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Research article

Changes in the fluorescence excitation and emissions spectra of heated and frying rapeseed oil and sunflower oil

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Abstract: *Frying is a popular method of cooking (meals preparation). Heating and deep-fat frying cause a series of chemical reactions, such as oxidation of polyunsaturated fatty acids and vitamin E, as well as formation of trans isomers and products of peroxidation. These chemical reactions cause organoleptic and nutritional changes in the product, which may have a negative effect on health. For this reason, the usefulness of many methods for evaluation of refined oils quality is investigated. The fluorescence spectroscopy is increasingly used for this purpose. The aim of the study was to monitor the changes in emission and excitation spectra of refined rapeseed oil and sunflower oil after processes of heating and frying frozen French fries. The obtained results show the differences between the shapes of fluorescence excitation and emission spectra of both oils due to the two processes and these changes depend on duration of both processes. This study indicates that fluorescence spectroscopy is a promising method for evaluation of changes in oils during heating or frying.*

Keywords: *fluorescence spectroscopy, vegetable oils, deep frying.*

Introduction

Vegetable oils are most often used in cooking, both in households and the food industry, due to the speed of preparation of dishes and the unique organoleptic qualities of the obtained products [1]. The general consumption of frying products, however, raises a lot of controversy, especially among doctors and dieticians. High temperatures used during frying in the presence of oxygen and water cause a number of significant chemical changes in fats. As a result of interactions between fats and fried ingredients, numerous compounds are also formed (cyclic fatty acid monomers, epoxides, some hydroxy acids) that have a negative effect on human health [2]. The biggest threat to health are secondary oxidation products, which are characterized by high biological activity. As a result of a series of reactions occurring during frying, the aldehydes, ketones and

acids that are formed damage cell membranes, intracellular structures and have cytotoxic and atherogenic properties [3]. Due to the popularity and high consumption of fried products (including French fries) among children and adolescents, the described impact of harmful substances on the human body becomes more important. A large number of households, catering units and industrial plants use vegetable oils multiple times, and in addition, they prefer cheaper products, not dedicated to use during frying. Using frying oil for several times results in a significant deterioration of the taste and health values of the prepared products. However, a properly prepared dish should be prepared during a single use of a portion of oil dedicated for frying.

Despite the documented negative impact of frying products on health, there still is a shortage of regular actions to control the quality of oils used to prepare dishes in catering business. That is why it is worth developing simple and quick methods allowing both the identification of frying oil and the number of thermal processes in which it was used. This decides about its suitability for consumption, and thus the safety of the consumer.

Currently, chemical and instrumental methods are used in food analysis processes. Instrumental methods based on spectroscopic methods are becoming increasingly important among analytical methods and they are successfully used to study various groups of food items, including vegetable oils [4]. Spectroscopic methods are based on measurements of absorption and emission of radiation of product components. According to Sikorska et. al. [5] methods based on the measurement of radiation emission show greater selectivity and sensitivity in comparison with absorption methods. The use of emission methods for analytical purposes is possible due to the natural occurrence of fluorescent compounds in food products or the addition of appropriate fluorescing or emission inducing compounds to them. Natural fluorescence is a characteristic feature of organic compounds having an aromatic nature or having conjugated double bond systems. In vegetable oils, absorption and emission properties are observed among others in phenolic compounds, tocopherol, chlorophyll, thermal oxidation products and oleic acid, which allows the use of spectroscopy in direct evaluation of their quality [4, 6]. So far, however, few papers have been published presenting the results of spectroscopic evaluation of vegetable oils subjected to frying and heating [7, 8, 9, 10, 11, 12]. In view of the above, a study was conducted to assess the changes in emission spectra and excitation of refined rapeseed and sunflower oil subjected to a frying process without and with the addition of frozen fries.

Experimental

Materials and Methods

The heating and frying process

The subject of the research were two refined vegetable oils i.e., rapeseed oil and sunflower oil. The tested products with a shelf-life date were bought at a local store at random. The tested material in the amount of 0.7 ml was placed

in a quartz cuvette of thickness: 1 × 1 cm. The samples were not diluted. The total number of samples tested was 10. The control test was fresh oil, not subjected to heating processes. The remaining samples were subjected to a frying process four times without and with the addition of frozen French fries.

