CIELAB and Thermal Properties of Sesame Food Oil Under Antocyanin and UV Influence

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One of the most serious problems of the food industry is lipid oxidation, which decreases nutritional quality, increases toxicity, and alters texture and color of the food in question. Research suggests that oxidation of lipids from the diet may play a direct role in the development of chronic diseases in the human body. Natural antioxidants may be added directly to foods as primary antioxidants, which donate hydrogen atoms to quench peroxyl radicals before they can further react with unsaturated lipids. Antioxidants significantly extend the shelf life of foods containing lipids susceptible to oxidation such as vegetable oils. Wild berries are a potential source of natural anthocyanin antioxidants. This paper presents experimental results obtained using antocyanins from Vaccinium Vitis - Idaea Fruits, upon color and thermal properties of sesame food oil, which was exposed to UV radiation.

Keywords: sesame oil, absorbance spectra, UV radiation, antioxidant influence, thermal stability

The oxidation of oils is a major concern to the food industry. The process of oxidation can lead to several changes to a food product which affect shelf-life and consumer acceptance. These include the development of rancid flavors and aromas, changes in color and texture, increased toxicity and a decline in the nutritional value of the food [1].

Oxidative rancidity of cooking oils refers to the undesirable odors and flavors which develop when such products are exposed to the oxygen in the air. The poly-unsaturated fatty acid portions of these foods react with oxygen to form peroxides. The peroxides decompose to yield a complex of mixtures, including aldehydes, ketones, and other volatile products. These products are responsible for *rancid* odors and flavors [2].

Factors that influence oil oxidation are: the temperature - considerable improvement in storage stability can therefore be gained by lowering the storage temperature; the presence of oxygen - the use of packaging materials with low oxygen permeability is desired; light - packages that exclude light can be used to protect the products against fat oxidation; metals such as copper, iron, manganese, and chromium increase rate of fat oxidation - the preferred storage containers are steel drums, tin, or nonmetallic materials such as plastic. Stainless steel is commonly used in processing plants so as to avoid excessive contact with metals that increase fat oxidation. [2]

Sesame (S*esamum indicum*, L.) is one of the oldest oilseed crops known to mankind and is the only cultivated S*esamum* species. Sesame seed has been considered to be important because of its high oil content (42–56%) and protein (20–25%), and also because it is a good source of minerals, particularly calcium, phosphorus, potassium and iron. Moreover, sesame oil is highly resistant to oxidation sesame oil contains a relatively high percentage of unsaponifiable matter (1–3%) which includes sterols, sterol esters, (mainly) γ-tocopherol, and unique compounds called sesame lignins (described below). Sesame oil is classified as a polyunsaturated, semi-drying oil containing about 82% unsaturated fatty acids. The major fatty acids, oleic and linoleic, are present in approximately equal amounts in the oil [3].

Food antioxidants are compounds that increase the resistance of oils to oxidation and consequent deterioration or rancidity. Natural antioxidants from fruit products, have also been shown to effectively reduce oxidative rancidity in ground meat products while providing additional sources of nutrients and flavor [2].

The definition of antioxidants, given in 1995 by Halliwell and Gutteridge, stated that an antioxidant is *any substance that, when present at low concentrations compared with that of an oxidizable substrate, significantly delays or inhibits oxidation of that substrate* [4, cited in 5].

The majority of the antioxidant capacity of a fruit or vegetable may be from compounds such as flavonoids, isoflavones, flavones, anthocyanins, catechins and isocatechins. [6] The berries fruits class contains in high proportion compounds with recognized antioxidant activity - flavonoids and polyphenols - due to the hydroxy groups, that can neutralize the oxygen radicals, responsible for the oxidation reactions [7, 8]. Main flavonoid subgroup in berries and fruits are anthocyanins. Anthocyanins, are pigments which belong to the secondary metabolite group of flavonoids, and are often responsible for the orange, red and blue colors in fruits. [8] The *Vaccinium Vitis - Idaea* berries contain also plentiful organic acids, vitamin C, vitamin A (as beta carotene), B vitamins (B_1, B_2, B_3), and the elements potassium, calcium, magnesium, and phosphorus.

The antioxidant activity of vegetable extracts depends on a proper solvent selection for extraction and isolation of all the active principles. The most common solvents used for the extraction of polyphenolics from plant material are methanol, ethanol, acetone, ethyl acetate, and their aqueous solvents [8].

