SPECTRAL SIMULTANEOUS DETERMINATION OF TARTRAZINE, ALLURA RED, SUNSET YELLOW AND CARAMEL IN DRINK SAMPLE BY CHEMOMETRIC METHOD

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ABSTRACT

The simultaneous determination of tartrazine, allura red, sunset yellow and caramel in quarternary mixtures and commercial preparation were performed by using the chemometric calibrations based on the use of UV-VIS spectra. The data obtained from experiments were processed by chemometric approaches, such as principal component regression (PCR). The absorbance data in the UV-Vis spectra were measured at 16 wavelenghth points in the UV-VIS spectra range 250-550 nm.. The proposed methods were validated by using synthetic ternary mixtures and applied to simultaneous determination of four colorants in drink.

Keywords: Sunset Yellow, tartrazine, allura red, caramel, principal component regression, chemometric approaches

INTRODUCTION

Food colorants may often be considered simply cosmetic in nature, but their role in the food industry is actually very significant. Colour is the first sensory quality which foods are judger and food quality and flavour are closely associated with colour. Consumers are conditioned to expect foods in certain colours and to reject any deviation from their expectations. The physchological basis for the need of food colours is established 1.

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Generally, spectrophotometry is used for determining these colorants and a prior separation is almost always involved, for these are a serious spectral overlap. The procedure of chemical separation is usually time consuming and often unsuccessful. An analysis that requires little or no separation is far more appealing. In order to avoid time-consuming clean-up procedures, attempts to resolve complex spectra by using instrumental approaches or various chemometric methods have been made 2.

The application of quantitative chemometric methods, particularly principal component regression (PCR) and partial least squares (PLS) to multivariate spectral data are used to determine the component concentration from the sample spectrum 3.

The basic concept of PLS regression was originally developed by Wold 4,5 and the use of the PLS method for chemical analysis in the analytical applications was also pioneered by Wold and co-workers 6.

In analytical chemistry, the wavelet transform method has been used in combination with other calibration techniques such as partial least squares (PLS) for the quantitative determination of active compounds in samples 7.

Among computer-controlled instruments, derivative techniques and multivariate calibration methods are playing a very important role in the multicomponent analysis of mixtures by Ultraviolet-visible molecular absorption spectrophotometry 8.

The aim of this work is to develop simple and accurate spectrophotometric methods for the simultaneous determination of tartrazine, allura red, sunset yellow and caramel in four-component mixture without the need for prior separation. The developed methods was applied to determine the amounts of four colorants in commercial drink sample. . The structure of the synthetic food colorants were shown Figure 1.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Analytical reagent grade chemicals were used, unless otherwise indicated. Tartrazine, allura red, sunset yellow and caramel are synthetic food colorants. Commercial product is a drink (Blood orange).

Stock solution of the food colorants, 10 mg/100 mL of each, were prepared in deionize water. Absorbance measurements were carried out by using

Pharma 1700 Spectrophotometer /SHIMADZU. UV-Vis spectrophotometer interfaced to an IBMSX-486 microcomputer for the spectral acquisition provided with a software . The absorbance measurements were carried out in two matchşng quartz 1.0 cm cells with a 1 mm path length.

