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Application of non-destructive fast methods for quality assessment of sunflower oil

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The sunflower oil is pressed from the seeds of the sunflower plant (*Helianthus annuus*). It contains high amounts of the essential fatty acid, linoleic acid. Sunflower oil is commonly consumed in foods. The quality of sunflower oil depends on the quality of the sunflower seeds to be processed, the storage conditions of the seeds before pressing and the refining conditions. The standard chemical methods used to determine the chemical content of the oils are usually time-consuming, labor-intensive and expensive. Therefore, we have tested four physical methods measuring refractive indices and their dispersion curves, color parameters, UV-VIS spectroscopic and fluorescence spectra that are related to the chemical structure and composition of the sunflower oils. The refractive indices of the samples were measured using a laser refractometer at wavelengths of 405 nm, 447 nm, 532 nm and 656 nm. The dispersion curves and the dispersion parameters were approximated using one-term Sellmeier model. The color parameters were obtained using a Lovibond PFX 880 spectrophotometer. The values for the refractive indices were compared to these, obtained by a standard method using the Abbe refractometer. These methods are fast, easy to perform and do not require any additional chemical agents. Four groups of sunflower oils – cold pressed, oil with added antioxidants and commercially refined and nonrefined sunflower oil, were investigated.

Keywords: refractive index, fluorescence, sunflower oil, quality assesment

INTRODUCTION

Sunflower oil is a popular vegetable oil derived from the seeds of the sunflower plant (*Helianthus annuus*) [1]. It is used for various purposes, including food and cosmetics.

Sunflower oil is a major source of high-quality edible oil, contributing to about 87% of vegetable oil production worldwide [2]. It is primarily produced for the development of high-oil varieties, which require fertile soil, adequate rainfall, and suitable environmental conditions. The global sunflower oil market is driven by the fluctuating prices of other vegetable oils, such as palm oil and soybean oil, and is in high demand in developing countries due to its healthier and more affordable alternatives to many counterparts [3].

Sunflower oil quality can be influenced by various factors, including: genotype and environment: Sunflower oil quality and yield depend on the plant genotype and its interaction with the environment [4]. Different sunflower cultivars have been developed to produce oils with specific fatty acid profiles, such as high stearic or high palmitic acid cultivars [5].

Temperature during the plant cycle: The effect of temperature during the plant cycle, from anthesis to maturity, on the fatty acid composition of sunflower oil has been reported to change the oleic/linoleic acid (O/L) ratio, known as unsaturation ratio, in the oil [5].

Seed quality and treatment: Seed quality, seed treatment prior to extraction, extraction method, and processing conditions can affect the properties and composition of sunflower oil [6].

Blending with other oils: Blending sunflower oil with other edible vegetable oils, such as linseed oil, grapeseed oil, and coconut oil, can improve its quality characteristics, such as acidity and stability to autoxidation.

In summary, sunflower quality assessment can involve various techniques and methods, depending on the specific goals and requirements of the assessment. These assessments can help improve the understanding of sunflower cultivation, production, and the quality of sunflower-based products. The objective of the present work is to study the capabilities of a group of physical methods for fast quality evaluation of the sunflower oils.

MATERIALS AND METHODS

Materials

Four types of commercially available sunflower oils – cold pressed, oil with added antioxidants and commercially refined and nonrefined sunflower oil, were chosen for analysis and their characteristics

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were compared. The samples were measured immediately after opening the bottle to avoid accelerated oxidation processes.

Refractive index measurement

The refractive index values of the samples investigated were determined by a laser refractometer and a standard Abbe refractometer. The measurements by Abbe refractometer were performed at a temperature of 20 °C with an accuracy of ± 1×10^{-4}.

The refractive index values of the samples were measured using a laser refractometer with a total experimental uncertainty of less than 2×10^{-4} by the method of the disappearing diffraction pattern for four laser wavelenghts – 405 nm, 445 nm, 532 nm and 635 nm at a temperature of 20 °C. The data obtained from the refractive index measurement at four laser wavelengths were used for the construction of dispersion curves using the one-term Sellmeier model for the fundamental absorption band [7].

Fluorescence spectroscopy

BroLight BIM-6002 fiber-optic spectrometer with spectral sensitivity in the range of 200-1100 nm was used to measure the fluorescence spectra of sunflower. An optical fiber of 200 µm diameter was used for more light on the probe and measurement of fluorescent and scattered light. A collimator with a 5 mm aperture lens was used to capture more light and direct it to the receiver. Using a 200 µm entrance slit, the resolution was approximately 8 nm. The sources used to measure the fluorescence spectra were light emitting diodes (LEDs) emitting light at wavelengths of 245 nm, 265 nm, 275 nm, 295 nm, 375 nm, 395 nm, 405 nm, 410 nm, 415 nm and 435 nm. Measurements at 395 nm were performed, since the fluorescence intensity at the indicated wavelength was strongest for the relatively weak fluorescence signal at an excitation time of about 100 ms.

