Walnut Food Oil Under UV Radiation - influence Upon CIELAB and Thermal Properties of Antocyanin Addition

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Lipid oxidation is one of the most serious problems of the food industry, because it increases toxicity, decreases nutritional quality, and, of course, alters texture and color of the food in question. Some 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 used as primary antioxidants, when added directly to foods. They 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 walnut food oil, which was exposed to UV radiation.

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

Oxidation of food oils can lead to several changes to a food product which affect shelf-life and consumer acceptance, so the process of oxidation is a major concern to the food industry. This process include the development of rancid flavours and aromas, changes in colour 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].

Oil oxidation may be influenced by several factors, such as: 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].

Walnuts (*Juglans regia* L.) contain kernels that have high content of glyceride oil. Regarding the fatty acid composition unsaturated fatty acids are dominating - oleic, linoleic and linolenic. Ratio of these acids determines the nutritional value of walnut oil. The presence of γ-tocopherol in the walnut oil - 88% of total tocopherols provides some level of protection against oxidation. Walnut oil is used as salad oil, because the oil phase emulsifies sauces. It is not used for cooking or heat treatment of products due to the presence of unsaturated fatty acids - 70%. Their oxidation leads to the appearance of unwanted taste and odor [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] Many type of berries fruits class have a high content of flavonoids and polyphenols, compounds with recognized antioxidant activity. This property is due to the hydroxy groups, which can neutralize the oxygen radicals (responsible for initiating and propagating the oxidation reactions) resulting more stable compounds [7]. 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 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 in organic chemistry [9], anorganic chemistry [10], and in food chemistry as well [11].

The thermal studies of different oils and of the studied mixtures indicated a high thermal stability [12].

Storage conditions play an important role in food quality, because UV radiation may damage food properties. This paper presents some aspects regarding the influence of

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Vaccinium myrtillus dried fruits extract upon CIELAB and thermal properties of walnut food oil under UV radiation.

Experimental part

Walnut food oil found on Romanian market was mixed in proportion of 2% concentrated extract from *Vaccinium myrtillus* dried fruits in ethanole. 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 walnut oil was storage at darkness. The process was repeated after 24, 48 and 72 h, respectively. The same experiment was performed with walnut 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 thermogravimetric (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 measeured the evolution of the extinction coefficient ε of walnut oil in different experimental conditions. The results are presented in figure below.

In figure 1 is presented the evolution of the molar absorbance coefficient for the raw oil during exposure to UV light; and in figure 2 is presented the evolution of the molar absorbance coefficient for the walnut oil with extract during exposure to UV light.

From these figures results that the addition of the extract makes the walnut oil more stable to light.

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 3 (a to d) were obtained.

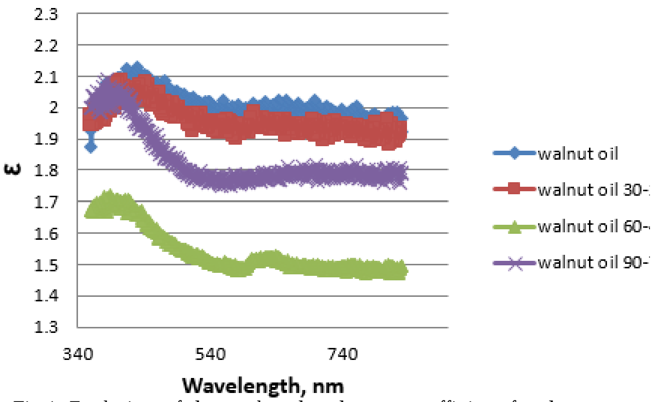


Fig.1. Evolution of the molar absorbance coefficient for the raw walnut oil during exposure to UV light for 30 min, after 24, 48, and 72 h, respectively

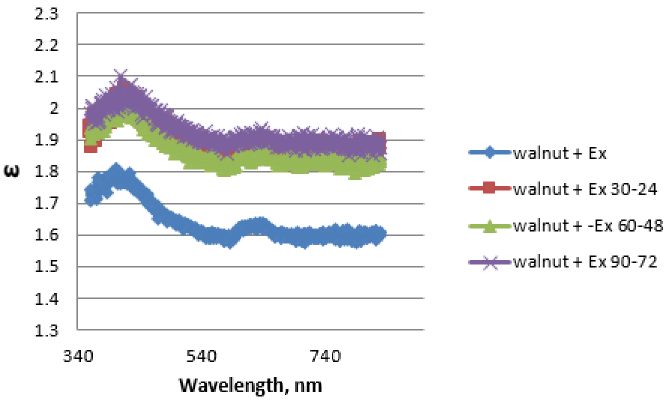


Fig.2. Evolution of the molar absorbance coefficient for the walnut oil with extract during exposure to UV light for 30 min, after 24, 48, and 72 h, respectively

