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IDENTIFICATION OF VEGETABLE OIL ADULTERANTS IN SUNFLOWER OIL THROUGH DISCRIMINANT ANALYSIS OF COLORIMETRIC PARAMETERS

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Abstract

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Mathematical discriminant analysis was applied to mixtures of sunflower oil and cottonseed or rapeseed oil and the differences in the color parameters and the content of pigments such as chlorophyll and beta carotene were demonstrated. The method suggested aimed at supporting quality control towards and easy and non-destructive determination of sunflower oil adulteration with vegetable oils. The significance of individual indices for the modeling was evaluated. The models were tested with results from other independent samples.

Key words: color parameters, sunflower oil, cottonseed oil, rapeseed oil, mahalanobis distances, canonical analysis

Introduction

The need for fast and efficient methods of food quality control has grown considerably in recent years (Ivanova and Milkova-Tomova, 2012; Milkova-Tomova and Ivanova, 2012). The increasing adulteration of olive oil and sunflower oil with cheaper vegetable oils has necessitated the use of discriminatory analysis for the discovery of differences between groups of natural oils and of adulterant-containing oils.

The objective of this paper was to analyze a database of colorimetric parameters and pigment content in mixtures of sunflower oil and rapeseed or cottonseed oil. To this end, the following issues needed to be addressed:

i) Choice of suitable sunflower oil samples, preparation of model systems containing rapeseed or cottonseed oil adulterants in concentrations between 10% and 50%, and database accumulation because of colorimetric analysis.

ii) Establishment of statistically significant differences between the indices of oil groups with different adulterant content and development of suitable models describing their characteristics.

Materials and Methods

Three commercially available vegetable oils have been investigated: sunflower oil, rapeseed oil, cotton oil correspondingly from Bulgaria, France and Turkey. Two systems of model mixtures from sunflower and rapeseed oil and form sunflower and cotton oil were prepared. Four measurements of the contents of pigments and color parameter were performed for each of the systems.

The samples were poured in 10 mm-wide cuvettes. The color parameters (index of lightness L^*, b^* and a^*) corresponding to the uniform color space CIELab (Commission Internationale de I Elairage Recommendations on uniform color spaces, 1978) are determinated by Lovibond PFX 880. It has been used for determining the beta carotene and chlorophyl content in the sunflower oil and its double mixtures with rapeseed oil and cotton oil. The specified colorimetric system has been selected and used because it is more suitable for working with pigments because it is simpler to use in practice and gives a very good assessment of the resulting colors obtained by mixing pigments.

The "Statistics" software has been used for the treatment of data. The distribution was found to be Gaussian by the Kolmogorov-Smirnov criterion (Geoffrey and McLachlan, 1992; Vandeginste et al., 1998)

For each of the model systems were formed groups with varying component of the contents of an admixture of rapeseed or cotton oil. The group of applied statistics and con-

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sultations with the Technical University of Berlin performed statistical processing of data. The “Statistics” software was used to establish the type of distribution of the indicators, dispersion and discriminatory analysis with a priori equal probabilities of falling into each group. The relations between the groups were précised using the mahalonobis distances.

Results and Discussion

Data were obtained after colorimetric analysis of double sunflower/rapeseed oil mixtures with admixture content from 10% to 50%. For this purpose, model systems were investigated. The color parameters (*x*. *y*) in the colorimetric systems XYZ index of lightness *L** and color parameters (*a**. *b**) corresponding to the uniform color space CIELab were analyzed. The basic statistical characteristics of the parameters studied were obtained. The results are presented in Table 1.

The values from the dispersion analysis are shown in Table 1. These show that there are statistically meaningful differences in the parameters considered. Using Tukey’s criterion for multiple comparisons it is found where these differences are which is sufficient for modelin.

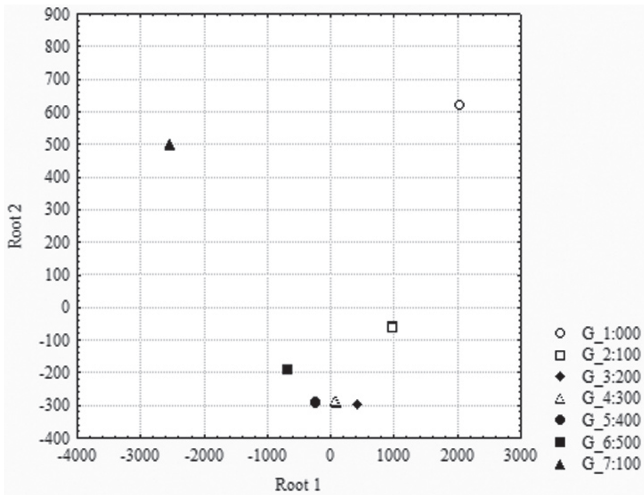
After application of a systematic analysis with grouping variable “rapeseed admixture content” discriminant functions guaranteeing 100% of recognition were obtained. The indices used in the modeling in the order of their inclusion in the model, were: color coordinate y, color coordinates X, Y, Z, index of lightness *L**, chlorophyll and beta carotene.