The process of heat treatment of oil and frying French fries was carried out separately for both types of oils tested. In the KENWOOD deep fryer, the DF-150 model, a litre of the tested oil was poured and subjected to a heating process without fries at 190°C for 10 minutes, then the oil was cooled to room temperature. This procedure was carried out four times. Next, each type of tested oils was heated together with frozen French fries. For this purpose, a litre of fresh oil was added to the deep fryer, and then 200 grams of frozen fries were added. The frying process was repeated four times using the same oil and each time a new batch of fries. The frying time for French fries was 10 minutes at 190°C. After each frying operation, the oil was allowed to cool down to room temperature (about 23°C) and subsequent analysis. Fluorescence measurements were taken within 24 hours of completing sample preparation. Before the spectroscopic tests, the material was stored in a refrigerator at a temperature of about 4°C.

Measurements

Examination of the prepared samples of rapeseed and sunflower oil was carried out in three following steps: (a) the measurements fluorescence excitation and emission bands of the oil in the native state (without heating), (b) the same measurements after each heating of the oil itself (no fries) to a temperature of 190°C and (c) the same measurements after each process of frying French fries. Fluorescence spectra were measured with a Perkin Elmer LS 50B spectrofluorometer using excitation with waves of the following lengths: 290 nm, 320 nm, 375 nm, 405 nm, 450 nm. Excitation spectra of oil samples were recorded at wavelengths: 320 nm, 380 nm, 440 nm, 500 nm. The measurements were performed in the front-face geometry. The results obtained were developed using the OriginPro 9.1 (OriginLab, USA). The choice of wavelengths was made on the basis of the absorption and emission bands of the native fluorophores of both oils (see e.g. [5]).

Results and Discussion

Figs. 1 and 2 show the examples of collected fluorescence excitation and emission bands of rapeseed oil (RO) and sunflower oil (SO). In both cases, the emission bands of not heated, heated and fried oils samples were excited at the wavelength 290 nm, while the excitation spectra of all samples were recovered at the detection wavelength of fluorescence at 500 nm.

Fig. 1A represents the fluorescence emission bands of rapeseed oil and sunflower oil obtained for not heated samples (0x heated), heated four times (4x heated) and fried four times (4x fried). Both oils differ evidently in the shapes of their emission bands. They exhibit two maxima, i.e. at around 330 nm and around 420 nm, but with the opposed relations between the fluorescence intensities I_{330} and I_{420}, that is, $I_{330} < I_{420}$ for rapeseed oil and $I_{330} > I_{420}$ for sunflower oil. This

manifests different molecular composition of both kinds of oils under study. In Fig. 1B are shown, for a comparison purpose, the emission bands recorded for rapeseed oil and sunflower oil samples fried two times (2x fried) and four times (4x fried). The experimental data presented in Figs. 1A and 1B display evident changes of the emission spectra of all the oils samples studied and subjected to heating and frying of frozen fries. Both oils differ in the tendency of changes of the fluorescence intensities I_{330} and I_{420} under the heating and frying processes, namely in case of rapeseed oil I_{420} decreases but in case of sunflower oil I_{330} increases.

