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Detecting admixtures of vegetable oils in sunflower oil using physico-chemical methods

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Systems of sunflower oil containing rapeseed oil or cotton oil were studied. Data on the color characteristics of the specified sample mixtures in CIE *La* b** and XYZ colorimetric systems were obtained. The metric brightness, purity of color and metric angle were determined. Regressive dependencies between the specified parameters and the concentration of rapeseed or cotton oil admixtures were found, which permit the quantitative determination of the admixture content. The qualitative detection of the latter is possible using transmission spectra in the visible region and infrared spectra.

Key words: vegetable oils, infrared spectroscopy, color characteristics, fatty acid composition

INTRODUCTION

In recent years the purity of sunflower oil has become of great importance. There are different methods for identifying admixtures in it. These methods include determining the iodine number, saponification number, density, fatty acid composition (FAC) and viscosimetric measurements [1].

Some authors have used data on the content of fatty acids, triglycerides, tocopherols, etc., for detecting vegetable oil admixtures in sunflower oil and olive oil [2, 3]. However, detecting admixtures by determining their physicochemical characteristics is a difficult process, as the fatty acids found in various oils are almost the same. Most of the analytical techniques for the detection of adulterants rely upon chromatographic methods such as gas and liquid chromatography (GC and HPLC) [4–6]. The latter methods are expensive and time-consuming. That calls for cheaper, faster and simpler methods for detecting admixtures of other vegetable oils in sunflower oil.

The objectives of this study are as follows:

to investigate the potential and efficiency of infrared spectroscopy for detecting vegetable oil admixtures in sunflower oil as a fast, non-destructive and cheap method;

to use the possibilities of colorimetric analysis in the quantitative identification and determination of the admixtures.

MATERIALS AND METHODS

In the experiments commercially available sunflower oil (Bulgaria), cottonseed oil (Turkey) and rapeseed oil (France), as well as mixtures of sunflower oil / cotton oil and sunflower oil / rapeseed oil with concentrations of the admixtures ranging between 10% and 50 % were investigated.

Fatty acid composition of the pure oils (sunflower, rapeseed and cottonseed) was determined by gas chromatography. The total fatty acid composition was determined by GC after transmethylation of the respective sample with 2N methanolic KOH at 50 ºC according to Christie [7]. Fatty acid methyl esters (FAME) were purified by silica gel TLC on 20×20 cm plates covered with 0.2 mm Silica gel 60 G layer (Merck, Darmstadt, Germany) with mobile phase n-hexane:acetone 100:8 (by volume). GC was performed on a HP 5890 (Hewlett Packard GmbH, Austria) gas chromatograph equipped with a 30 m × 0.25 mm (I.D.) capillary InnoWax column (cross-linked PEG, Hewlett Packard GmbH, Austria) and a FID. The column temperature was programmed from 165 ºC to 240 ºC at a rate of 4 ºC/min and held at each value for 10 min; injector and detector temperatures were 260 ºC. Nitrogen was the carrier gas at a flow rate of 0.8 cm^3 /*min*; split was 100:1. Identification was performed by

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comparison of retention times with those of a standard mixture of fatty acids subjected to GC under identical experimental conditions [8].

The specified colorimetric system was selected because of its suitability for working with pigments, simple use and possibility of assessing the resulting colors obtained by mixing pigments. The samples were poured into 10 mm-wide cuvettes. The color parameters (index of lightness L^*, chroma C^* and hue h_{ab}) corresponding to the uniform color space CIELab [9], were determined on a Lovibond PFX 880 device using a standard light source at wavelengths from 420 nm to 710 nm selected by means of 16 narrow-band interference filters. These filters have translucency peaks at every 20 nm but the measuring system was programmed in such a way as to interpolate light at intervals of 5 nm. Lovibond PFX 880 was used for determining the β -carotene and chlorophyll content in the sunflower oil and its double mixtures with rapeseed oil and cotton oil. The device features a special program through which the β -carotene and chlorophyll contents in the product are determined from the readings obtained from the RYBN color scale, designed for determining the color characteristics of transparent products.