The mahalanobis distances were calculated. As evident from the data in Table 2, the degree of statistically significant differences for the various groups can be evaluated.

Canonical analysis was performed for a better illustration of the results obtained. The results are shown in Figure 1.

Table 2
The mahalanobis distances for sunflower oil and rapeseed oil samples

№	C, % Rapeseed oil	Percentage of rapeseed oil						
		0	10	20	30	40	50	100
1	0	0						
2	10	1.9	0					
3	20	4.2	4.6	0				
4	30	5.6	1.0	0.1	0			
5	40	7.3	1.9	0.5	0.1	0		
6	50	9.8	3.6	1.7	0.9	0.4	0	
7	100	25.1	15.2	11.2	9.0	7.0	4.8	0



1-0% rapeseed oil; 2-10% rapeseed oil; 3-20% rapeseed oil; 4-30% rapeseed oil; 5-40% rapeseed oil; 6-50% rapeseed oil; 7-100% rapeseed oil

Fig. 1. Object grouping by rapeseed oil percentage in the sunflower oil

Table 1
Basic statistical characteristics for the sunflower oil group with rapeseed oil admixture

Rapseed	0%		10%		20%		30%		40%		50%		100%		p
	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	
x	0.3208	0.0006	0.3806	0.0004	0.4152	0.0008	0.4329	0.0006	0.4488	0.0003	0.4580	0.0003	0.4752	0.0002	.000
y	0.3335	0.0004	0.4172	0.0003	0.4636	0.0015	0.4835	0.0004	0.5011	0.0009	0.5064	0.0005	0.5103	0.0003	.000
X	85.4217	0.0214	77.2933	0.0388	72.9733	0.0602	69.7850	0.0308	68.2933	0.0450	55.0317	0.0826	64.5867	0.0163	.000
Y	88.9150	0.0187	84.9800	0.0908	81.9883	0.0621	77.5750	0.0464	76.2583	0.0538	60.8233	0.0878	69.3000	0.0141	.000
Z	92.4250	0.0187	41.2750	0.1559	20.1933	0.0609	13.7967	0.0761	8.1567	0.0535	4.4350	0.0423	2.0133	0.0450	.000
L*	95.5300	0.0268	93.7383	0.0325	92.6883	0.0240	90.6833	0.0197	90.0367	0.0121	82.3317	0.0475	86.6633	0.0497	.000
a*	-3.092	0.0402	-11.062	0.0117	-13.648	0.0371	-13.620	0.0228	-13.408	0.0133	-11.088	0.0098	-7.278	0.0483	.000
b*	7.9450	0.0281	48.4083	0.0306	72.3550	0.0339	86.3233	0.0207	100.6667	0.8017	102.8467	0.8585	125.7917	0.0508	.000
Chlorofil	0.0083	0.0075	0.1695	0.0085	0.3005	0.0188	0.4083	0.0098	0.5077	0.0043	0.6078	0.0143	9.4645	0.0541	.000
Carotene	2.2733	0.0650	15.4000	0.0518	25.5750	0.0464	34.1517	0.0581	43.7717	0.0500	53.2633	0.0216	134.9017	0.0840	.000

With the increase in the rapeseed oil in the samples, the cholorophyll and beta-carotene sharply increased, which evidently influenced the color parameters. The green component in the mixtures under consideration increased ($a^*\leq 0$). Some of the dependencies of the considered parameters vs. the rapeseed admixture content are shown in Figure 2.

A similar study was performed to distinguish sunflower oil samples containing cottonseed oil from natural sunflower oil samples. As a result of a statistical analysis, the basic statistical characteristics of the analyzed parameters were obtained. The results are presented in Table 3.

After application of a systematic discriminate analysis with grouping variable "concentration of admixture of cottonseed oil", discriminant functions guaranteeing 100% recognition were found. The indices included in the modeling were the color coordinates *Y*, *Z*, lightness *L** and color parameter *a**, *b** in the CIELab colorimetric system, chlorophyll and beta-carotene. In this group color parameters characterizing small color differences in the mixtures participated in the model. whereas in the sunflower oil/rapeseed oil group the color parameters of the XYZ colorimetric system intended for more significant color differences between samples were predominant. The mahalanobis distances between the centroids of individual samples were obtained. Their values are presented in Table 4. All distances guarantee sample recognition. The model was tested with values of the specified parameters of a sunflower oil sample, which did not participate in the modeling. The sample was classified into the pure oil group of the model oil/cottonseed oil mixtures. The results were illustrated by a canonical analysis. The object grouping is shown in Figure 3.

