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Simultaneous determination of Dopamine and Ascorbic acid in real samples by Partial Least Squares method

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Abstract: Partial least squares (PLS) is multivariate calibration method that allows simultaneous determination of several analyte in spite of their overlapping spectra. In this research, a spectrophotometric method using PLS is proposed for the simultaneous determination of ascorbic acid (AA), dopamine (DA). The linear concentration ranges for AAand DA were 1.73–28.66, 1.89–151.23 (ng mL^{-1}), respectively. However, PLS was applied to design calibration set based on absorption spectra in the 220–300 nm range for 16 different mixtures of AA, DA in all cases. Cross validation method was used to select the optimum number of principal components (NPC). The NPC for AA and DA was found to be 2 by PLS. Prediction error sum of squares (PRESS) of AA, DA were 0.58 and0.74.For PLS Satisfactory results were achieved for the simultaneous determination of AA and DA in some real samples such as human urine, serum and plasma.
Keywords: Dopamine and Ascorbic acid, Partial Least Squares method.

1. Introduction

Ascorbic acid (AA) and dopamine (DA) are the compounds of great biological and chemical interest that play important roles in the Operation of the human metabolism, central nervous and renal systems [1].Ascorbic acid has been used forthe prevention and treatment of common colds, mental illnesses,infertility, cancers, and in some clinical manifestationsof HIV infections [2]. Dopamine (DA) was discovered to be an important neurotransmitter in mammalian central nervous system in the late 1950s and it is found in high amounts in a region of the brain known as the “caudate nucleus” [3].Therefore, it is essentialto develop simple and rapid methods for the determinationof these biological molecules in a routine analysis.Several methods such as electrochemical methods [4-10], HPLC methods [11], fluorescence [12] and spectrophotometric methods [13] have been developed for the quantitation of AA and DA, some of which were difficult to operate and use expensive instruments[14]. Partial least squares (PLS) is multivariate calibration method that allow simultaneous determination of several analytes in spite of their overlapping spectra [15-25]. In this research, a spectrophotometric method using PLS is proposed for the simultaneous determination of ascorbic acid (AA) and dopamine (DA). [2]. DA andAA usually coexist in physiological samples such as blood and urine, and the AA concentration (0.2–0.4 mmol L^{-1}) is generally 100 to 1000 times that of DA. This makes itdifficult to detect DA electrochemically because AA and UA can be oxidized at a potential close to that of DA at bare electrodes [14]. To the best of our knowledge, in the literature, there has been no report on the simultaneous determination of AA and DA by UV–VIS spectrophotometric measurements using multivariate calibration. The present work addresses UV–Vis spectrophotometry which has been applied for quantitative simultaneous determination of

AA and DA by PLS regression that performed in the PLS fashion for the calibration and validation of the proposed method and resolve two mixtures of AA and DA in synthetic and real samples.

2.1. Reagents

All reagents used were of analytical-reagent grade. Thewater utilized in all studies was double distilled anddeionized. Solutions of Ascorbic acid and Dopamine with concentration wereprepared by dissolving appropriate amounts of reagents (Merck, Darmstadt, Germany) in distilledwater.To adjust the pH of phosphate buffer and its salts was used.

2.2. Instrumentation

A Shimadzu 2100 UV–visible spectrophotometer (Shimadzu, Japan), A Jenway model 3510 pHmeter was used for pH measurements. An electronic analytical balance (220LA, ADAM) was used for weighting the solid materials.

2.3.Software and hardware

To check the data MATLAB and PLS programs 2007 are used for data processing.

2.4. Procedure

A 0.041 g of AA, 0.047 g of DA were dissolvedin a little amount of water separately and then dilutedwith a buffer solution to 25.0 mL. Theconcentrations of each stock solutionwere 10^{-2}mol L^{-1}. Then they were used to set up the calibrationset with concentration established according to themixture design. An independent prediction set of ternary mixtures,randomly established, was prepared to validate the elaboratedmultivariate model.

2.5. Multivariate calibration

Multivariate calibration methods, such as PLS, requirea suitable experimental design of a standard belongingto the calibration set in order to provide a good prediction. The first step in the simultaneous determination of the analytesby PLS methodologie involved constructing a calibrationmixture for the mixtures of AA and DA. For thispurpose, a synthetic set of 16 solutions of mixtures of AA and DAwere prepared in the concentration ranges. Fromthese series, 9 solutions were chosen for calibration setaccording to the mixture design for three component systems(Table 1), and 7 solutions, that were chosen randomly, wereused for prediction set (Table 2).

Table 1. Concentration data of the calibration set for two component system using mixture design.

DA[b] μg mL^{-1}	AA[a] μg mL^{-1}	Mixture No. of
1.70	1.80	1
1.70	37.80	2
1.70	75.00	3
1.70	113.00	4
1.70	150.00	5
8.50	1.80	6
8.50	37.80	7
8.50	75.00	8
8.50	113.00	9
8.50	150.00	10
13.63	1.80	11
13.63	37.80	12
13.63	75.00	13
13.63	113.00	14
13.63	150.00	15
21.44	1.80	16

AA=ascorbic acid DA= dopamine

Table 2 Added and found results of the synthetic mixture of AA and DA for PLS.