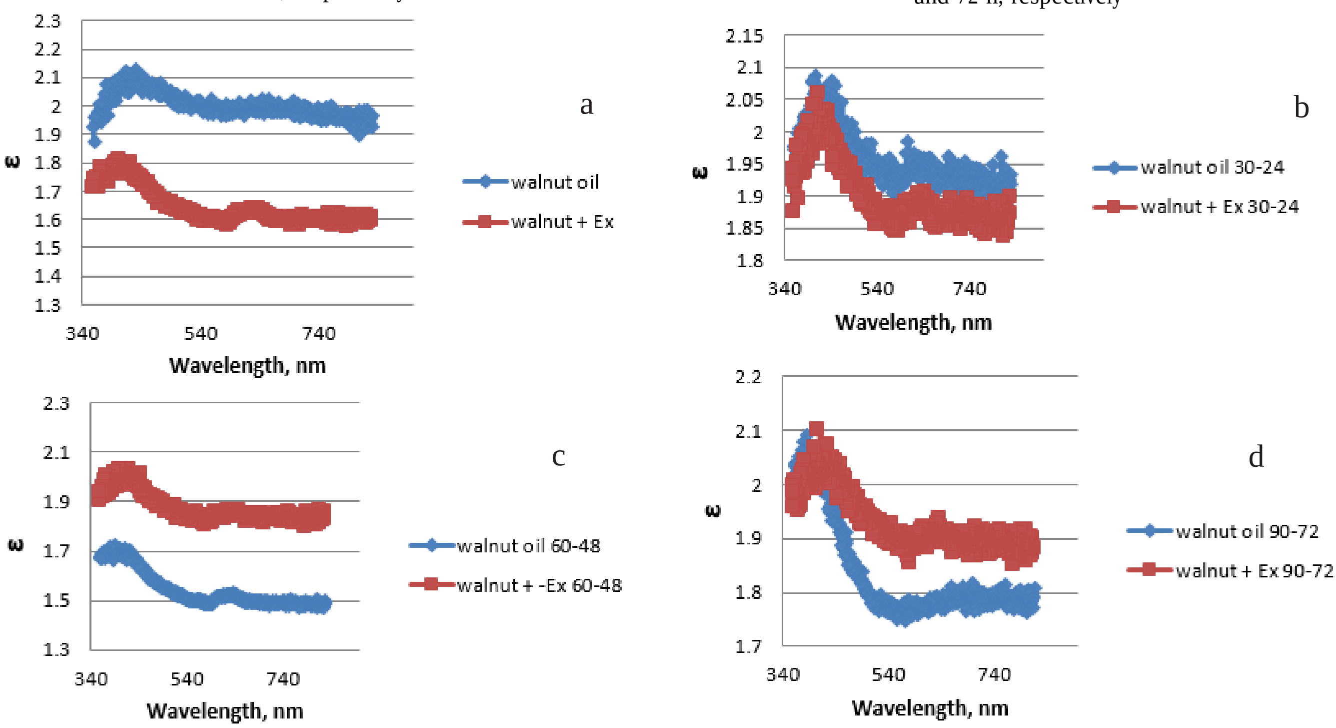


Fig.3. Comparing the evolution of the molar absorbance coefficient for the raw oil and the oil with extract for the different periods of exposure to UV light a)before the exposure; b) 30 min of exposure after 24 h; c)30 min of exposure after 48 h; d) 30 min of exposure after 72 h

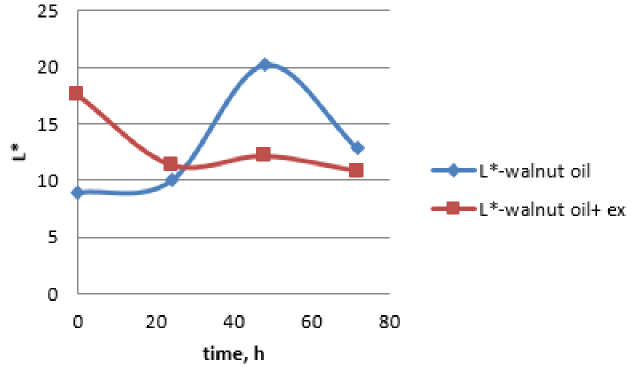


Fig.4. The evolution of the luminosity - *L**, for the walnut raw oil, and for the walnut oil with extract

