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Overall color parameter as a parameter determining the level of oxidation of olive oil

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ABSTRACT

Edible fats are an important part of a human daily diet. They have a significant effect on the proper functioning of the human body. During frying, the oil is chemically modified and the fats consumed should have the highest oxidation stability. The subject of the study were samples of olive oil bought at local markets in Gdansk. Samples were heated at 20 °C, 60 °C, 100 °C, 140 °C and 180 °C. The aim of the study was to determine the differences in the level of oxidation of selected edible oils which were heated. Studies were performed using spectrophotometric techniques. The dependence between the level of oxidation of the olive oil samples and the value of the overall color parameter was determined. Based on the results obtained, the lower value of the color parameter overall, means that the oil is more degraded. The used procedure is characterized by an uncomplicated and low cost consuming stage of the preparation of the sample for analysis and also enables rapid analysis.

***Keywords*:** analytical chemistry, food analysis, edible oils, olive oil, overall color parameter, thermal degradation

1. INTRODUCTION

Growing consumer awareness about the role of fats in the daily diet of man has increased the consumption of vegetable oils. Consumers are beginning to see edible oils not only as a source of energy but also as a pro-health food [1]. They are supposed to deliver polyunsaturated fatty acids and fat-soluble vitamins to the body [2]. It is important to consume oils of the highest quality. Vegetable oils are most commonly used in the frying process. This is a type of food processing technique. It involves the heat treatment of food submerged in animal fat or vegetable oil. The temperature of this process usually ranges from 150 °C to 190 °C [3]. During frying, the oil undergoes degradation due to chemical changes: hydrolysis, oxidation, cyclization and polymerization reactions. During this process, a number of thermal degradation products such as aldehydes, ketones, esters, alcohols, alkenes, alkanes, aromatic hydrocarbons or short chain carboxylic acids are formed [4,5]. The resulting chemical compounds are responsible for the desired flavor, taste and color of the fried food, and for its crispy texture. Some of these substances, such as PAH compounds, however, exhibit mutagenic properties and can cause cancer [6,7]. On the other hand, chemical compounds such as aldehydes can contribute to diabetes or atherosclerosis [8]. It is essential that edible oils used in the frying process of the food have a high oxidative stability and low amount of oxidation catalysts such as metals such as iron, nickel, copper, water or free fatty acids [9].

Olive oil is a very valuable vegetable oil. It is well-known and used worldwide [10]. Mediterranean region accounts for about 98% of all olive trees grown around the world. The largest producers of olive oil and its consumption are responsible for the Mediterranean countries, i.e. Greece, Spain, Portugal, Italy, as well as Algeria, Morocco, Syria, Tunisia and Turkey [11]. European Union countries are the largest producers of olive oil, including Spain, Italy and Greece. Other big producers of olive oils are countries in the Middle East (Turkey, Syria, Lebanon, Israel) and North Africa (Tunisia, Algeria, Morocco, Libya) [12].

Olive oil is an oil obtained from the fruit of an olive tree using mechanical and chemical methods, as well as mixing with other types of oils [13]. The nature and quality of the oil determines its chemical composition. The oil production process determines its chemical composition. Important factors are: olive-growing, olive variety, olive-ripening stage at the time of harvest, oil processing.

Oxidation of triglycerides and their derivatives in olive oil results in changes in chemical, nutritional and sensory properties of oil that affect oil quality [14,15]. In accordance with the applicable norms [16,17] peroxide value, extinction K_{232}, K_{270} and sensory evaluation serve to assess the oxidative degradation of olive oil. Other reference methods used to evaluate oil quality are: oxidative stability determination using Rancimat Test and determination of fatty acids by gas chromatography. However, these are time-consuming methods, as well as requiring expensive and complicated apparatus facilities.

The aim of this work was to present a research methodology to determine the level of oxidation of samples of olive oil. The procedure used is characterized by an uncomplicated and low cost consuming stage of preparation of samples for analysis and also enables rapid analysis.

2. EXPERIMENTAL

2. 1. Materials

The object of study were the edible oils samples which were bought at local markets in Gdansk. Two types of olive oil have been selected: refined and extra virgin olive oil. For all refined and unrefined oils, three different producers were selected. Oil samples were stored in sealed containers at low temperature in a dark place. This was to prevent self-oxidation

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of oil samples. Samples of unrefined oils are more susceptible to self-oxidation, since their packaging is usually made of brown or green glass. This action is intended to reduce the possibility of fat degradation due to the effects of light radiation. Refined oils are less susceptible to oxidation because during refining process they are purified from chemicals which could reduce the durability of edible oil. This way these oils can be stored longer, even in plastic, transparent packaging.