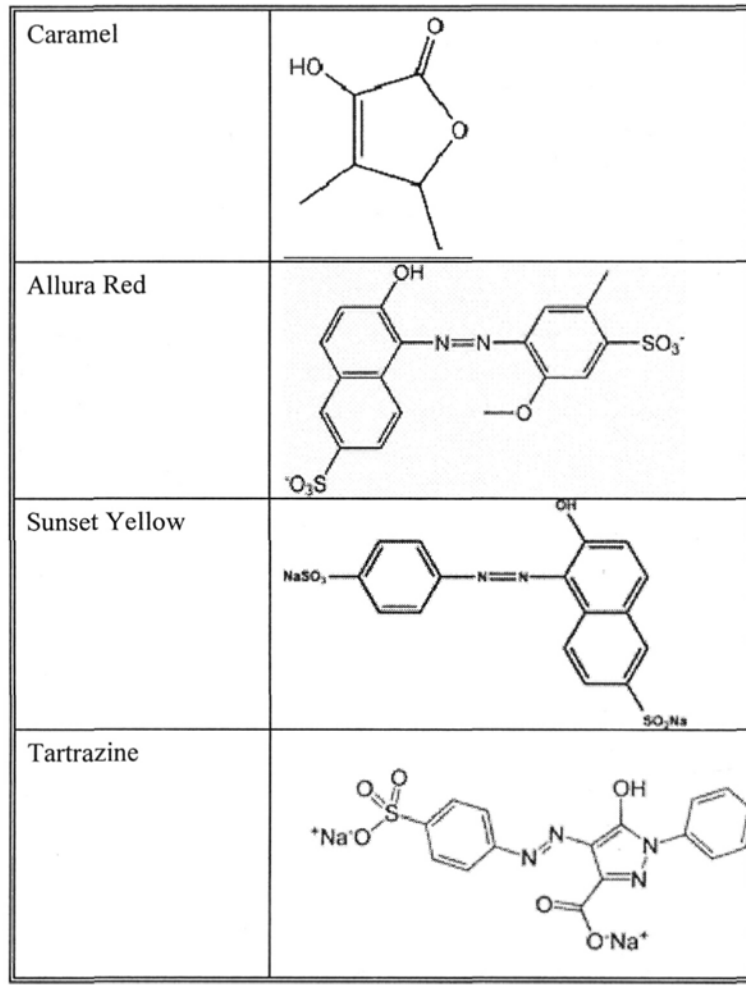

Fig. 1: Structural formula of studied synthetic food colorants.

2.2. Absorbance Measurements

The absorption spectra were recorded between 250 and 550 nm with an interval of 0.1 nm between each two point and were contrasted with corresponding blanks. The spectra were giving 6100 experimental points for each spectrum. The calibration matrix was prepared 16 solutions containing mixtures of four components in different ratios and optimized and calculated by using PCR calibration , both to analyze the spectra obtained and to calculate the concentration of the analytes in the real samples. Additional softwares Panorama (LabCognition) was used for all the treatment of the absorbance-concentration data and the statistical calculations.

3. PROCEDURES

An aliquat of sample containing between 0,4 and 16 (μg/mg) of the colorants (alone or in mixtures) was placed in a 25 mL volumetric flask and deionize water was added. The mixture was shaken for 20 min and packed in a 1 nm cell. Blanks were prepared in the same way as described for the standards and contained all the reagents except the colorants.

3.1. Procedure for real sample:

For this purpose, an amount volume to 20 mL samples in drink (commercial product, Blood Orange). The sample was transferred to 25 mL calibrated flask and dissolved in water mechanically.

3.2. Principal Component Regression:

In the spectral work, the following steps were applied to the fundamental concept pf PCR :

The original data obtained in absorbance (A) and concentrations (C) of analytes were reprocessed by mean-centering as Ao and Co , respectively.
The covariance dispersion matrix of the centered matrix Ao was computed. The normalized eigenvalues and eigenvectors were calculated starting from square covariance matrix. The number of the optimal principal components (eigenvectors) is selected by considering only the highest values of the eigenvalues. The other eigenvalues and their corresponding eigenvectors are

eliminated from our study.Using the ordinary linear regression C=a + b x A , we calculated the coefficients a and b. To reach this objective firstly we determined the coefficient b as b= P x q, where P is the matrix of eigenvectors and q is the C-loadings given by q=D x TT x Ao. Here TT is the transpose of the score matrix T. D is a diagonal matrix having on the components the inverse of the selected eigenvalues. Knowing b we can easily find a by using the formula a= C mean – A mean x b, where AT mean represents transpose of the matrix having the entries the mean absorbances values and C mean is the mean concentration of the calibration set . The algorithm described here permitted us to calculate the amount of analyte in sample by using equation, C = a + b x A.