For each of the sample groups (sunflower oil and rapeseed oil, or sunflower oil and cottonseed oil) the mahalanobis dis-

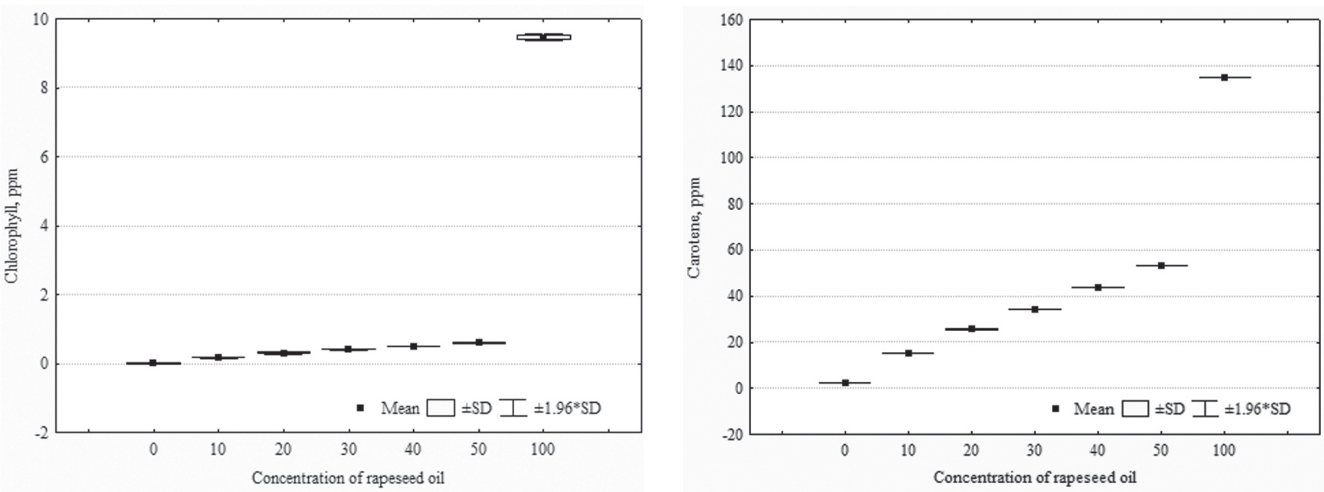


Fig. 2. Dependencies between some of the parameters and the rapeseed oil concentrations

Table 3
Basic statistical characteristics for the sunflower oil group with cottonseed oil admixtures

Cotton	0%		10%		20%		30%		40%		50%		p
	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	Mean	St. D	
x	0.3224	0.0001	0.3272	0.0007	0.3332	0.0004	0.3351	0.0003	0.3382	0.0002	0.3414	0.0005	.000
y	0.3356	0.0004	0.3432	0.0025	0.3507	0.0004	0.3534	0.0004	0.3585	0.0014	0.3611	0.0006	.000
X	83.5917	0.0585	82.7500	0.4637	79.9050	0.6718	77.9583	0.4723	69.6200	0.2409	73.4017	0.2596	.000
Y	87.0783	0.0549	86.1050	0.1971	83.8983	0.4922	81.3633	0.4567	73.3900	0.0790	77.4083	0.0488	.000
Z	88.6667	0.0489	83.5633	0.0638	75.5167	0.1067	72.4417	0.0937	62.2717	0.0608	64.0483	0.0970	.000
L*	95.0583	0.2654	94.8917	0.4294	93.2900	0.1778	92.3033	0.4939	88.7200	0.0787	90.5667	0.0175	.000
a*	-3.1983	0.0133	-4.0217	0.1015	-4.7083	0.0343	-5.0583	0.1143	-5.2000	0.1684	-5.3217	0.0847	.000
b*	9.1467	0.0280	12.0950	0.0592	16.0750	0.1077	17.2000	0.0510	18.8367	0.0880	20.5667	0.0446	.000
Chlorofil	0.0135	0.0021	0.0192	0.0023	0.0032	0.0020	0.0043	0.0023	0.0005	0.0008	0.0003	0.0005	.000
Carotene	2.6583	0.0571	3.6150	0.0505	4.8950	0.0274	5.3450	0.0586	6.0833	0.0423	6.6533	0.0826	.000

tances were calculated and canonical analysis was simultaneously performed because mahalanobis distances provide an idea of the specific features of the examined group in the original space, whereas canonical representations are in a bidimensional space. They serve for a better visualization of the particular groups since their canonic variables are linear combinations of the initial physical indices.