Parameters such as chroma (C^*) and hue (h_{ab}) are defined by formulas (1) and (2):

$$C^* = \left[\left(a^*\right)^2 + \left(b^*\right)^2\right]^{1/2}, \quad (1)$$

$$h_{ab} = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

The infrared spectra of sunflower oil and of its double mixtures with 50% content of rapeseed or cotton oil, respectively, were obtained. The spectra were collected using a Nicolet 6700 FTIR spectrometer with a spectral resolution of 2 cm^{-1}, accumulating 32 scans.

To record spectra, approx. 50 μL of the oil was dissolved in 5 % CCl_4. The cuvette used was 4 mm thick and 10 mm wide. The cuvette was carefully cleaned by twice scrubbing with hexane followed by acetone and was dried with a soft tissue before filling with the next sample. The transmission IR spectrum of all diluted standards and oil samples were recorded under the same parameters and background was subtracted from each one. These spectra were recorded as absorbance values at each data point. The spectral reconstruction was carried out in two steps:

-The spectrum of the diluent was subtracted from the spectrum of the diluted oil to eliminate the spectral contributions to measure the dilution factor (r).

-The resulting spectrum was then multiplied by $(1–r)^{-1}$ to correct for dilution as to reconstitute the oil spectrum.

For the sunflower oil and all sample systems, the transmission spectra within the interval from 400 nm to 750 nm were measured on the Lovibond PFX 880 device.

RESULTS AND DISCUSSION

The results for the fatty acid composition of the pure vegetable oils are given in Table 1.

Table 1. Fatty acid composition of sunflower, rapeseed and cottonseed oils

Fatty Acid, %	Sunflower oil	Cottonseed oil	Rapeseed oil
C14:0	-	0.7	-
C16:0	9.7	23.5	5.1
C16:1	0.3	0.6	0.3
C18:0	4.8	2.6	1.9
C18:1	28.2	20.6	66.3
C18:2	56.7	51.0	17.4
C18:3	-	0.3	7.1
C20:0	0.3	0.4	0.7
C20:1	-	-	1.2
C22:0	-	0.3	-

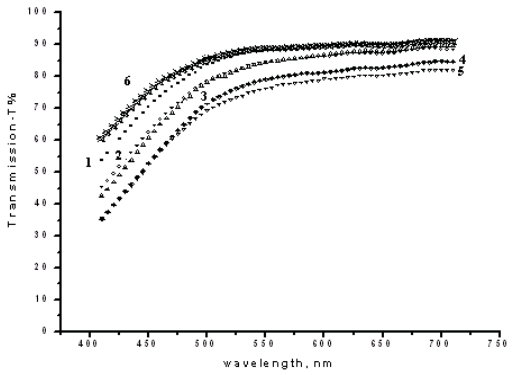

Fig. 1. Transmission spectra of sunflower oil and of its double mixtures with cotton oil. 1-10% cotton oil+90 % sunflower oil; 2–20% cotton oil+80 % sunflower oil; 3–30% cotton oil+70 % sunflower oil; 4-40% cotton oil+60 % sunflower oil; 5-50% cotton oil+50 % sunflower oil; 6- sunflower oil.

The transmission spectra of sunflower oil and of its double mixtures with cotton and rapeseed oil are presented in Figures 1 and 2. The addition of cotton oil to sunflower oil creates turbidity and lowers the product transmittance. The latter is a sign of the presence of an admixture in sunflower oil. It cannot,

however, serve to identify the admixture as cotton oil due to the lack of a characteristic absorption band. It is evident from the graph that the area under the spectrum decreases with the content of cotton oil in the mixture. The linear dependence *Area* = –84.78.C +25656 is found with a correlation coefficient R = 0.9.