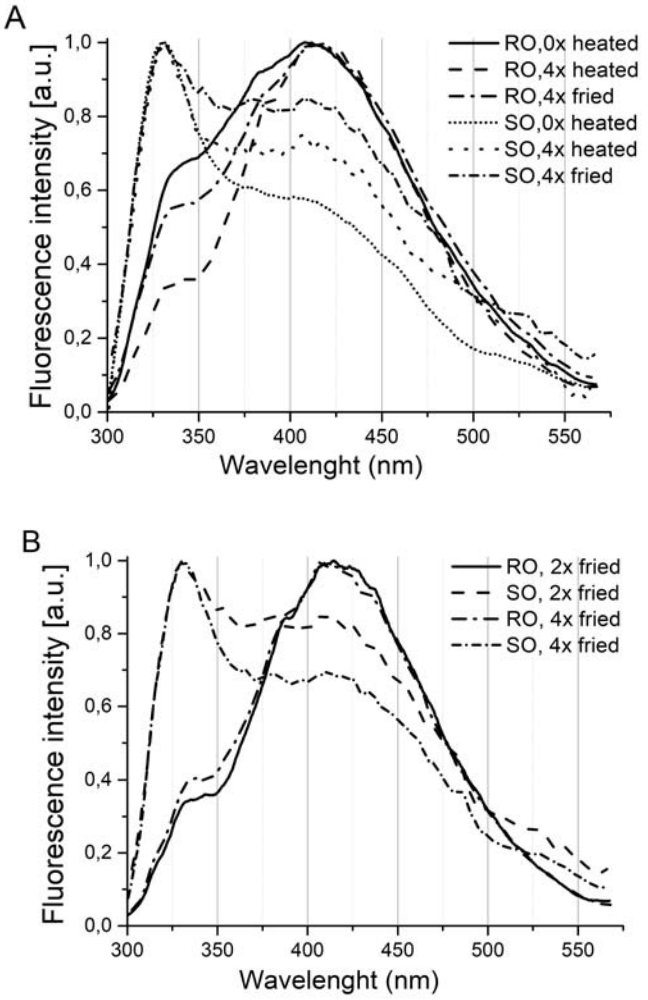

Figure 1. Changes of fluorescence emission spectra of refined vegetable oils (sunflower (SO) and rapeseed (RO)) subjected to the processes of heating and frying frozen fries. Emission bands collected at excitation wavelength 290 nm

In the excitation spectrum (λem = 500 nm) of sunflower oil, three bands are observed with a maximum of 323 nm, 342 nm and 385 nm for both the untreated sample as well the sample subjected to heating for four times (Fig. 2A). The obtained excitation spectrum of rapeseed oil, subjected to fourfold heating and frying French fries, can be characterized by the presence of four bands with maximum values at wavelengths of 310 nm, 325 nm, 360 nm and 390 nm (Fig. 2B). Characteristic bands with a maximum of 310 nm and 325 nm are not observed in the non-heated trial (Fig. 2A).

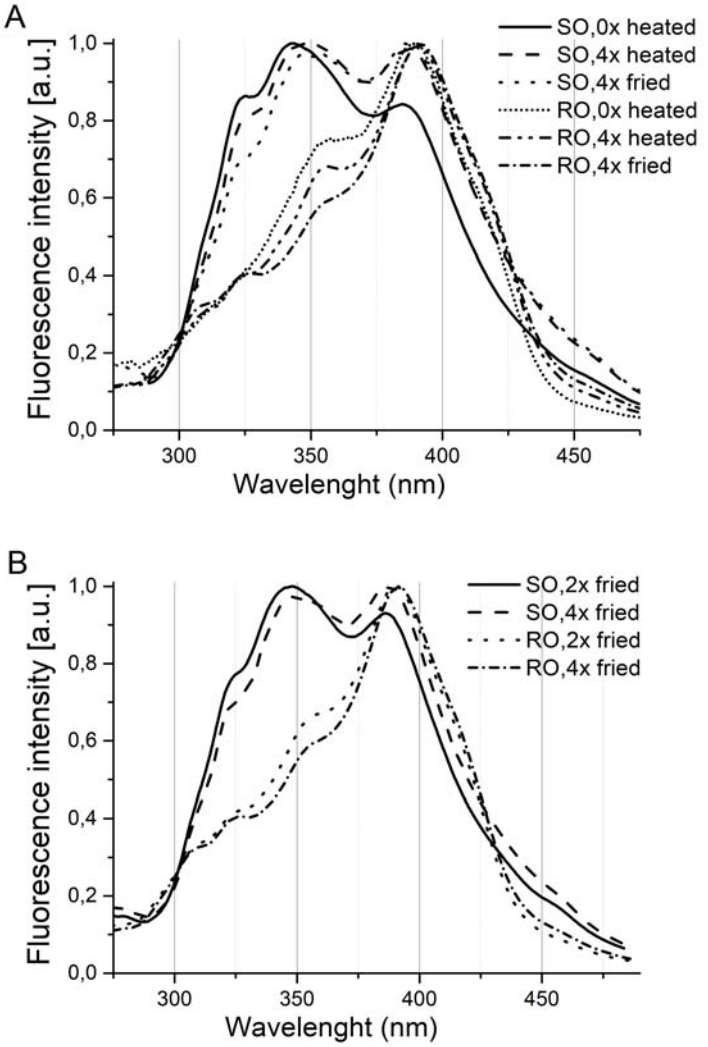

Figure 2. Changes of fluorescence excitation spectra of refined vegetable oils (sunflower (SO) and rapeseed (RO)) subjected to the processes of heating and frying frozen fries. Excitation spectra collected at emission wavelength 500 nm