2. 2. Sample preparation

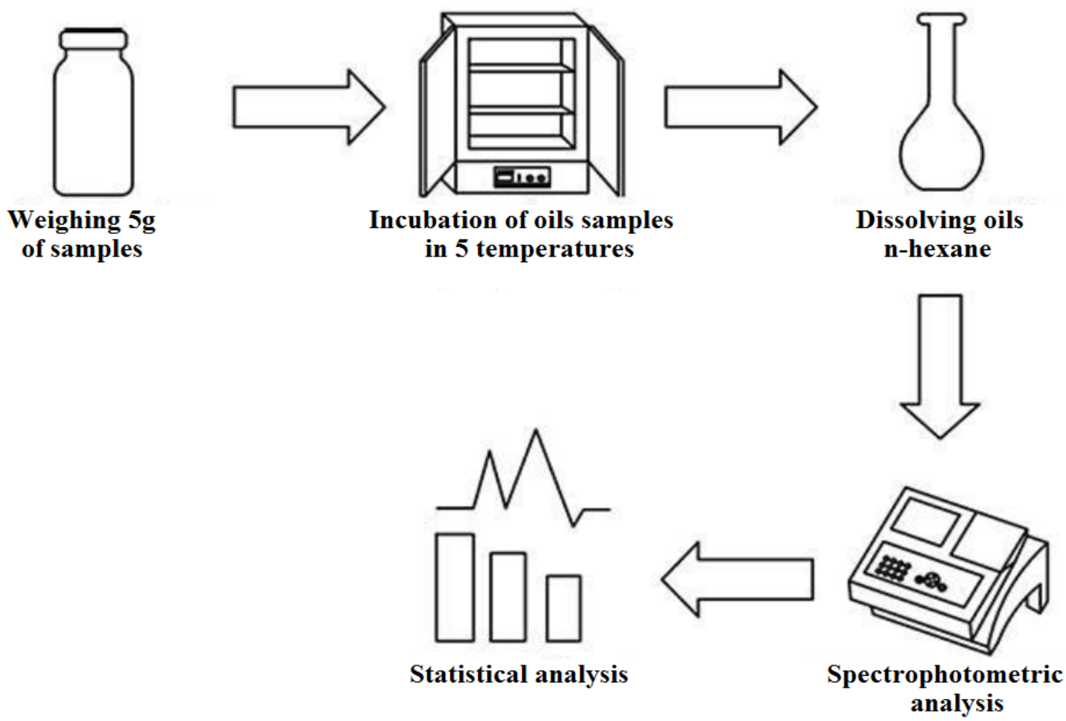

Figure 1. Diagram of the analytical procedure

The analytical procedure presented in the study consisted of five basic stages. The first two steps consisted in weighing the appropriate sample amount of selected edible oils (5 g) into 20 ml glass vials. The vials were capped with a Teflon seal. The samples prepared were heated for 24 h at 5 different temperatures (20 °C, 60 °C, 100 °C, 140 °C and 180 °C). Heating caused thermal degradation of the samples. After incubation of the oil samples, was the weighing the corresponding amount and then dissolve them in n-hexane (99%, POCH S.A.). Such mixtures were subjected to spectrophotometric analyzes. The last step was the interpretation of data. The diagram of the analytical procedure used is shown in Figure

2.3. Determination of the overall color parameter in olive oil samples

The requirements for the determination of the overall color parameter for refined oils are laid down in Polish Standard PN-A-86908:2000 [18]. In this work, the values of this parameter were studied for both refined and unrefined oil samples to compare differences in