CIELAB analysis are used in many different experiments, for instance: in organic chemistry, [9, 10], in anorganic chemistry [11], and in food chemistry as well [12, 15].

Different mixtures based on vegetable oils and mineral oil are analyzed from the point of view of thermal stability, using the differential scanning calorimetry (DSC) and

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thermal gravimetric (TG) analyses. The results were comparatively evaluated with reference to vegetable oils. [16, 17]

Storage conditions play an important role in food quality, in particular in food oils case, because UV radiation may damage their properties. The change in color indicates the oxidation of the unsaturated fatty acids present in food oils. The aim of this paper is to establish the influence of *Vaccinium Vitis - Idaea* dried fruits alcoholic extract addition upon CIELAB properties of sesame food oil under UV radiation, highlighting the necessity of using antioxidants when storage food oils.

Experimental part

Experimentals were perform using sesame food oil with the following composition in fatty acids: saturated fatty acids – 10.2%, mono-unsaturated fatty acids – 36.5%, poly-unsaturated fatty acids – 37%, among them being linoleic acid 36.8% and linolenic acid - 1% [18]. The composition of *Vaccinium Vitis – Idaea* extract was presented in [8] and its color properties in [13]. The concentrated extract from *Vaccinium Vitis - Idaea* dried fruits in ethanole was prepared according to the recepice presented in [8]. *Vaccinium vitis idaea* (4 g) were extracted with 1:10 (w/v) aqueous ethanol 94% by volume in a shaker at 400 rpm at room temperature for one hour, and then centrifuged at 2000 rpm for 6 min and the supernatant was collected, filtered and stored in a freezer.

The sesame oil was mixed in proportion of 2% with the concentrated extract from *Vaccinium Vitis – Idaea* fruit. The mixture was put under UV radiation for 30 min , using a UV lamp – Vilber Lourmat VL-6.C-230V 50/60Hz S/N:07 23148. After the exposure, the sesame oil was storage at darkness. The process was repeated after 24, 48 and 72 h, respectively. The same experiment was performed with sesame oil containing no extract.

The color analysis of the oils was conducted using a Cary-Varian 300 Bio UV-VIS colorimeter. All color data were expressed by *L*, a*, b**, where *L** corresponds to lightness; *a** corresponds to the transition from green (- *a**) to red (+*a**); and b* corresponds to the transition from blue (-*b**) to yellow (+*b**).

The international standards and the nomenclature for the measurement of color used by the food industry were defined by the Commission Internationale de l'éclairage (CIE) in 1931. In the present study, the CIELAB system (*L*, a*, b**) was used. The equipment was set up using the following parameters of the $BaSO_4$ reference: *L** =99.9996, *a** = 0.0021 and *b** = -0.0028 - in the case of absorption spectra; and : *L** =99.9994, *a** = 0.0073 and *b** = 0.0128 0028 - in the case of transmittance spectra.

The thermogravimetric (TG)/derivate thermo-gravimetric (DTG) analysis were performed with a NETZSCH TG 209F1. Approximately 3÷7 mg of sample was heated in an Al_2O_3 crucible, with 5°C/min. in nitrogen atmosphere, within the range of temperature 20° ÷ 600°C.

Results and discussions

Absorbance spectra measured the evolution of the molar absorbance coefficient ε of sesame oil in different experimental conditions. The results are presented in figure 1.

Comparing the evolution of the molar absorbance coefficient for the raw oil and the oil with extract for the different periods of exposure to UV light, the representations in figure 1 (a to d) were obtained.

Studying these figures, one can observe that the variation of the molar absorbance coefficient is do not depend on UV exposure when using the fruit extract, but in the case of oil exposure without the extract, the molar absorbance coefficient is lower when increasing UV exposure. That means that the addition of the extract makes the sesame oil more stable to light.

It can be observed that after a longer period of exposure to UV light, the raw sesame oil changes its absorbance characteristics more obvious. But, by addition of the *Vaccinium Vitis - Idaea* dried fruits extract this property remains unchanged.