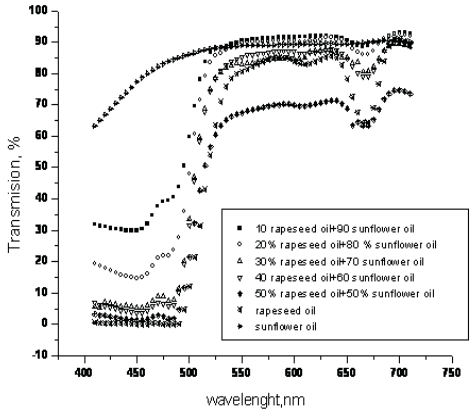

Fig. 2. Transmission spectra of sunflower oil and of its double mixtures with rapeseed oil

The presence of rapeseed oil admixture in sunflower oil, however, can easily be detected on the basis of the translucency spectrum in the visible range. Rapeseed oil has a marked absorption band in the interval from 630 nm to 680 nm, and there is no such band in the sunflower oil. The presence of rapeseed oil admixture up to 10 % results in the appearance of an absorption band typical of rapeseed oil. This fact can be used for the fast and easy detection of rapeseed oil in sunflower oil. In the case of low concentrations (C≤ 20%) of rapeseed oil, transmission abruptly drops in the spectral range from 400 nm to 500 nm. The presence of 10% rapeseed oil in sunflower oil leads to a two-fold decrease in transmission at λ = 420 nm. The characteristic absorption band in the 630 to 680 nm spectral range and the transmission between 15 % and 40 % in the 400 nm to 500 nm range present an opportunity for the identification of small concentrations (below 10%) of rapeseed oil.

The transmission coefficient T at λ = 690*nm* decreases with the concentration of cottonseed oil in model systems of sunflower and cottonseed oils. A regression dependence of the type $T = f(C)$ with a correlation coefficient R = 0.88 was established as T = –0.14× C + 92.27. A dependence of the same type was valid for model systems of sunflower and rapeseed oils at λ = 670*nm* with $T=-0.28C+89=65$ and a correlation coefficient R= 0.89, where C is the admixture concentration. The dependence of the transmission on the admixture concentration was determined at λ = 690*nm* nm which is the transmission minimum of rapeseed oil.

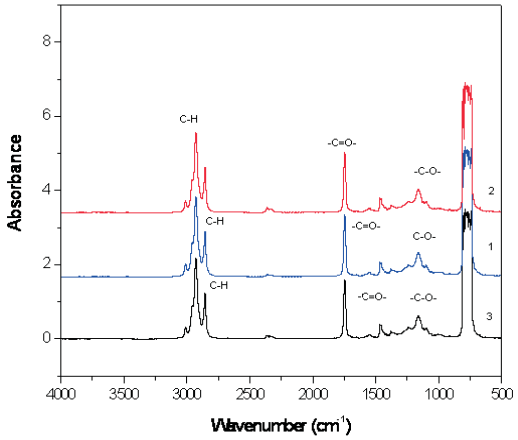

Fig.3. Infrared spectra of sunflower oil and of its mixtures with cotton and rapeseed oil 1-sunflower oil, 2–50% cottonseed oil+50% sunflower oil, 3–50% rapeseed oil+50% sunflower.

The biggest changes in the transmission for the admixtures of rapeseed oil in sunflower oil are in the 400 nm to 500 nm spectral range. For each of the two groups used as substitutes of sunflower oil, correlations between transmission T and concentration C were looked for at λ = 470*nm* nm, at which largest differences were registered. For admixtures of rapeseed oil in sunflower oil the exponential dependence $T = 65.11 \times e^{-0.057}$ with R^2= 0.99 was found. For the same wavelength, the difference in transmission for cotton and sunflower oil is smaller and the dependence is linear, namely, T = –0.416C + 79.93 with R= 0.95.

The infrared spectra of sunflower oil and its double mixtures with rapeseed and cotton oil in a proportion of 1:1 in the interval from 500 cm^{-1} to 4000 cm^{-1} are presented in Figure 3.

Two peaks observed at 1747 cm^{-1} and 1160 cm^{-1} are due to the stretching vibrations of the aldehyde group (*C=O*) and ester group (*C–O*), respectively. In the region of the former peak, infrared energy is absorbed due to the carbon-oxygen bonds in the oil and it is often used for determining the level of oxidation.

