS model in detection of minerals was compared with PRM as a linear model. The pure concentration and spectral profiles were obtained using MCR-ALS. EFA and SVD were used to distinguish the number species. The stability constants of the complexes were derived using RAFA. Finally, RBF-PLS was utilized for simultaneous determination of minerals in pharmaceutical formulation and various vegetable samples.

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1. Introduction

Both calcium and magnesium are two of the most important minerals in the body which play an essential role in bone mineral structure. For example, almost 99% of body's calcium is in bone tissue [1]. The remaining 1% is related interplay that takes place in the body. However, this 1% is so important that its deficiency causes some disorders. Magnesium is a cofactor in large a number of reactions including energy metabolism, protein and nucleic acid synthesis [2]. Approximately half of the total magnesium in the body is present in hard tissue and less than 1% of it is found in blood [3]. Hypocalcaemia and hypomagnesaemia (also hypercalcaemia and hypermagnesaemia) are an imbalance for abnormally low levels (or high levels) of calcium and magnesium in the body that have been correlated with a cluster of metabolic abnormalities and associated chronic diseases [4,5]. Generally, calcium and magnesium help to prevent osteoporosis, manage blood pressure, reduce breathlessness (asthma) and maintain a healthy heart and muscle [6–8]. Because of these important roles and for maintaining balance and cellular reactions dependent on them, especially when determination is considered for trace levels, there is an increasing need for the development of simple and selective analytical methods in bioscience, clinical diagnosis, and pharmaceutical, food and other industries. Most methods for the determination of calcium and magnesium simultaneously or in combination with other minerals are based on

UV–Vis spectrophotometry due to its advantages including low cost, fast response, non-destructive nature, accuracy and reliability particularly when associated with chemometric approaches. The spectrophotometric simultaneous determination of minerals in aqueous solution or an organic medium is generally based on the complexation reaction between the analytes and a chromomeric reagent [9–11], absorbance spectral overlap of corresponding complexes is the main limitation in quantification, it requires the use of multivariate calibration (MVC) as an analytical method. However, in spite of the obtained results being very good, two aspects of the method were not satisfactory enough for the authors. The first unsatisfactory aspect of the method is that it focuses less on determination values of stability constants of complexation reactions. The stability constants can be the key parameters for the investigation of equilibria in solution and in many fields such as agricultural and environmental studies, pharmaceuticals and the food industries [12,13]. Second, no attempt has been done to investigate the interaction of the complexation reactions between ligand and metal ion.

Also, the literature inspection revealed that flame atomic absorption spectroscopy (FAAS), capillary electrophoresis electrochemical methods and ion chromatography have also been reported [14–17]. Many of these methods employ expensive instruments and/or material, high purity solvents and often pretreatment steps of samples are required. MVC methods seem to be the most appropriate technique for showing the best performance in the multi component quantitative mixture from different types of absorptive spectral and electrochemical data [18]. However, the problem which restricts the application of

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methods such as partial robust-M regression in simultaneous multi component determination is the intrinsic non linearity observed in the system. The radial basis function-partial least squares is a chemometrics approach to non-linear projection to PLS modeling using radial basis functions (RBFs) to provide a non-linear inner relation [19]. The distinguishing characteristic of the RBF-PLS is its flexible non-linear modeling ability; it can take into account the nonlinear characteristics and approximate various non linearities in the data sets. RBF-PLS has attracted the interest as a modeling tool for MVC in spectrophotometry, electrochemistry and mass spectrometry [20–22].

One of the outstanding characteristics of soft modeling methods such as multivariate curve resolution with alternating least squares is that there is no need for any previous knowledge, either chemical or mathematical, to analyze the system under investigation. However, the performance of these methods depends greatly on local properties of the data set and can positively influence the resolution of the system [23,24]. Rank annihilation factor analysis has become the most common approach used in spectroscopic methodologies for determining the stability constants of complexation reactions, in addition to its utilization in quantitative applications [25–27].

In this investigation, first the RBF-PLS method was proposed for simultaneous determination calcium and magnesium by applying spectrophotometric measurements based on their complexation reaction with calmagite (Fig. 1) at pH 10.20. The analytical performance of RBF-PLS model was compared with PRM model as a linear model. Then, the MCR-ALS was applied to the resolution of the complex overlapping spectra, and to interpret the extracted spectral and concentration profiles of any pure chemical species identified. RAFA was applied to determine the stability constants of the complexes. Finally, the ensuing method was used to determine Ca^{2+} and Mg^{2+} in pharmaceutical formulation and various vegetable samples.