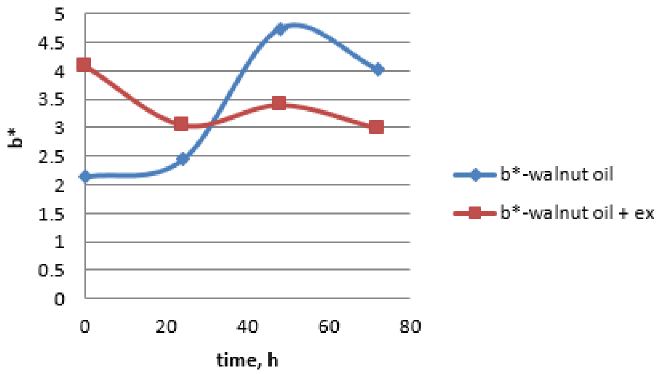


Fig.6. The evolution of the parameter *b**, for the walnut raw oil, and for the walnut oil with extract

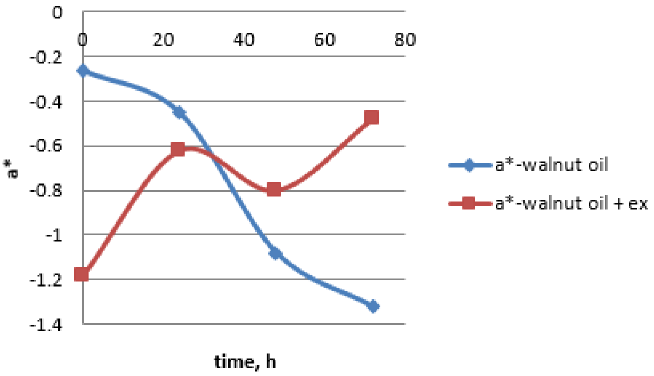


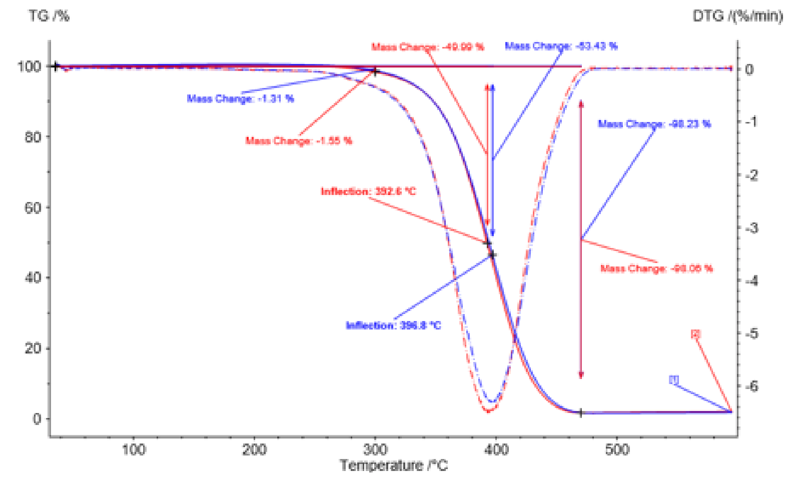
Fig.5. The evolution of the parameter *a**, for the walnut raw oil, and for the walnut oil with extract