During the frying and heating process in vegetable oils, there are a number of changes regarding natural ingredients and their products that can be monitored using spectroscopic methods, including fluorescence methods. Despite the underlined potential [4, 5] of fluorescence spectroscopy, only a few studies are available, in which this method was used to determine the degree of oxidation of oils in the heating process [6-8, 11-16, 18]. It should be emphasized that this paper focuses on the heating process and the frying of food products.

Tena et. al. [8], when analyzing olive oil, observed a decrease in the fluorescence intensity in the range of 300-380 nm along with the length of the heating time and a shift of the bands towards longer wavelengths. In contrast, in our own studies it was found that the intensity of emission spectra in the 300-350 nm range also decreased along with the heating and frying times, but without significant changes in the location of maximum values (Fig. 1A). The observed differences are attributed to changes in the content of individual forms of tocopherol and phenolic compounds [17]. Further test results using fluorescence spectroscopy methods to monitor the oxidation of vegetable oils (including sunflower oil), as discussed by Cao [18], may confirm the above observations. Cao [18] emphasized the relationship between the fluorescence intensity and the concentration of lipid oxidation products and the tocopherol concentration level. The increase in the intensity in the range of 400-500 nm is probably caused by the fluorescence of primary and secondary oxidation products. On the other hand, the change in intensity in the range 300-350 nm is the result of a decrease in the level of tocopherols and phenolic compounds. Similar results were presented by other authors. Cheikhousman [7] and Poulli [15] observed a decrease in the intensity of the bands corresponding to the tocopherol fluorescence and a simultaneous increase in the intensity of the bands in the region of 325-465 nm during heating.

Fluorescence spectroscopy due to its sensitivity and selectivity to organic and inorganic compounds has been recognized in many studies on photo-oxidation monitoring and thermal changes in vegetable oils.

In the light of these studies, fluorescence spectroscopy is considered an appropriate technique for assessing the oxidation state.

Differences in the spectroscopic values of the investigated oils as well as their changes occurring during heating and frying of fries demonstrated in the paper (Fig. 1A, 1B, 2A, 2B) suggest their potential in identifying the type of oil and the degree of its consumption (multiplicity of frying processes carried out on a single portion of oil), e.g. during the quality control of catering services. This may exert a significant impact on health, especially in relation to the risk of carcinogenic compounds formed during frying [19].

Due to the complexity of spectroscopic methods, as most authors, we were unable to avoid some methodological errors that could affect the correctness of the interpretation of the obtained results. Limitations of work include lack of fluorescing substances using chemical analytical methods and lack of analysis

of diluted samples. However, the purpose of this paper was to determine a simple, direct method allowing to indicate the degree of changes in emission and absorption spectra that occur under the influence of heating and frying for a particular type of oil. This paper does not discuss the pathomechanism of the material changes in the frying process. The study of undiluted samples was also dictated by the desire to obtain information on the emission of compounds present in small amounts or characterized by low fluorescence yield, which consists in obtaining a full spectroscopic image of the tested sample. Due to the fact that many chemical compounds that are naturally found in food products exhibit natural fluorescence, fluorescence methods can be an attractive tool for testing food. Currently, spectroscopic methods are used to assess the quality of – among others – vegetable oils, dairy products, and alcohol products.

Conclusion

1. Spectroscopic spectra of non-heat-treated rape and sunflower oils showed individual spectroscopic features characterized by changes in the intensity and shape of the emission and excitation spectra, suggesting the possibility of using this method to identify the type of oils.
2. Reducing the intensity of the emission waves under the influence of heating, both without and with the addition of French fries, suggests the use of spectroscopic methods in assessing the degree of consumption of frying oils.
3. Based on our own research and literature reports, it can be concluded that fluorescence methods can be used in the assessment of food quality and can be an alternative to the current time-consuming chemical tests.

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