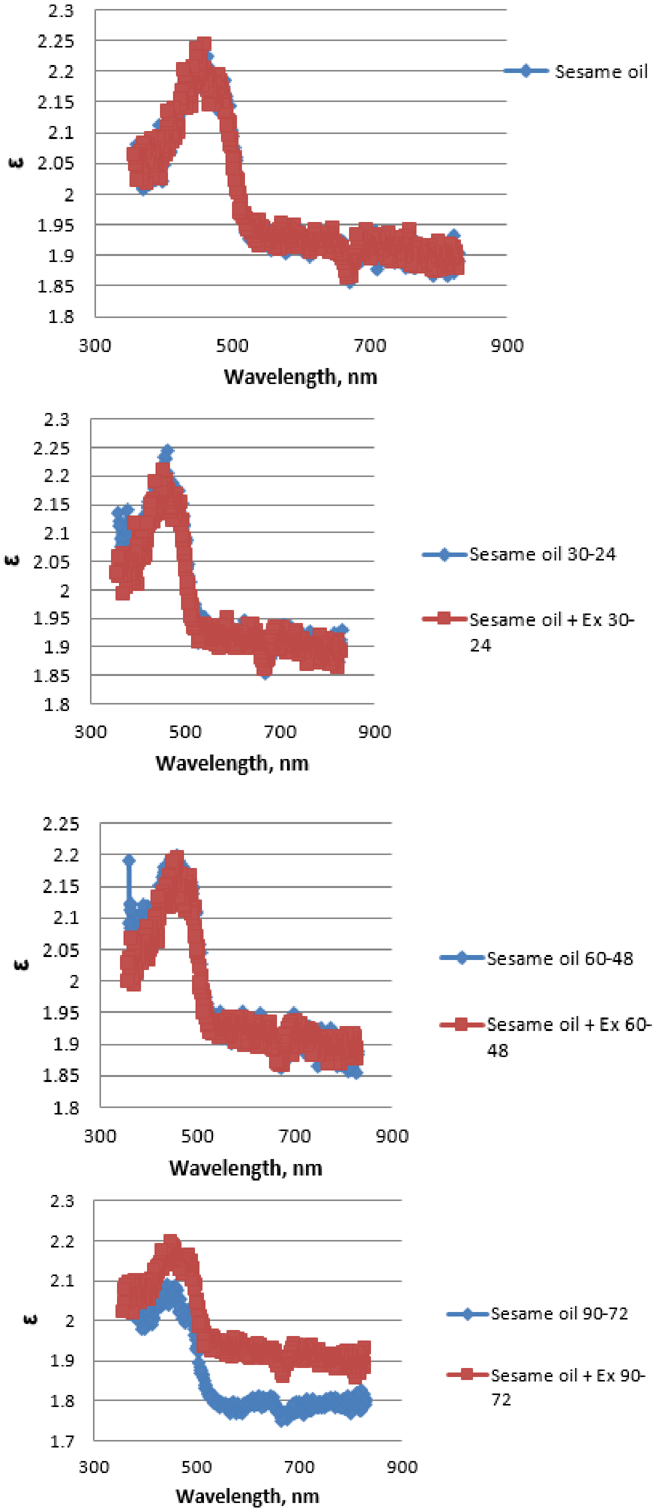


Fig.1. Comparing the evolution of the molar absorbance coefficient for the raw oil and the oil with extract for the different periods of exposure to UV light a) before the exposure; b) 30 min of exposure after 24 h; c) 30 min of exposure after 48 h; d) 30 min of exposure after 72 h

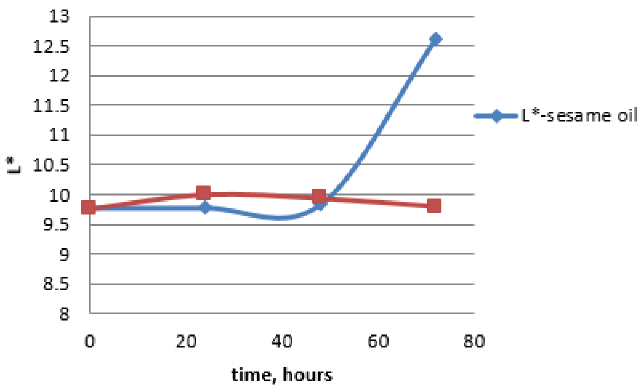


Fig.2. The evolution of the luminosity - *L**, for the sesame raw oil, and for the sesame oil with extract