There also are two peaks attributed to the bending vibrations in methylene (CH_2) groups and C-H stretching vibrations, which appear at 1465 cm^{-1} and 2929 cm^{-1}, respectively.

For the specified wavelengths 2929 cm^{-1} and 1747 cm^{-1}, the peak height increases upon addition of cotton oil, and decreases when the

same concentration of rapeseed oil is added. A similar decrease in the peak height is observed when corn and soybean oil are added as admixtures to olive oil [10].

The investigation carried out shows that infrared spectroscopy makes it possible to detect cotton oil and rapeseed oil admixtures in sunflower oil. In future studies, the obtained results will be used for identifying correlation dependencies between the peak height or peak area in the infrared spectrum and the concentration of the admixture in sunflower oil.

The β -carotene and chlorophyll content of sunflower oil and of its double mixtures with cotton oil and rapeseed oil was investigated. The obtained data are presented in Table 2.

Table 2. Data on the chlorophyll *a* and β-carotene content in sunflower oil and in its double mixtures with cotton oil and rapeseed oil.

Concentration of the admixture C %	Sunflower oil+ rapeseed oil			Sunflower oil + cotton oil		
	x	β - carotene ppm	Chlorophyll *a* ppm	x	β - carotene ppm	Chlorophyll *a* ppm
10	0.3803	15.36	0.162	0.3266	3.52	0
20	0.4145	25.54	0.286	0.3329	4.87	0
30	0.4323	34.10	0.397	0.3348	5.30	0
40	0.4487	43.73	0.504	0.3383	6.05	0
50	0.4579	53.25	0.597	0.3410	6.58	0
sunflower oil	0.3202	2.23	0	0.3202	2.23	0

Table 3 Color parameters of sunflower oil and its double mixtures with cotton oil or rapeseed oil.

Concentration of the admixture. C %	Sunflower oil + rapeseed oil						Sunflower oil + cotton oil					
	L	*a*	*b*	ΔE_{ab}	*C*	h_{ab}	*L*	*a*	*b*	ΔE_{ab}	*C*	h_{ab}
10	93.72	-11.07	48.41	41.30	49.66	-77.11	94.57	-3.93	12.08	3.05	12.70	-71.98
20	92.71	-13.62	72.36	65.35	73.63	-79.34	93.16	-4.68	15.98	7.21	16.65	-73.68
30	90.70	-13.63	86.33	79.26	87.40	-81.03	92.75	-4.96	17.16	8.48	17.86	-73.88
40	90.03	-13.40	100	92.81	100.89	-82.37	88.65	-5.05	18.76	11.61	19.43	-74.93
50	82.30	-11.09	102.06	95.40	102.66	-83.80	90.56	-5.25	20.55	12.37	21.21	-75.67
0	95.51	-3.06	7.93	-	8.50	-68.90	94.87	-3.19	9.14	-	9.68	-70.76

There is no chlorophyll in pure sunflower oil, and the β -carotene content is low, ranging from 2.23 ppm to 2.61 ppm. The presence of cotton oil admixture in sunflower oil results in an increase of the β -carotene content to 6.58 ppm, and the presence of rapeseed oil admixture - to 53.25 ppm. The presence of chlorophyll *a* in sunflower oil from 0.162 ppm to 0.597 ppm is a sign of the presence of rapeseed oil from 10% to 50%. When cotton oil is added, the chlorophyll *a* content in sunflower oil remains unchanged and cannot therefore be used as a parameter for detecting cotton oil admixtures in sunflower oil. Oil with 3 – 7 ppm of β -carotene contains cotton oil admixtures, and oil with above 10 ppm of β -carotene contains rapeseed oil admixtures. The dependence between the transmission coefficient at $\lambda = 670nm$ and the content of chlorophyll in the rapeseed oil-containing samples was obtained: $T = -4.46\ Chlorophyl + 94.23$ with a correlation coefficient R = 0.95.