AA			DA			No. of Mixture
Recovery (%)	Found (µg mL-1)	Added (µg mL-1)	Recovery (%)	Found (µg mL-1)	Added (µg mL-1)	
89.11	14.27	16.02	90.21	34.10	37.82	1
98.83	17.20	17.41	97.52	73.14	75.00	2
98.50	19.06	19.36	98.85	111.71	113.00	3
99.53	31.00	21.41	98.79	148.19	150.00	4
96.50	21.28	23.39	90.00	1.62	1.80	5
103.35	26.32	25.47	93.30	35.27	37.80	6
98.14	26.02	26.52	99.44	74.58	75.00	7
98.14	28.09	28.62	98.74	111.58	113.00	8
104.08	31.62	35.39	98.16	147.25	150.00	9

3. Results and discussion

3.1. Found of λ_{max} for Ascorbic acid and dopamine

According to the Stock of two analytes solution, Stock solutions were prepared from each analyte and the absorption is measured at pH=7 and 25 ºC separately. A max wavelength of 288 nm for dopamine and 266 nm for Ascorbic acid was found respectively.

3.2. Register absorption spectrum of real samples

In this step conjunction with Repeat multivariate calibration stage, with a choice of three multivariate calibration solution for each real samples (plasma, serum and urine) absorbed the two analytes to be measured simultaneously. For this purpose, the desired solution by adding 500 ml any one of real samples simultaneously in a solution of ascorbic acid and dopamine absorption is measured Figures 1 to 3.

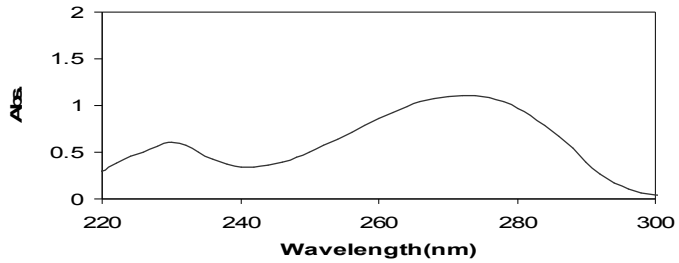

Fig.1. Simultaneous the absorption spectrum of dopamine and ascorbic acid, with concentrations 1.13 and 1.03 ng mL^{-1} respectively in plasma samples at pH=7, 25 $^{\circ}$C

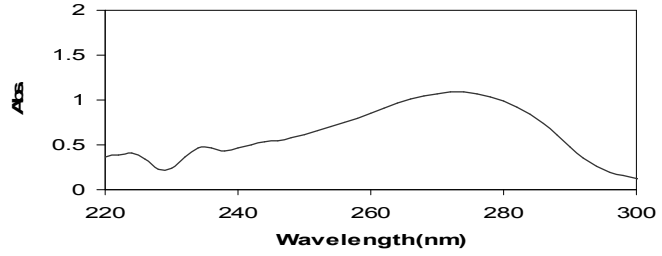

Fig.2. Simultaneousthe absorption spectrum of dopamine and ascorbic acid, with concentrations 1.13 and 1.03 ng mL^{-1} respectively in urine samples at pH=7, 25 $^{\circ}$C

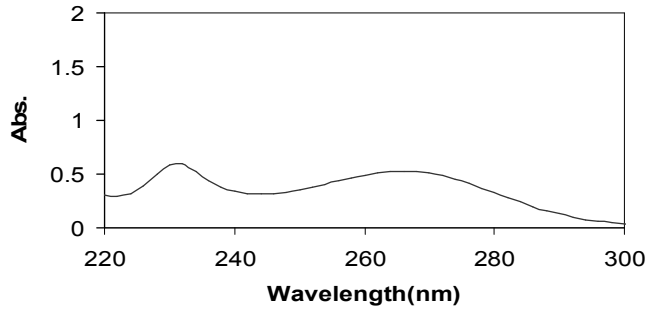

Fig.3. Simultaneousthe absorption spectrum of dopamine and ascorbic acid, with concentrations 1.13 and 1.03 ng mL^{-1} respectively in serum samples at pH=7, 25 $^{\circ}$C

3.3. Univariate calibration

The temperature has no appreciable effect on the spectra of theanalytes, so 25 ºC was chosen as a suitable temperature in thisstudy. Furthermore, pH = 7.0 was selected to obtain sufficientdata points in biological conditions. The individual calibrationcurves for each analyte have been determined by plotting theabsorbencies at the corresponding λ_{max} versus the analytes'concentration in the linear range for AA and DA (Figs. 4,5). Line equations and R^2 are also shown in Fig(4,5). The λ_{max}that recorded for AA andDA were 266.0 and 288.0 nm respectively.