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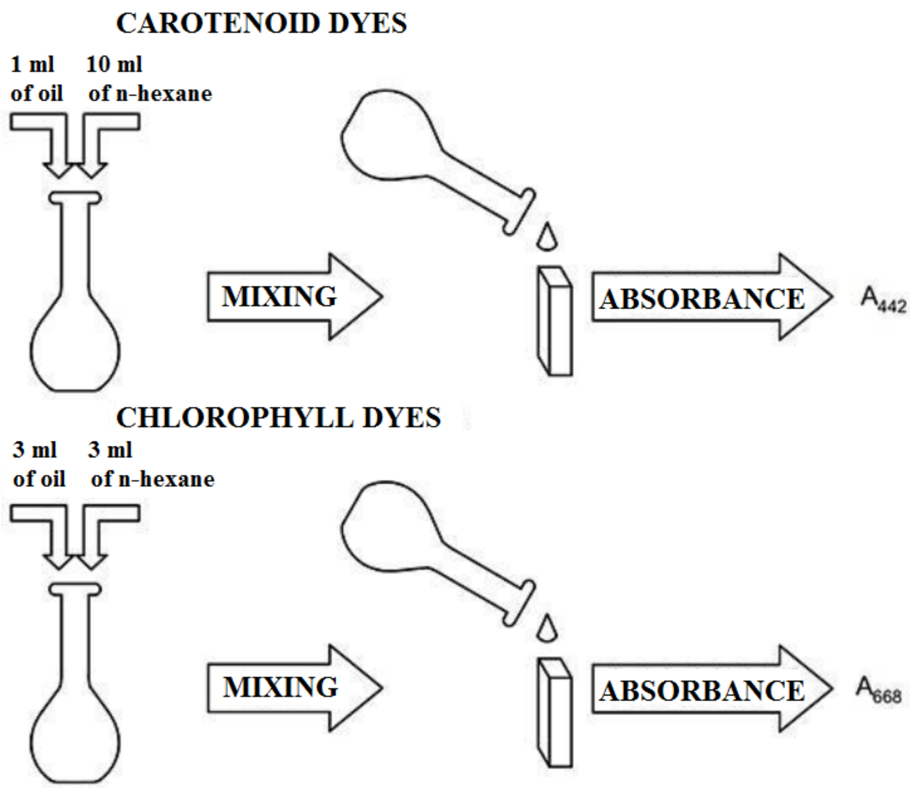
the color content of these oils. Using the procedure described in the abovementioned standard, the oxidation stability of the sample can be estimated. Calculation of this parameter is not time-consuming. The principle of the method of determining the value of the overall color parameter is shown in Figure 2. When studying this parameter, absorbance is measured for diluted oil samples at specified wavelengths in the visible light range.



$$B = 1000\ (A_{442} + A_{668})\ [-]$$

Figure 2. Diagram of the analytical procedure

Pharo 300 Spectrophotometer (Merck) was used to measure the absorbance of the prepared solutions. Absorption measurements were performed at 442 nm for carotenoid colorants and at 668 nm for chlorophyll colorants, respectively. Determining the value of the overall color parameter does not require special measuring conditions.

3. RESULTS

Monitoring of carotenoid and chlorophyll colorants in oil samples is very important because these substances contribute to lowering the oxidative stability of oils. Chlorophyll dyes are considered oxidation catalysts [19-21] but carotenoid dyes can act as antioxidants

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[22-24] but also as pro-oxidants [25,26], depending on the conditions in which the oil is stored or the oil being treated.
The Figure 3 shows the change in oil color depending on the sample heating temperature. As the temperature of the sample incubation increased, the color of the oil became brighter.

Figure 3. Photo showing the color change of samples of refined olive oil depending on the temperature of their incubation (from the left: 20 °C, 60 °C, 100 °C, 140 °C and 180 °C)

After performing the spectrophotometric analyzes, the results are presented as the dependence of the overall color parameter on the incubation temperature of the oil samples (Figure 4) or as the dependence of carotenoid and chlorophyll dyes content in the oil samples on the incubation temperature of these samples (Figure 5).