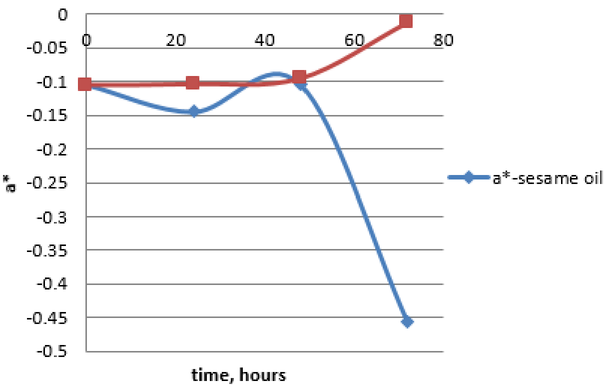
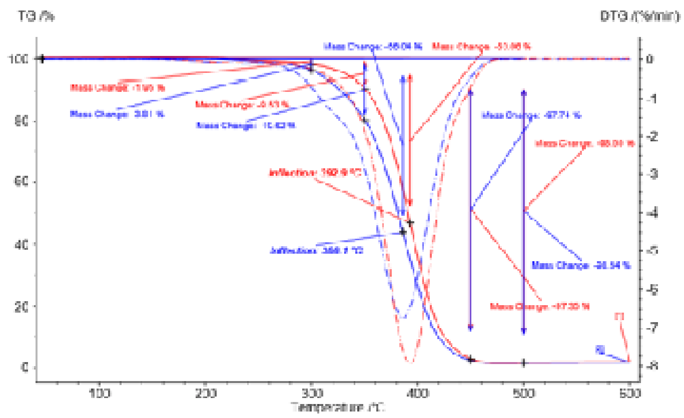


Fig.3. The evolution of the parameter *a**, for the sesame raw oil, and for the sesame oil with extract

The CIELAB characteristics of the sesame oil and for the sesame oil with extract, in the experimental conditions exposed above, are presented in the following figures.

In figure 2 is presented the evolution of the luminosity - *L**, in figure 3 the evolution of the *a** parameter, and in figure 4 the evolution of the *b** parameter.



curve S1 and curve S5

Fig.5. Comparing the TG/DTG curves for the raw sesame oil and the oil with extract for the different periods of exposure to UV light; a) before the exposure (S1 and S5); b) 30 min of exposure after 24 h (S2 and S6);

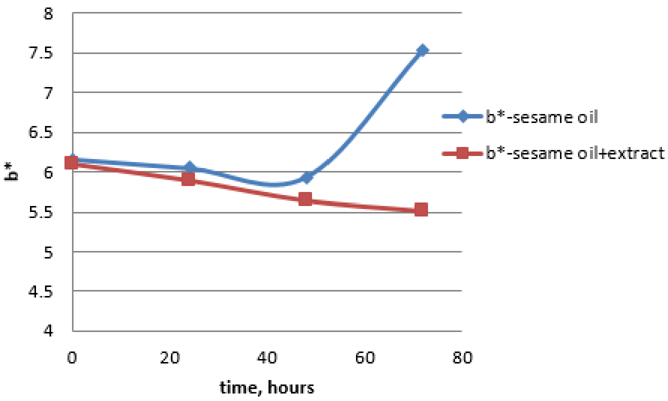


Fig.4. The evolution of the parameter *b**, for the sesame raw oil, and for the sesame oil with extract

The changes in CIELAB properties appear after 50 h under UV radiation, for the raw sesame food oil. The amount of antocyanin addition to sesame oil was small, only 2%, so its color did not influence the color properties of the oil. Taking this into account, it can be observed that the CIELAB characteristics: luminosity - *L**, parameter *a** and parameter *b** are more stable when the sesame oil is treated with the extract.

The luminosity is approximately constant when using *Vaccinium Vitis - Idaea* dried fruits extract even at 90 minutes under UV exposure, in compare to the untreated oil. That means that oxidation of fatty acids did not appear in this period of time.

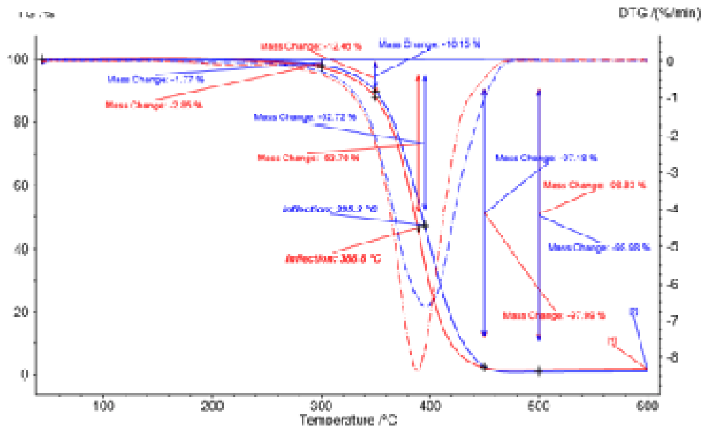
The *a** parameter, which determines the quality of red - green color and the *b** parameter, which determines the quality of yellow – blue color, also remain constant up to 60 minutes of exposure, so the UV radiation did not influence the CIELAB properties of sesame oil when using *Vaccinium Vitis – Idaea* extract in compare to the untreated oil.