Color parameters measurement

The color parameters for the sunflower oil samples were determined in a CIELab colorimetric system after preliminary tempering of the samples. VISIONlite ColorCalc software package and Helios Omega spectrophotometer with 10 mm cuvette were used.

Luminance L and color characteristics a and b in a CIELab colorimetric system, color coordinates X,Y,Z and chromaticity coordinates x, y in a XYZ colorimetric system were determined. For the case of the present study, CIELab is more informative, as it is designed for small color differences.

The color intensity C_{ab} and hue angle h_{ab} can be determined according to the following dependencies:

$$C_{ab} = \sqrt{a^2 + b^2} \quad (1)$$

$$h_{ab} = \text{arctg}(b/a) \quad (2)$$

RESULTS AND DISCUSSION

Fluorescence spectroscopy is proving to be a fast, easy and possibly non-destructive technique for the analysis of sunflower oil. With the increase in the price of sunflower oil in Bulgaria and the ever-increasing imports, the creation of libraries of fluorescence spectra is useful for the development of methods to assess the quality, authenticity and geographical origin of sunflower oil.

Most samples have a characteristic peak at around 580 nm associated with oxidation as a result of exposure to temperature changes during transport, storage, bottling or as a result of exposure to direct sunlight. The fluorescence spectra are presented in Fig. 1.

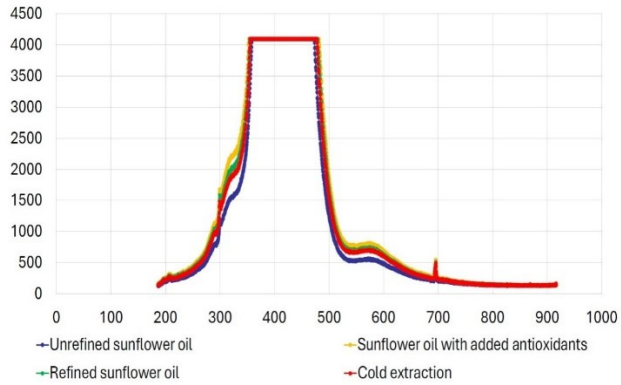

Fig. 1. Fluorescence spectra of sunflower oil samples

Two fluorescence maxima are clearly distinguishable:

- Peak I with maximal intensity in the range 580-590 nm;
- Peak II with maximal intensity around 696 nm.

Peak I can be attributed to the oxidation of the fatty acids and tocopherols [8], while Peak II displays a low intensity between 304 and 387 a.u. and can be linked to pigments like carotenoids and chlorophyll [9]. The positions of the peaks of the different samples match almost completely and differ only in intensity. The only type of oil that displays a shift of 10 nm in Peak I is the sunflower oil with added antioxidants. The aforementioned peak is linked to the oxidation of the samples, with refined sunflower oil with added antioxidants possesing the hightest value of 758 a.u., followed by regular

refined sunflower oil with a value of 732 a.u. This latter result can be attributed to the fact that during the refining process a major part of the minor components that possess antioxidant effects in the sunflower oil (including vitamin E) are lost. This is linked to the high procentage of polyunsaturated fatty acids contained within vegetable oils [10]. Unrefined sunflower oil possesses the lowest intensity of Peak I (535 a.u.). This can be due to its production procedure preserving the compounds that possess antioxidant effects, which in turn leads to its lower oxidation.

Good positive corelation was found between the intensities of the flourescence peaks (caused by the pigments and the oxidising compounds ($I_{696} = 0.69 * I_{581} - 83.52$)) with the determination coefficient $R^2 = 0.73$. Similar correlation for olive oil is reported by Kyriakidis and Skarkalis [11].

The color measurements of both colorimetric systems (XYZ and CIELab) show that the color parameters of the second colorimetric system (meant for detection of small color differences) are more useful for both customers and analysers. Within the color range of the colorimetric system CIELab, the color parameters a* and b* can be given in polar coordinates by calculating the color C and hue h, which are linked to the perseption of the human eye. The color shade is considered a qualitative attribute dwhen determining the color.