For the different brands of sunflower oil, as well as for each of the investigated sample systems, data on the color coordinates *a** and *b** in the CIE *La*b** colorimetric system were obtained; the color coordinate x in XYZ colorimetric system, as well as the metric lightness *L**, the metric chroma *C** and the metric angle of the hue of the color h_{ab} were calculated. The color differences ΔE_{ab} between sunflower oil and its double mixtures with rapeseed or cotton oil were calculated. The data are presented in Table 3. The translucency spectra were recorded using a 1 cm wide cuvette, without dilution.

The data presented in Table 3 clearly show that the addition of cotton oil or rapeseed oil admixtures leads to an increase in the values of the color coordinate *в**. This fact indicates that both admixtures lead to an enhancement of the yellow hue of the product. The higher values of the color coordinate x are connected with the higher β-carotene content.

The presence of admixtures in sunflower oil causes turbidity, and hence a decrease in the value of the metric lightness *L** of the product. The presence of cotton oil admixtures leads to a decrease in the specified value by 2 or 3 units, while the presence of rapeseed oil leads to a decrease in the *L**value up to 10 units. There is a correlation dependency between the metric lightness *L** and the concentration of the admixture when rapeseed oil is added to sunflower oil: $L^* = -0.1689\ ^*C + 95.75$ with a

correlation factor R= 0.96, but this dependency, when cotton oil admixture is added, has a relatively low correlation factor, and is, therefore, not mentioned in the discussion.

Table 4. Correlation dependency between the color parameters and the concentration of admixtures in the sample.

Sunflower oil + rapeseed oil		Sunflower oil+ cotton oil	
Linear dependences	R	Linear dependences	R
ΔE_{ab}=1.3564*C+34.131	0.93	ΔE_{ab} =0.2305*C+1.6282	0.95
h_{ab}= – 0.1639*C–75.815	0.99	h_{ab} = 0.0864*C–71.43	0.95
x = 0.0026*C+0.3439	0.93	x =0.0004*C+0.3232	0.80

The knowledge of the type of the admixture in sunflower oil and the color characteristics of the sample makes it possible to determine the concentration of the admixture. For this purpose, linear regression dependencies of the type $\Delta E_{ab} = f(C)$, $h_{ab} = f(C)$ and $x = f(C)$ were identified. The specified dependencies, together with their correlation factors, are presented in Table 4.

CONCLUSIONS

It is possible to detect admixtures of rapeseed oil in concentrations from 10 to 50 % to sunflower oil on the basis of the translucency spectrum in the visible range and the presence of an absorption band at 670 nm. An absorption band in the interval from 630 nm to 680 nm and a transmission coefficient between 15% and 40% in the 400 to 500 nm range of a sunflower oil sample is a solid indication of the presence of low concentrations (up to 20%) of rapeseed oil adulterant.

The adulteration of sunflower oil by cottonseed oil (up to 50%) leads to a decrease in the transmission coefficient T in the interval from 400 to 500 nm. There is no absorption band found in the visible spectrum.

In the infrared spectrum at a fixed λ, the peak height increases with the addition of cottonseed oil and decreases with the addition of up to 50% of rapeseed oil. Through the infrared spectrum it is possible to detect adulterants of rapeseed or cottonseed oils in quantities lower then 50%. Future studies are recommended to investigate the relationship between the characteristics of the IR spectra and the concentration of adulterant oils in the range from zero to 25%.

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ОТКРИВАНЕ НА ПРИМЕСИ ОТ РАСТИТЕЛНИ МАСЛА В СЛЪНЧОГЛЕДОВО МАСЛО ЧРЕЗ ОПТИЧНИ МЕТОДИ

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(Резюме)

В настоящата работа са изследвани моделни системи от слънчогледово масло в смес с рапично или памучно. Получени са данни за цветовите характеристики на посочените моделни смеси в CIE *La*b** и XYZ колориметрични системи. Определени са метричната светлота, чистотата на цвета и метричният ъгъл. Показано е, че съществуват регресионни зависимости между посочените параметри и концентрацията на примеса от рапично или памучно масло. Чрез тях е възможно количественото определяне на примеса, а качественото му откриване е възможно чрез получаване на спектъра на пропускане във видимата част на спектъра и провеждане на инфрачервена спектроскопия.