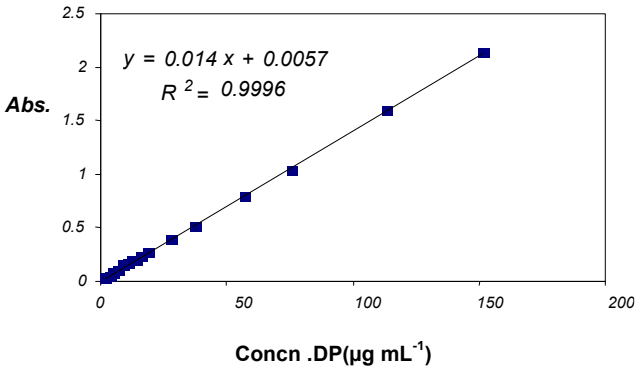

Fig.4. calibration curve for Dopamine

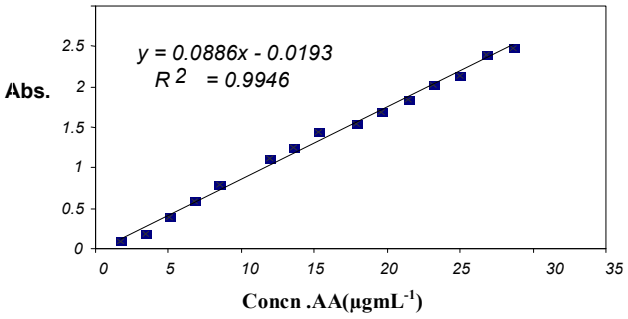

Fig.5. calibration curve for ascorbic acid

3.4. The optimal parameters

Several methods are available to obtain the important factors. One of these methods is cross-validation method.PRESS indicates the model's ability to predict the concentration samples.For the second time was a

factor all over again and the process is repeated n times PLS algorithm is implemented by a factor of 2.PRESS amounts so as to apply a factor equal to the total number of standards continue (Figs.6, 7).

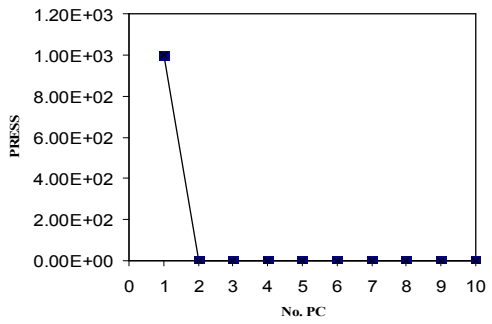

Fig.6. PRESS graph based on the factors in prediction of dopamine concentrations.

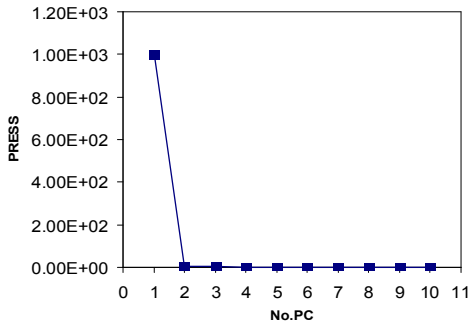

Fig.7. PRESS graph based on the factors in prediction of ascorbic acid concentrations.

3.5. Determination of Dopamine and Ascorbic Acid in real samples

Using the model created by PLS, it applied to real samples. Table 1 shows the results of PLS model in some real sample such as serum, urine and plasma .The results obtained PLS models able to predict the concentrations of dopamine and ascorbic acid recovery in the range of 93.45% to% is 111.1 in real samples.

Table 1.Application of presented method to tablet samples.

Ascorbic Acid (*μ*g/mL)			Dopamine (*μ*g/mL)			number solution	real samples
% Recovery	**found**	**added**	**% Recovery**	**found**	**added**		
102.32	8.71	8.51	111.10	2.00	1.80	1	**serum**
102.94	14.00	13.66	105.55	1.92	1.80	2	
93.45	20.00	21.42	103.70	39.00	37.80	3	
105.88	1.82	1.74	105.50	1.95	1.80	4	**Plasma**
98.13	21.00	21.44	111.10	2.00	1.80	5	
101.39	19.60	28.16	96.56	37.01	37.80	6	
94.11	1.60	1.75	97.77	37	37.80	7	**Urine**
105.88	9.00	8.55	101.85	38.54	37.80	8	
96.32	13.12	13.66	103.17	39.0	37.80	9	

4. Conclusion

The main purpose of this study was the measurement of ascorbic acid and dopamine in the standard samples and real-time such as plasma, serum and urinary tract. Therefore, due to the two overlapping spectral data PLS good ability to separate analyte spectra overlap and predicted concentrations of synthetic and real.This method compared to other methods such as chromatography and electrochemistry, easier, cheaper and better selectivity. So we can PLS as a potential method to measure species used in real samples, particularly clinical.

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