The TG/DTG curves of the sesame raw oil and of the sesame oil with extract in different experimental conditions are presented in figure 5 (a to d).

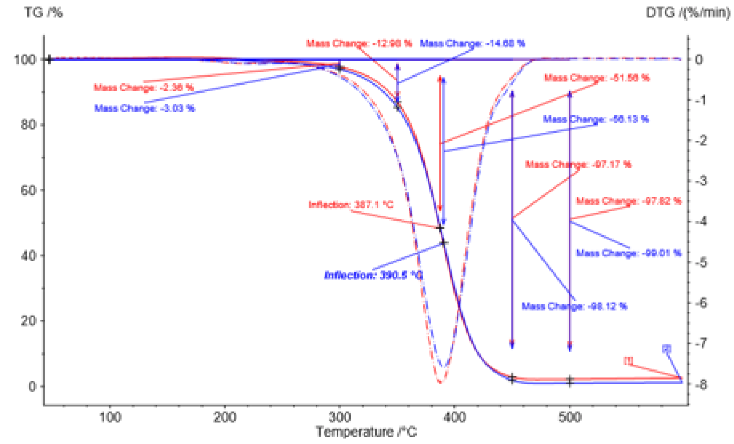
In all cases the following results were obtained:

-until 300°C the mass loss was in very small amount, between 1.77 and 3.81%

-total mass loss appears at 500°C.



curve S1 and curve S6



c) curve S3 and curve S6

Fig.5. Comparing the TG/DTG curves for the raw sesame oil and the oil with extract for the different periods of exposure to UV light; c) 30 min of exposure after 48 h (S3 and S7); d) 30 min of exposure after 72 h (S4 and S8)

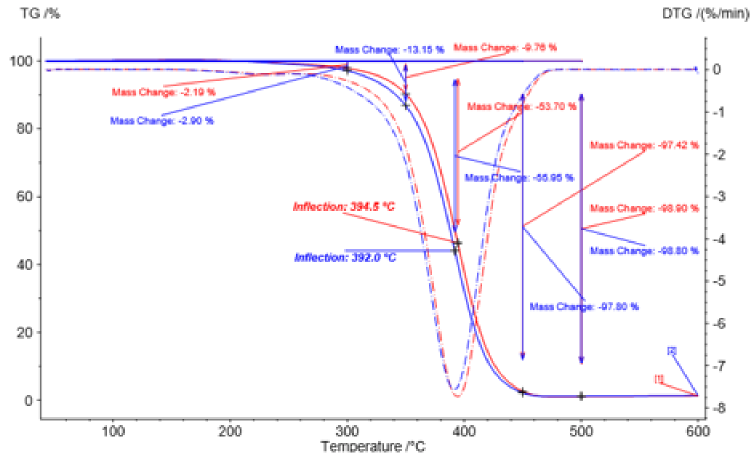


Table 1
INFLECTION POINTS FOR ALL EXPERIMENTAL CONDITIONS

Sample	S1	S2	S3	S4	S5	S6	S7	S8
Inflection point, °C	392.9	388.8	387.1	394.5	386.1	395.2	390.5	392.0

The inflection points – which represent the temperature for maximum decomposition – for all experimental conditions mentioned above are presented in table 1.

Addition of the *Vaccinium Vitis - Idaea* extract to the studied sesame oil samples does not significantly influence the thermal degradation.

Conclusions

The experiments reveal that storage conditions, which depend on UV radiation, affect the quality of the food oil, modifying its color by fatty acids oxidation, if it is not treated with an antioxidant product.

In conclusion, it can be said that by addition of *Vaccinium Vitis - Idaea* dried fruits extract to sesame oil, its color properties after exposure to UV light modify only slightly, compared to the raw oil, when the color properties modify very much, especially at long periods of exposure to UV light.

Regarding the thermal analysis, we conclude that the thermal stability is influenced only in small amount by addition of antocyanin extract to the sesame oil under the radiation process.

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