Notes

Simultaneous Determination of Colorant Mixtures Used in Cosmetics by Partial Least-Squares Multivariate Calibration Spectrophotometry

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Quinoline Yellow (C.I. 47005), Sunset Yellow (C.I. 15958), Tartrazine (C.I. 19140) and Brilliant Blue FCF (C.I. 42090) are four synthetic colorant matters widely used as additives in cosmetic products. Quinoline Yellow (QY) E-104 is a colorant approved by the European Union for use in cosmetics, except in the area around the eyes.[1] Sunset Yellow (SY) E-110 is an azo dye to which some people have an allergic reaction.[2] Tartrazine (TT) E-102 is a synthetic product that can produce urticaria, asthma, a running nose and other discomfort in susceptible individuals.[3] Finally, Brilliant Blue FCF (BB) E-133 is a synthetic dye under consideration by the E.U. for an "E" prefix. Due to such difficulties in using these additives, only small amounts can be used in the manufacturing of cosmetic products[4] and analyses are needed.

The analytical techniques that have been used for the analysis of these chemicals are mainly the following: differential pulse voltammetry with a solid electrode or with a dropping mercury electrode[5–7], liquid chromatography[8], high-performance liquid chromatography[9] and UV-spectrophotometry.[10,11] The main obstacle in the spectrophotometric determination of mixtures of these colorants is the overlapping of their spectra. However, in recent years complex mixtures of chemicals with similar spectral characteristics have been resolved by applying multivariate analysis methods of partial least-squares (PLS), originally proposed by Wold.[12] PLS methods have been applied to the determination of mixtures of flavour enhancers in foods[13] or aromatic aldehydes in biological samples[14] among other applications.

Since the four colorants studied here show similar chemical structures, they present a high spectral overlapping, and their simultaneous determination is hard when conventional methods are used. Hence, we propose the utilization of the PLS statistical method for treating of the analytical signal and absorbance, and to resolve quaternary, ternary, binary mixtures and single determinations of the above-cited colorants.

In general, a multivariate calibration model is constructed from instrumental response data collected for a set of multicomponent samples of known concentrations with respect to the analytes of interest. In these cases we used partial least-squares regression, PLS. This method is based on the concentration of the total information of a response matrix in the fewest number of new variables, called principal components or factors, which can describe the significant information contained in multivariate data, such as the spectra, kinetics and chromatographic peaks. Its main difference with other multivariate calibration methods, as a principal-component regression (PCR), is that PCR uses only information of the response matrix and PLS uses the response matrix and the concentration matrix for calibration in order to define which dominant factors in the response data are most relevant to the concentration of the components. The orthogonality of the principal components is lost in the PLS model. Two forms of the algorithm exist, namely, PLS-1 and PLS-2. The former calibrates each analytes individually, while the latter can model a number of components simultaneously.

In this work, since PLS-1 provided the most accurate predictions, it was applied in the proposed method for determining these colorants in commercial cosmetic products as colognes, facial tonics, deodorants, after shave lotions, bath gels, bath salts and shampoos. In all cases the obtained results are satisfactory.

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Experimental

Apparatus and software

A Perkin-Elmer Lambda 2 spectrophotometer (with a 10-mm cell) interfaced with an IBM SX-486 microcomputer for spectral acquisition and subsequent manipulation of the data was used to perform the absorbance measurements.

A Crison 501 digital pH-meter with saturated calomel and glass electrodes and an Agitaser 2000 rotating agitator were also used.

The GRAMS-386 level I version 1.0 software package[15] with PLS plus version 2.1 G applications software, was used for a statistical treatment of the data and applications of the PLS methods.

Reagents

Quinoline Yellow water soluble (Aldrich Chemie) (100 μg/ml), Sunset Yellow (Utter Laboratorios España S.L.) (100 μg/ml), Tartrazine (Utter Laboratorios España S.L.) (100 μg/ml) and Brilliant Blue FCF (Aldrich Chemie) (50 μg/ml) stock solutions were prepared by exact weighing of the standards and subsequent solution in water. These solutions were stable for at least one month. Working solutions were prepared from stock solutions diluted by reverse-osmosis water in all instances. All of the solvents and reagents were at least of analytical grade, and reverse-osmosis water was used.