4. RESULTS AND DISCUSSION

The colorants used in this study are chemically related compounds. Figure1. show the absorbance-wavelenght curves of these colorants.

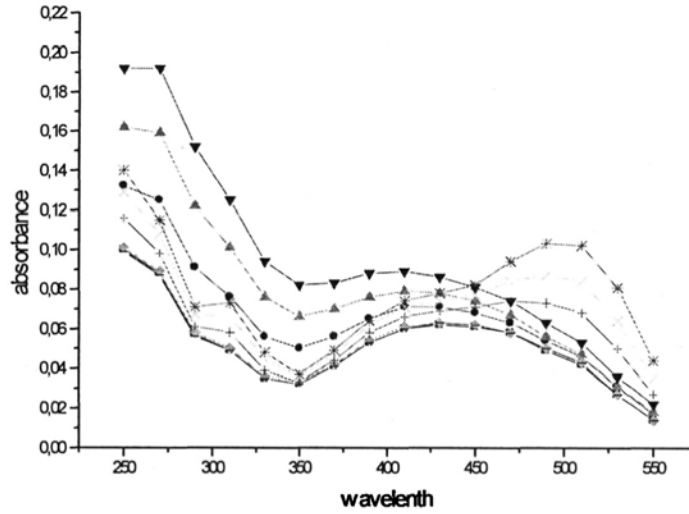

Fig. 2: UV-VIS spectra of tartrazine, allura red, sunset yellow and caramel in deionize water.

It is obvious that spectra of these four colorants are overlapped seriously Fig.1. indicates the absorption spectra absorption spectra of food colorants in the spectral region 250-550. The determination of colorants in the mixtures is

not possible by traditional spectrophotometric method, due to the interference of the spectra of these colorants for the different concentration ratios. The obtained results of this method were compared with those obtained by two numerical methods.

In the MLR and PCR methods, the training set was randomly prepared by using 16 ternary mixture solutions. The absorbance data were obtained by measuring the absorbance values at 16-wavelength set with interval of $\Delta\lambda$: 20 nm in the spectral range of 250 and 550 nm as shown Fig.1.

By using the PCR algorithm and by using the optimum number of factors calculated in the cross-validation process for four colorants, the following equations were obtained;

Ccaramel = 5,86 - 218 A1 + 10,2 A2 - 569 A3 + 909 A4 + 782 A5 - 186 A6 - 1313 A7 + 1660 A8 + 84.0 A9 - 1024 A10 + 428 A11 - 212 A12 + 383 A13 - 611 A14 + 213 A15

Callura red = - 2,75 + 127 A1 + 150 A2 + 144 A3 - 411 A4 - 290 A5 + 67,7 A6 + 505 A7 - 959 A8 + 158 A9 + 413 A10 - 191 A11+ 30,7 A12 - 88,1 A13 + 280 A14 - 134 A15

Csunset yellow = 2,18 - 136 A1 - 44.4 A2 - 25,4 A3 + 27,9 A4 + 274 A5- 19,1 A6 - 90,9 A7 + 331 A8 + 46.2 A9 - 283 A10 + 28,5 A11 + 88.7 A12 + 157 A13 - 255 A14 + 98,0 A15

Ctartrazine = - 12,8 + 819 A1+ 64,5 A2 - 397 A3 + 500 A4 - 1342 A5 - 106 A6 + 836 A7 - 1272 A8 - 77,0 A9 + 678 A10 - 30,0 A11 - 534 A12 - 488 A13 + 961 A14 - 561 A15

Where Ccaramel, Callura red, Csunset yellow, Ctartrazine are the concentration of food colorants, respectively. The absorbance values measured at fifteen point for the samples were introduces into the above equations. As a result, the concentration of each colorant in drink sample was succesfully determined.

Commercial product analysis

The experimental results (μg/mg) of PCR to commercial product in this work shown in table3. We observed that the results obtained in these methods are very close to each other.