Mahalanobis distances represent individual groups better than canonical variables because they give an idea of the dynamics of the change in the distance between the group centroids. Greater differences were observed between the centroids of groups with admixture between 40-50% and natural sunflower oil. They were more essential for cottonseed oil admixtures than for rapeseed oil admixtures.

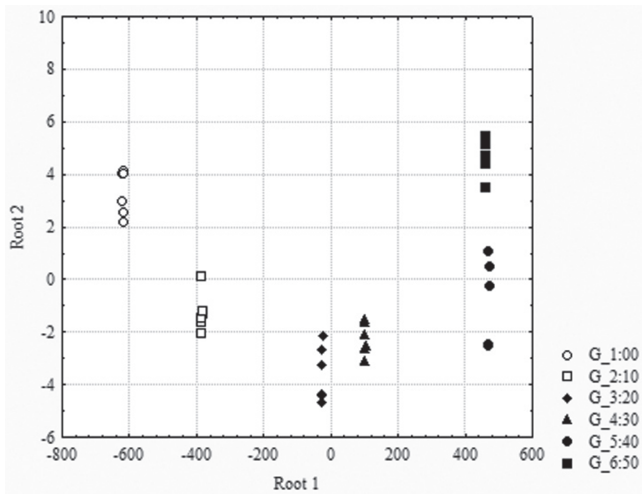
The data in Tables 2 and 4 clearly show a considerable difference in the mahalanobis distances between the groups of sunflower oil and vegetable oil mixtures and natural sunflower oil, which guarantees 100% recognition of admixture presence in a tested sample. It would be more difficult to discern two neighboring groups containing admixtures with a difference up to 10%. Hence, the suggested discriminant analysis can successfully be used to qualitatively discern natural sunflower oil from sunflower oil containing rapeseed and cottonseed oil admixtures.

Table 4
Mahalanobis distances for sunflower oil and cottonseed oil samples

№	C, % Cottonseed oil	Percentage of cotton oil					
		0	10	20	30	40	50
1	0	0					
2	10	0.6	0				
3	20	4.2	1.6	0			
4	30	6.2	2.8	1.2	0		
5	40	14.3	8.8	3.0	1.7	0	
6	50	14	8.6	2.8	1.6	0.02	0

The checking of independent samples is of basic interest. We studied samples with varying rapeseed content in the 0 to 100 % range. The models were used to classify the samples. The results on the corresponding mahalanobis distances to the corresponding groups are presented in Table 5.

It is worth noting that samples containing from 25% to 33% of rapeseed oil were referred to the group of those with 50% rapeseed oil. The two samples with 100% of rapeseed were accurately classified. In studying sample 5, a lack of a characteristic line of rapeseed oil absorption was noticed. As seen in the table, this sample is at the greatest distance from pure rapeseed and closest to pure oil. Sample 6 is at relatively equal distances of 20% and 30% of rapeseed oil, which can be interpreted as the rapeseed percentage in it being within the same limits. Sample 7 is declared as sunflower oil and is accurately classified into the group of 100% oil.



1-0% cottonseed oil; 2-10% cottonseed oil; 3-20% cottonseed oil; 4-30% cottonseed oil; 5-40% cottonseed oil; 6-50% cottonseed oil

Fig. 3. Object grouping by cottonseed oil percentage in the sunflower oil

Table 5
Mahalanobis distances of independent samples

№	Squared Mahalanobis Distances	Percentage of rapeseed oil						
		0%	10%	20%	30%	40%	50%	100%
1	25% rapeseed oil-75% sunflower oil	9.25	3.8	2.07	1.25	0.74	***0.09***	3.55
2	33% rapeseed oil -67% sunflower oil	15.91	9.5	7.16	5.77	4.84	***2.79***	4.06
3	Rapeseed oil sample 1	22.1	13.78	10.34	8.34	6.62	4.5	***0.17***
4	Rapeseed oil sample 2	19.27	11.57	8.47	6.66	5.18	3.12	***0.5***
5	Rapeseed oil sample 3	***0.11***	1.14	2.76	3.75	5.02	6.78	19.06
6	Sunflower oil sample 1	3.7	0.61	***0.2***	0.22	0.52	1.09	8.96
7	Sunflower oil sample	***0.44***	0.84	2.13	2.95	4.05	5.48	17.14

Conclusions

The existence of differences in the values of the investigated parameters was statistically proven. This makes discriminant analysis an efficient tool for the qualitative distinction of natural sunflower oil and adulterated oil containing admixtures from other oils. The models and the associated mahalanobis distances enable the classification of unknown samples.

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