Absorbance measurements

The absorption spectra of standard solutions of the colorants against ethanol were recorded at between 400 and 800 nm every 0.5 nm, with a scan speed of 480 nm/min, and were stored in a disk file. The absorbance of colorant species was measured in a 10-mm cell showing the following maxima wavelengths: 416.5 nm for QY, 485 nm for SY, 430 nm for TT and 629 nm for BB (Fig. 1).

Procedures

Procedure for standards. To an aliquot of a sample containing between 25.0 and 500.0 μg of QY, 25.0 and 200.0 μg of SY, 25.0 and 600.0 μg of TT and 25.0 and 200.0 μg of BB placed in a 50-ml calibrated flask, appropriate volumes of water and ethanol were added to make the mark, ensuring in all cases 70%(v/v) of ethanol. Then, 20 ml of this solution was transferred into a 100-ml separatory funnel and 16 ml of CH_2Cl_2 was added. The mixture was shaken for 1 min and the hydroalcoholic phase containing the colorants was transferred into a 10-ml calibrated flask, making the mark with ethanol. Absorbance measurements were performed against ethanol and the spectra were stored on a disk file.

Procedure for real samples.

Colognes: An aliquot, typically 20 ml, is taken and the procedure for standards is applied.

Bath salts: A weighed amount is dissolved in a medium of ethanol/water 70/30 (v/v). An aliquot, typically 20 ml, of this solution is taken in order to apply the procedure for standards.

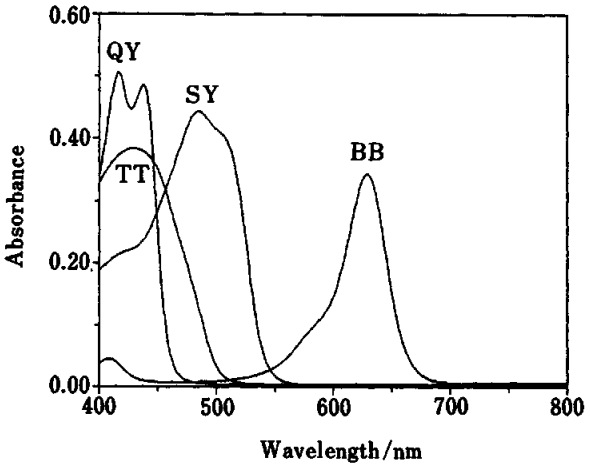

Fig. 1 Absorption spectra of Quinoline Yellow, Sunset Yellow, Tartrazine (5 μg/ml) and Brilliant Blue FCF (2 μg/ml) in the hydroalcoholic phase.

After shaves, deodorandts and facial tonics: An aliquot is taken to make a medium of ethanol/water 70/30 (v/v). An aliquot, typically 20 ml, of this solution is taken to apply the procedure for standards.

Bath gels and shampoos: After a weighed amount is dissolved in water, an aliquot of this solution is taken to make a medium of ethanol/water 70/30 (v/v). An aliquot, typically 20 ml, is taken in order to apply the procedure for standards.

Results and Discussion

Calibration and selection of the number of factors

A training set of 26 standard samples was taken from different quaternary and ternary mixtures (Table 1) randomly selected to span the concentration range expected in a real sample. The PLS model was developed in the PLS-1 mode using the spectral region between 400 and 700 nm, which implies working with 601 experimental points per spectrum, because this is the zone with the maximun spectral information for the components of the mixture.

The optimum number of factors selected for PLS-1 was nine for QY, four for SY and TT and five for BB.

The number of factors selected for QY using the criterion of Haaland and Thomas[16,17] was nine, higher than expected, with the four first factors containing the largest variability (Fig. 2). In spite of this, because a calibration matrix with four factors for QY led to worse results in the prediction of synthetic samples (both QY and BB), the nine-factors matrix was chosen.