Table 2
Recovery results of synthetic mixtures by the proposed methods.

Karamel		PCR		Allura Red		PCR		
NO	ACTUAL	PREDICTION	R%	NO	ACTUAL	PREDICTION	R%	
1	4,0000	4,2444	106,11	1	0,4000	0,4002	100,05	
2	8,0000	8,0619	100,7738	2	0,4000	0,3996	99,9	
3	12,0000	12,0638	100,5317	3	0,4000	0,3919	97,975	
4	16,0000	15,9784	99,865	4	0,4000	0,4075	101,875	
5	4,0000	4,0599	101,4975	5	0,4000	0,3975	99,375	
6	4,0000	3,9953	99,8825	6	0,8000	0,8057	100,7125	
7	4,0000	3,956	98,9	7	1,2000	1,1764	98,03333	
8	4,0000	3,8706	96,765	8	1,6000	1,5636	97,725	
9	4,0000	3,9289	98,2225	9	0,4000	0,3817	95,425	
10	4,0000	3,9239	98,0975	10	0,4000	0,4031	100,775	
11	4,0000	4,0541	101,3525	11	0,4000	0,391	97,75	
12	4,0000	4,0212	100,53	12	0,4000	0,3995	99,875	
13	4,0000	3,9679	99,1975	13	0,4000	0,3737	93,425	
14	4,0000	4,0921	102,3025	14	0,4000	0,4042	101,05	
15	4,0000	3,9721	99,3025	15	0,4000	0,3965	99,125	
16	4,0000	3,9094	97,735	16	0,4000	0,397	99,25	

Table 2. Cont'd:

Sunset Yellow		PCR		Tartrazine		PCR	
NO	ACTUAL	PREDICTION	R%	NO	ACTUAL	PREDICTION	R%
1	0,4000	0,3735	93,375	1	0,8000	0,8018	100,225
2	0,4000	0,396	99	2	0,8000	0,8011	100,1375
3	0,4000	0,3984	99,6	3	0,8000	0,7909	98,8625
4	0,4000	0,4005	100,125	4	0,8000	0,7929	99,1125
5	0,4000	0,3832	95,8	5	0,8000	0,7844	98,05
6	0,4000	0,3908	97,7	6	0,8000	0,7993	99,9125
7	0,4000	0,4067	101,675	7	0,8000	0,8348	104,35
8	0,4000	0,3964	99,1	8	0,8000	0,7949	99,3625
9	0,4000	0,4089	102,225	9	0,8000	0,7551	94,3875
10	0,8000	0,7871	98,3875	10	0,8000	0,7981	99,7625
11	1,2000	1,2088	100,7333	11	0,8000	0,8047	100,5875
12	1,6000	1,5872	99,2	12	0,8000	0,799	99,875
13	0,4000	0,3763	94,075	13	0,8000	0,7936	99,2
14	0,4000	0,374	93,5	14	1,6000	1,5887	99,29375
15	0,4000	0,3987	99,675	15	2,4000	2,4687	102,8625
16	0,4000	0,3933	98,325	16	3,2000	3,2	100

Table 3.
Experimental results of the drink sample by two methods.

	Caramel	S.Yellow	A.Red	Tartrazine
PCR	130,78	44,65	48	12,9

5. CONCLUSIONS

In this investigation,the plot of predicted concentration of colorants vs. actual colorants (for example: allura red) shown in figure3. The fit of data to a straight line (with a r2:0,9978) confirms the excellent predictive ability of the plot used in this study. Meanwhile, the correlation coefficients of such plots for individual colorants. Emphasize the high linear relationship between the predicted and the actual concentration.

Mean recoveries for PCR were found between 90,3 %- 100,%. For all points, low prediction errors and high correlations coefficients emphasize the high linear relationship between the predicted and actual concentrations. The results obtained with this ternary mixture and some ratios of component concentrations show excellent predictive ability of this methods.

6. REFERENCES

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