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

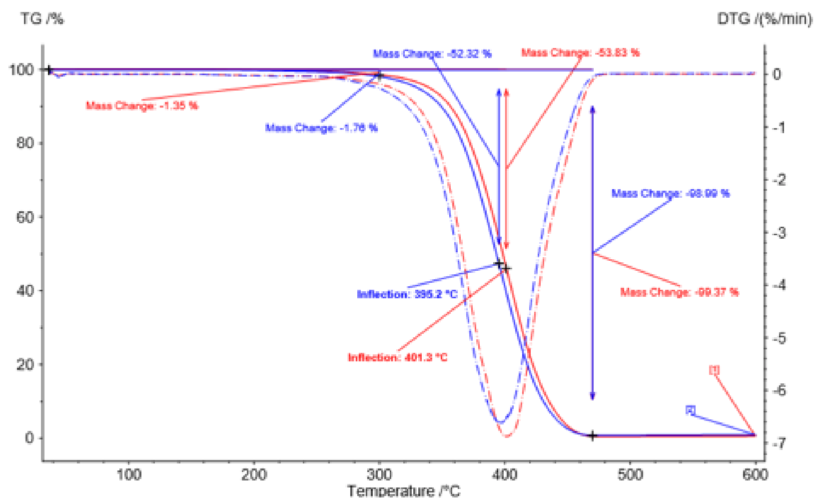
The CIELAB characteristics of the walnut oil and for the walnut oil with extract, in the experimental conditions exposed above, are presented in the following figures.

In figure 4 is presented the evolution of the luminosity - *L**, in figure 5 the evolution of the *a** parameter, and in figure 6 the evolution of the *b** parameter.

The changes in CIELAB properties appear after 50 h under UV radiation, for the raw walnut food oil.

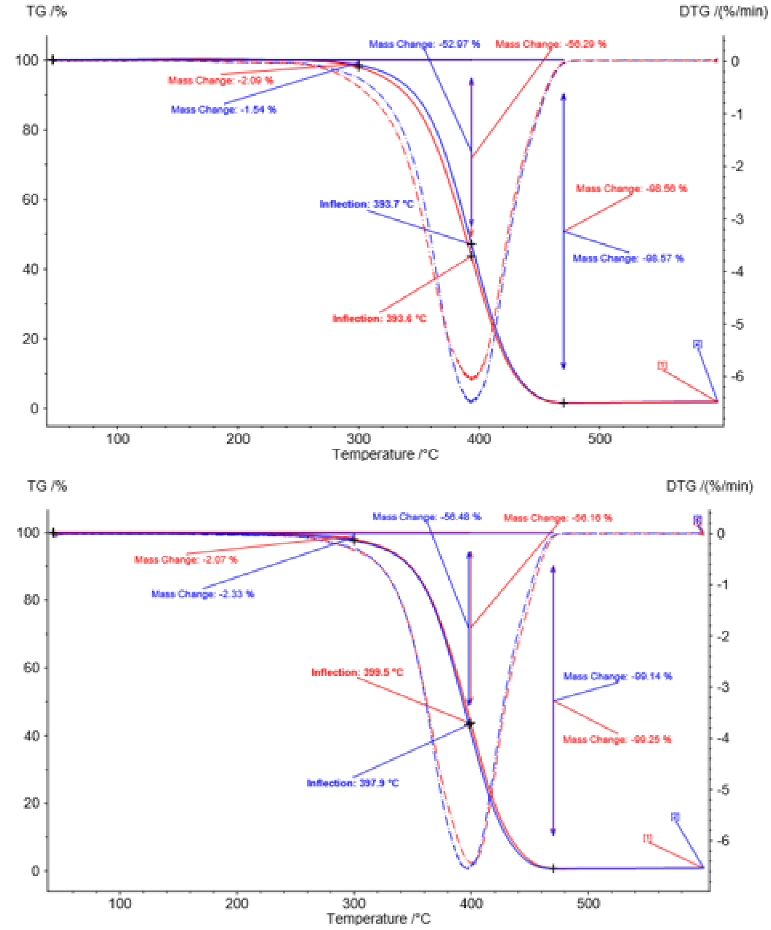


a



b

Fig.7. Comparing the TG/DTG curves 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

d

Fig.7. Comparing the TG/DTG curves for the raw oil and the oil with extract for the different periods of exposure to UV light; c) 30 min of exposure after 48 h; d) 30 min of exposure after 72 h

It can be observed that the CIELAB characteristics: luminosity - *L**, parameter *a** and parameter *b** are more stable when the walnut oil is treated with the extract.

The TG/DTG curves of the walnut raw oil and of the walnut oil with extract are presented in figure 7. In all the cases the following results were obtained:

-until 300°C the mass loss was in very small amount, between 1.3 and 2.33%

-a major decomposition process appear during 392 to 400°C, with a mass los between 49.99 and 56.29%

-total mass los appear at 470°C

Conclusions

The experiments reveal that storage conditions, which depend on UV radiation, affect the quality of the food oil, modifying its color, 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 walnut 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 not influenced by addition of antocyanin extract to the walnut oil under the radiation process.

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