Statistical parameters

The values of the root-mean-square difference RMSD (CV), which is an estimate of the absolute error in a

Table 1 Concentration (μg/ml) data for the different mixtures used in the calibration set

Standard	QY	TT	SY	BB
1	5.0	0.0	12.0	2.0
2	9.0	0.0	5.0	0.5
3	0.0	2.0	10.0	2.0
4	3.0	5.0	0.0	3.0
5	10.0	4.0	3.0	0.0
6	2.0	7.0	5.0	0.0
7	7.0	5.0	6.0	0.5
8	8.0	7.0	3.0	1.0
9	7.0	2.0	10.0	1.0
10	8.0	4.0	7.0	0.5
11	7.0	3.0	8.0	1.0
12	5.0	5.0	6.0	1.0
13	7.0	8.0	3.0	1.0
14	0.5	5.0	7.0	1.5
15	5.0	0.5	5.0	1.5
16	5.0	1.0	10.0	1.5
17	5.0	5.0	7.0	2.0
18	5.0	5.0	0.5	2.0
19	5.0	6.0	0.5	2.0
20	0.5	3.0	5.0	2.5
21	3.0	6.0	0.0	2.5
22	0.0	3.0	8.0	2.5
23	3.0	4.0	7.0	3.0
24	2.0	7.0	3.0	3.0
25	1.0	3.0	6.0	0.0
26	1.0	0.0	10.0	4.0

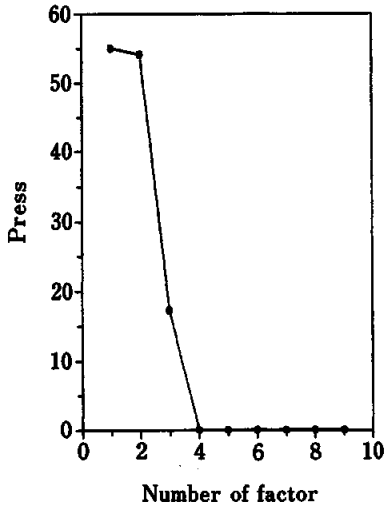

Fig. 2 PRESS plot for Quinoline Yellow by applying the PLS-1 method.

prediction by cross-validation for each component in the calibration matrix, are summarized in Table 2. The squared correlation coefficients (R^2), obtained when plots of actual *versus* predicted concentration were constructed (the mean spectral residuals values (MSR)), are also included in Table 2.

Table 2 Statistical parameters obtained by application of the PLS method

Component	Factor	RMSD (CV)	R^2
QY	9	0.041879	0.9998
TT	4	0.033781	0.9998
SY	4	0.084718	0.9993
BB	5	0.018516	0.9997

Table 3 Determination of QY, TT, SY and BB in cosmetic products

Cosmetic products	Dye/μg ml^{-1}			
	QY	TT	SY	BB
Cologne 1	1.12			
Cologne 2		5.66		
Cologne 3				1.34
Cologne 4		4.90		0.60
Cologne 5		8.80[b]	7.52[b]	
Bath salt		238[a]		
After shave				8.50
Bath gel 1			8.50[a,b]	
Bath gel 2	4.17[a]			1.52[a]
Shampoo 1	17.0[a]			1.74[a]
Shampoo 2		9.80[a]	5.58[a]	
Deodorant		3.24		0.68
Facial tonic		1.20		0.53

a. mg/kg. b. Standard addition.

Table 4 Recovery study in real samples

Cosmetic product	Dye (%recovery)			
	QY[a]	TT[a]	SY[a]	BB[b]
Cologne 2	105.0		99.0	101.0
Afther shave	105.0	107.0	107.0	
Shampoo 1		106.0	99.0	
Shampoo 2	108.0			94.0
Facial tonic	107.0		102.0	

a. 5.0 μg/ml. b. 2.5 μg/ml.

Applications

Applications to real samples. Previous to a determination of the colorants in commercial cosmetic samples its identification was carried out by thin-layer chromatography.[18]

Afterwards, the optimized PLS-1 model was applied to the analyses of samples of cosmetics containing one or more of these chemicals. In order to test the accuracy of the method in real samples these samples were spiked with diverse amounts of colorants not present in the initial product. The percentage of recovery founded is given in Table 3. Cosmetic samples were analyzed using in each case five replicates. Table 4 shows the results obtained for the colorants present in real samples.

As shown in Table 4, the degree of precision for the cosmetic samples in those cases in which the sample were spiked with analyte was found to be satisfactory, with a percentage of recovery of between 91.0 and 108.0% in all instances.

On the other hand, the proposed method can be applied to a simultaneous determination of these four colorants in some cosmetic products (eau de toilette), recording their spectra after a clean-up of the colorants with Cl_2CH_2.

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