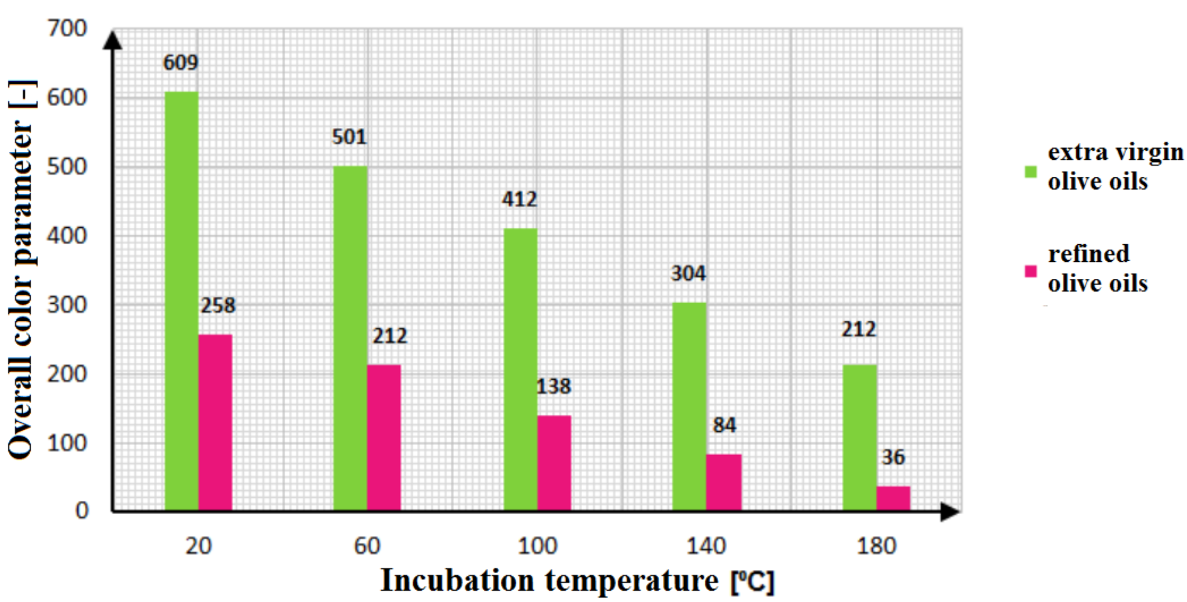

Figure 4. Dependence of overall color parameter on incubation temperature of refined and unrefined olive oil samples

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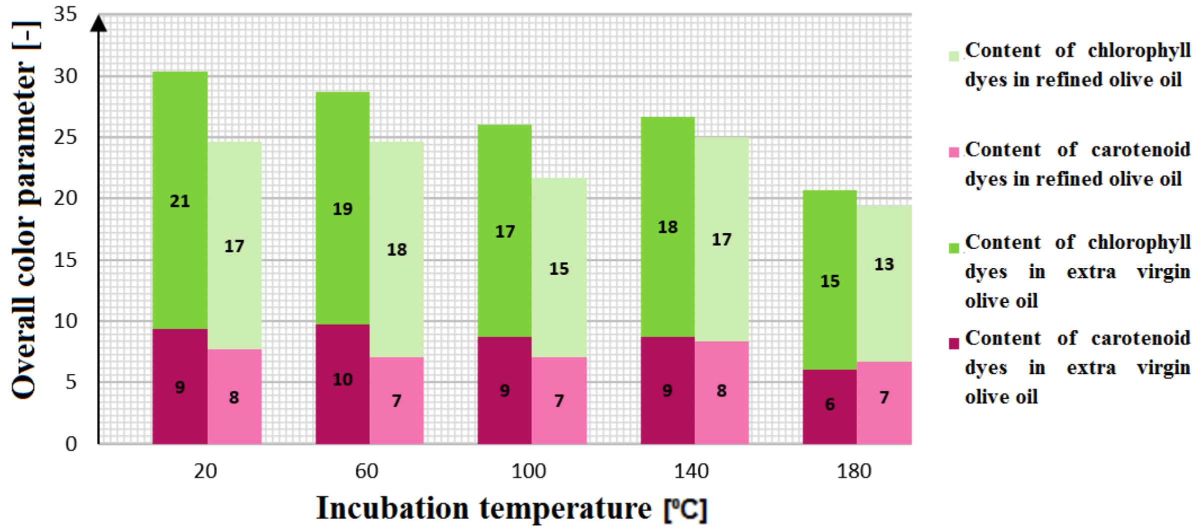

Figure 5. Dependence of the content of carotenoid and chlorophyll dyes on the incubation temperature of refined and unrefined olive oil samples

The use of the reference method described in PN-A-86934:1995 [27] allowed for a defined value of the overall color parameter for selected olive oil samples subjected to thermal degradation. Carotenoid and chlorophyll colorants were also investigated during the study. As the incubation temperature of oil samples was changed, the values of the overall color parameter of the oils were also changed. The higher the incubation temperature of the samples, the less the content of dye contained therein. This indicates the low stability of chlorophyll and carotenoid dyes. Based on the data presented in Figure 4, it can be seen that samples of extra virgin olive oil had a much higher overall color value than refined olive oil samples. This is due to the fact that the refined oils are subjected to adsorption bleaching, so that the dyes contained therein are removed [28]. Based on Figure 5, it can be seen that, in all olive oil samples, both refined and unrefined, the proportion of chlorophyll dyes was significantly higher than that of the carotenoid pigments. These results are consistent with the literature [29], the high content of chlorophyll dyes in olive oil is responsible for its greenish color.

4. CONCLUSIONS

Based on the results obtained, the lower value of the overall color parameter, means that the oil is more degraded. The method used to evaluate the quality of edible oil using spectrophotometric assays enables rapid analysis without the need for costly analytical equipment. The overall color parameter is not a sufficient indicator of the quality of oils subjected to thermal degradation. Despite the fact that dyes are non-volatile compounds and do not form part of the volatile fraction of edible oil samples subjected to thermal degradation, they have a significant effect on the oxidation of oils. Reducing the content of dye in oil samples due to the effects of high temperature may mean that these dyes have

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been converted into derivatives. This was due to the oxidation of other substances present in the sample. Therefore, it was decided that in the future, the results obtained from the spectrophotometric analysis will be compiled with the results obtained using gas chromatography technique, which is one of the reference methods.

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