2. Theoretical background

2.1. Multivariate non-linear and linear calibration techniques

2.1.1. Radial basis function-partial least squares (RBF-PLS)

Suppose X and y are the matrices containing the initial independent and dependent variables, a non-linear relationship is established using RBFs by transforming X to the A matrix, where A is the commonly called activation matrix. The Gaussian functions are the most common RBFs. Therefore, each element inside the i th row and j th column of A can be expressed by,

$$a_{ij} = \exp\left(-\frac{\|c_j - x_i\|^2}{\sigma_j^2}\right) \quad i, j = 1, 2, \dots, m \quad (1)$$

where $\| \cdot \|$ is a measure of Euclidean distance, x_i is an input object taken from the i th observations, c_j and σ_j are the center and the width of j th the RBF, which are calculated as:

$$c_j = x_j \quad j = 1, 2, \dots, m \quad (2)$$

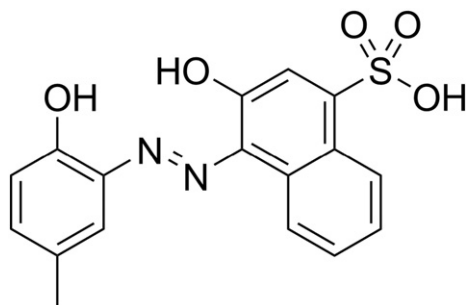


Fig. 1. Molecular structure of calmagite.

$$\sigma_{j1} = \sigma_{j2} = \frac{e}{m} \sum_{i=1}^m \|x_i - x_j\| \quad (3)$$

where e is a positive number. The resulting symmetrical ($m \times m$) matrix A has ones on its diagonal. Then the PLS procedure will be applied to optimize two objective functions: to minimize the variance of the prediction while maximizing the covariance of the A and y data. It means that the following PLS model is built:

$$y = TC + E = (AA^T)C + E \quad (4)$$

where T is the score matrix of A containing k PLS component (latent variables), C is the regression coefficients or loadings matrix, A^T is the transpose matrix of A and E is the residual matrix. Finally, in the prediction step for estimation of the composition of the unknowns from a measured data set, X_{unk} , the y_{unk} is calculated according to the following equation:

$$y_{\text{unk}} = A_{\text{unk}}A^TC \quad (5)$$

in which A_{unk} is the activation matrix of X_{unk} [19,28]. The remaining parameters formerly have been introduced.

2.1.2. Partial robust M-regression (PRM)

One of the disadvantages of classical least squares methods is that it assumes that data distribution is equal to the imposed model distribution. In particular, in the absence of normality and the presence of outliers the prediction ability of these methods is extremely low. This drawback has been heeded by robust statistics to construct a robust version of robust linear MVC models such as PRM. PRM allows a better fit and is more predictive by finding an outlier free subset of the data. Full details of the theoretical PRM model which was introduced by Serneels et al. and the detection outliers using robust principal component analysis (rPCA) to create a distance-distance plot can be obtained in Refs. of [29–31].

2.1.3. Performance estimation of multivariate calibration models

Determining the optimum number of RBF-PLS parameters (the width parameter, σ , and the number of latent variables) and PRM factors are an important prerequisite to achieve correct quantitation of these models. Probably the best known and oldest variant is the LOO_{CV} procedure. It is performed by estimating n in the calibration models for n sample of the calibration set. In order to evaluate the performance of the different models, root mean square error in cross validation (RMSE_{CV}), root mean square errors of prediction (RMSEP), relative error of prediction and squared regression coefficient (R_p^2) were calculated as follows:

$$\text{RMSE}_{\text{CV}} = \sqrt{\frac{\sum_{i=1}^n (C_{\text{pred},i} - C_{\text{true},i})^2}{n}} \quad (6)$$

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^m (C_{\text{pred},i} - C_{\text{true},i})^2}{m}} \quad (7)$$

$$\text{REP}(\%) = \frac{100}{\bar{C}_{\text{true}}} \sqrt{\frac{1}{m} \sum_{i=1}^m (C_{\text{pred},i} - C_{\text{true},i})^2} \quad (8)$$

$$R_p^2 = 1 - \frac{\sum_{i=1}^m (C_{\text{pred},i} - C_{\text{true},i})^2}{\sum_{i=1}^m (C_{\text{true},i} - \bar{C}_{\text{true}})^2} \quad (9)$$

where $C_{\text{pred},i}$ and $C_{\text{true},i}$ are true and predicted concentrations of each component in the sample i , respectively and \bar{C}_{true} is the average true concentration. n and m are the number of samples in calibration and

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