ID: 2022

Simultaneous Determination of Trace of Ca(II) and Mg(II) in Water and Pharmaceutical Products by Partial Least Squares (PLS) Method

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ABSTRACT

The quantitative prediction ability of partial least squares method applied to conventional and derivative UV-VIS absorption spectra is tested. This method is based on the complexation reaction between Ca(II) and Mg(II) with bromopyrogallol red (BPR) ligand in a micellar medium (Tween 80) adjusted by buffer solution, containing sodium hydroxyd (NaOH 0.1M)/ sodium tetraborate ($Na_2B_7O_4$, $10H_2O$ 0.05M), to pH10. In the numerical method, a training set was prepared by using 14 samples containing these metals simultaneously in the calibration range. The proposed methods were validated by using synthetic binary mixtures and applied to the simultaneous determination of Ca(II) and Mg(II) in multivitamins, physiological serum and commercial drinking water samples. The results were compared each other, the derivative mode gave better results in all cases. We concluded that the application of differentiation techniques prior to PLS algorithms could be advantageous in the cases of high spectral overlapping.

Keywords: UV-Visible derivative spectrophotometry; Partial Least Squares (PLS-2); Calcium; Magnesium

1 Introduction

Calcium (Ca) and magnesium (Mg) are essential nutrients necessary for numerous biological functions within the body. They are mentioned together because they mostly function as a group. Both elements are crucial for the optimal health and functioning of the bones, muscles and heart [1-3]. To function optimally in the body, magnesium must be balanced with phosphorus, calcium, potassium and sodium. Together with calcium, magnesium is involved in muscle contraction and blood clotting. Calcium promotes the processes while magnesium inhibits them. It is this interaction that helps to regulate blood pressure and the functioning of the lungs. [4-6]. Partial least squares (PLS) is among the most widely used chemometric technique to solve data analysis problems. This method has frequently been used in quantitative spectral analysis to obtain selective information from unselective data. The combination of derivative techniques with multivariate calibration methods has been employed [7-13].

2 Experimental

2.1 Apparatus

Ordinary and derivative spectra were recorded with a Schimadzu 2101 UVPC spectrophotometer equipped with PC computer. The absorption spectra of the reference and analyte solutions were carried out in 1cm quartz cells over the range of 400-800nm. Differentiation was performed according to the simplified least squares procedure of Savitzsky and Golay, a value of $\Delta\lambda$ = 4 nm was found optimal for smoothing. PLS algorithm was modelled using MATLAB 7.0.

2.2 Procedures

Multivariate calibration methods such as PLS require a suitable experimental design of the standard belonging to the calibration set in order to provide good prediction. Two sets of standard solutions were prepared. The calibration set contains 14 standard solutions. The composition of the calibration mixtures has been varied in the linear range of the analytical signal of each component ; 0.8-4.8 µg/ml for Ca (II) and 0.5– 3 µg/ml for Mg (II). For prediction set, it was used 6 test mixtures .The conventional absorption

DOI: 10.21467/abstracts.169 ISBN: 978-81-970666-4-1 (eBook)

spectra were recorded and the first-derivative spectra (Δλ = 4nm) were calculated. The spectral region between 510 and 720 nm (420 experimental points per spectrum) was selected for analysis.