All samples have high brightness. The distribution of color parameters in the samples according to the CIELab colorimetric system is presented in Fig. 2 and all values are listed in Table 1. The color of the sunflower oil is due to carotenoids and chlorophyll pigments [12]. For all samples parameter a has low values, and if the error in the measurement apparatus is taken into account, for refined samples the parameter approaches negative values. This observation strongly confirms the Moyano thesis which states that the parameter a is positive for unrefined and cold-pressed oils and negative for olive oils and refined sunflower oil [13].

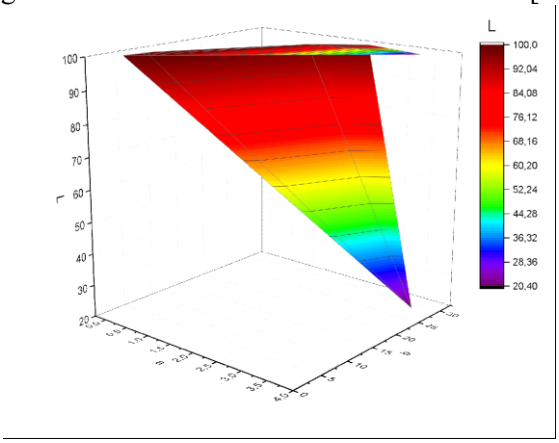

Fig. 2. Dependence between brightness and color parameter in CIELab colorimetric system

All samples have similar high luminosity, with the exception of the cold-pressed one. Similar fact has been reported by O'Brien [14]. The positive b component is attributed to the yellow color of the samples, caused by the presence of carotenoids [15]. The hue of the samples splits them in two groups: those with hue angle close to 90° (for refined samples) and those with angle between 82° and 85° (for unrefined and cold-pressed samples).

Table 1. Color parameters of sunflower oils

Sample	x	y	X	Y	Z	L	a	b	C	h
Cold extraction	0.53	0.446	3.7	3.1	0.2	20.5	3.6	28	28.3	82.7
Unrefined sunflower oil	0.481	0.427	114.7	101.9to	22.1	100	2.4	29.9	30	85.4
Biser	0.457	0.411	119.1	107.2	34.5	100	0.2	6.1	6.1	88.5
Sunflower oil with added antioxidants	0.458	0.413	108.1	97.2	30.4	98	0.2	7.6	7.6	88.6

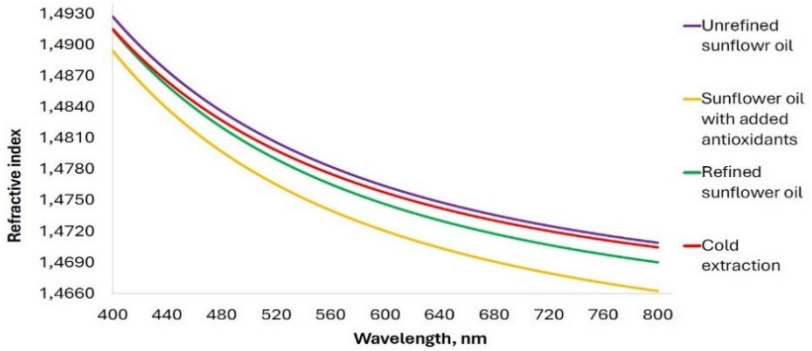

Fig. 3. Refractive index dispersion curves of the sunflower oil samples

Table 2. Refractive indices measured by Abbe refractometer at 20 °C

Sample	Cold extraction	Unrefined sunflower oil	Refined sunflower oil	Sunflower oil with added antioxidants
Refractive index	1.4730	1.4718	1.4730	1.4690

According to the search results, the refractive indices of sunflower oil are as follows: 1.461 - 1.468 below 20 ºC, 1.461 – 1.4735 at 20ºC [16].

It is important to note that the refractive index of sunflower oil can vary depending on factors such as temperature and specific type of sunflower oil being used. Using the Sellmeier's coefficients obtained from the refractive index data the dispersion curves of the refractive index were calculated for all samples in the spectral range (400-800) nm and plotted in Fig. 3.

It was found that the values of the refractive index for sunflower oil with added antioxidants are significantly lower than for the other investigated oils. These changes also can be associated with oxidation as a result of exposure to temperature changes during transport, storage, bottling or as a result of exposure to direct sunlight.

The refractive indices of the samples measured by using a standard Abbe refractometer are presented in Table 2.

It can be seen from the results shown in Table 2 that the sunflower oils with added antioxidants has the lowest refractive index value compared to other samples.

CONCLUSION

These initial studies imply that all offered physical techniques are connected and may be helpful in quickly identifying and evaluating the sunflower oil quality.

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