3 Results and discussions

Selection of the optimum number of factors is very important step before constructing the models. The prediction residual error sum of squares (PRESS) was calculated using a maximum number of initial factors of 8 (half the standards + 1). The Haaland and Thomas criteria was used, so, the selection of the optimal number of factors involves the comparison of PRESS selected for the models with the minimum PRESS. The optimum number of factors used for building PLS-2 models by conventional and derivative modes were found to be 6 for Ca(II), 6 and 5 for Mg(II), respectively. It is necessary to indicate that PRESS values for the derivative mode are smaller than those of the conventional mode. The validation set consisting of the synthetic binary mixtures of these metallic ions was employed to check the calibration of PLS-2. Mean recoveries and relative standard deviations for conventional PLS-2 were found as 95.55% and 1.62% for Ca (II), 96.73% and 1.79%; for Mg(II). The PLS-2 derivative mode shows mean recoveries and relative standard deviations of 99.21% and 1.50% for Ca (II), 98.70% and 1.65% for Mg(II).
The proposed methods, were applied for simultaneous determination of calcium and magnesium in real matrix samples. For this purpose, three real samples were analyzed commercial multivitamin (Additiva, manufactured by Dr. Scheffler, Germany), physiological serum (Saidal Pharm. Ind., Algeria) and drinking water (from commercial drinking water manufactured by IFRI, Algeria). The results of the prediction obtained by the present methods are summarized in Table 1 and compared with those obtained by atomic absorption spectrometry (reference method). These results show that derivative PLS-2 model is able to predict calcium and magnesium in these samples with better precision than conventional PLS-2 model.

Table 1. *Assay results for pharmaceutical preparations and drinking water.*

	Reported (SAA)		Found (PLS-2) Original data		Found (PLS-2) First-derivative data	
	Ca(II)	**Mg(II)**	**Ca(II)**	**Mg(II)**	**Ca(II)**	**Mg(II)**
Multivitamins	3.99	0.75	4.12	0.83	4.02	0.74
Human serum	1.115	3.065	1.15	3.12	1.09	3.07
Drinking water	2.62	0.63	2.51	0.56	2.64	0.65

4 Conclusion

Multivariate calibration approach PLS-2 is applied on conventional and first derivative absorption spectra. The results obtained on data set of calcium and magnesium mixture demonstrate that the application of PLS-2 method, for simultaneous determination of Ca^{2+} and Mg^{2+}, has proven that it provides adequate prediction for quantitative determination of these ions based on their reaction with bromopyrogallol red chromogenic reagent in Tween 80 micellar media. Another relevant point is that the application of differentiation techniques prior to the application of PLS algorithm is recommendable in this case.

References

[1] F. Kargin, K. Seyrek, A. Bildik, S. Aypak, Turk. J. Vet. Anim. Sci. 28 (2004)609-612.
[2] A.Schauss. Life Sciences Press: Tacoma, WA., 1995.
[3] P.O. Webster, Magnesium. *Am. J. Clin. Nutr.*, 45 (1987) 1305-1312.
[4] H. Ebel, T.Gunther. J. Clin. Chem. Clin. Biochem.,18: 257 (1980).
[5] Hyman Katz and Remo Navone.Joumal AWWA, Vol. 56, No. 1 (JANUARY 1964) 121-123
[6] J. Paluch M. Kozak J. Kochana M. Wieczorek, Analytical Letters, Vol. 51, No. 14 (2018).
[7] Yamane Takeshi, Goto Eiichi. Talanta, Vol.38, Issue 2, February 1991, pp. 139-143.
[8] Abbas Afkhami, Tayyebeh Madrakian, Maryam Abbassi Tarighat. Food Chemistry 109(3) (2008) 660-669.
[9] Kuldeep Kaur, Ashok Kumar Malik, Baldev Singh,. J. Pharm. Sci. 33 (2009) 123-136
[10] D. Venkat Ratnam, V. Bhardwaj, M.N.V. Ravi Kumar, Talanta 70 (2006) 387–391.
[11] P. Lopez Garcia, M.I. Rocha Miritello, Santoro, E.R.M. Kedor-Hackman, A. Kumar Singh, J. Pharm.Biomed. Anal. 39 (2005) 764–768.
[12] G. Gumus, H. Filik, B. Demirata, Anal. Chim. Acta 547 (2005) 138–143.
[13] Namita Kapoor, Sateesh Khandavilli, Ramesh Panchagnula, J. Pharm. Biomed. Anal. 41 (2006) 761–765

ISBN: 978-81-970666-4-1
Series: AIJR Abstracts
DOI: 10.21467/abstracts.169