Electrophysical methods for controlling the quality of vegetable oil in a digital economy

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Abstract. The article considers the possibility of controlling the quality of vegetable oil by electrophysical methods. In model experiments, refined sunflower oil sold in retail was selected as objects of research. During model studies, samples of vegetable oil were oxidized in air at a temperature of 120°C until the values of peroxide value (PV) were close to the maximum allowable 10 µE kg⁻¹. The dependence, allowing evaluating the effect of the polar products of vegetable oil oxidation on the change in the coordinates of the identification point, was determined by the results of these studies. When developing operational control of the degree of purification of vegetable oil at the stages of refining, samples were studied under industrial conditions. In each sample, the values of acid and peroxide values were determined, as well as the coordinates of the identification point. The technical result of these studies is the development of a single operational digital method to establish the degree of purification of vegetable oils with the requirements of current regulatory documentation at the stages of refining.

1. Introduction

The development of digital technologies in modern society has found wide application in various sectors of the economy—from industrial production to services that contribute to improving the quality of life [1, 2]. Digital technologies are rapidly developing in industries related to the production and sale of food products [3–6]. However, the digital transformation of food quality and safety control during production, storage and sale is difficult due to the lack of appropriate technological solutions for operational control methods.

When controlling the quality of food products, physicochemical methods are used, the implementation of which is possible only with the use of special equipment and professional engineers and experts. The lack of operational technological control of food quality can lead to the formation of toxic products and their use will harm human health. Vegetable oils are such foods.

Vegetable oils play a huge role in human nutrition, and are a source of unsaturated fatty acids and biologically active substances [7]. A complex technological process for the production of vegetable oils, including exposure to high temperatures, can lead to the formation of oxidation products in them. This may be offset by the presence of natural antioxidants [8, 9]. Thanks to natural antioxidants, vegetable oils retain their value when used in various food technologies [10]. However, the main assortment of vegetable oils in the trade is represented by refined deodorized oils, in which antioxidants are not enough to prevent oxidative processes.
Manufacturers store oilseeds or crude oil for its uniform production in accordance with consumer demand, for the continuous supply of vegetable oil to the population throughout the year. During storage and production, especially of refined vegetable oils, a series of transformations of a complex food system occurs with the likelihood of the formation of hydrolysis and oxidation products that are harmful to human health. Therefore, one of the important factors in ensuring the quality and safety of vegetable oil is the implementation of quality control during storage and at individual stages of production.

The number of operational methods for monitoring the quality of vegetable oil is currently limited. A multisensory system ‘electronic tongue’ with multidimensional processing of the obtained data was developed [11]. The system consists of four different chemical sensors that respond to a particular taste. Technically, this is implemented using a special microchip with millions of tiny channels designed to select molecules of a strictly defined size. A methodology for the rapid assessment of three indicators of the quality of vegetable oils using an electronic language and the optimization of oil sample preparation procedures for potentiometric analysis have been developed. Based on the studies, a regression equation was obtained that allows us to predict the values of peroxide and amides values and the concentration of total tocopherols. Similar electronic nose systems allow identifying the type of vegetable oil, which was studied using different types of olive oil as an example [12–14]. To identify the varietal origin of olive oil, it was proposed to use the method of capillary electrophoresis in PCR – RFLP based on single nucleotide polymorphism (SNP) [15]. As a result of numerous studies, the SNP database was created, including oil from 10 varieties of Greek olives [16–18]. Based on NMR and chemometrics, a computer expert system was created with a MATLAB script to assess the quality of oilseeds and vegetable oils at the stages of its production from the point of view of their botanical origin [19].

During the production of vegetable oils, the largest changes in its composition occur during refining under the influence of high temperatures. A spectral method based on the analysis of Raman scattering data that provides information on the structure of oils is proposed. Mathematically processed spectral data show that the greatest formation of thermal decomposition products and the loss of cis double bonds occur in sunflower oil [20]. All methods presented require the use of expensive equipment and cannot be used to automate the control of the quality and safety of vegetable oils in the production process.

The aim of the work is to study the possibility of using electrophysical methods to control the quality and safety of vegetable oil in the production process.

2. Methods
To study the possibility of using electrophysical methods in assessing the quality of vegetable oil, model experiments were carried out, and then quality control at different stages of production.

To conduct model experiments used refined sunflower oil of various manufacturers. Sunflower oil was purchased in the retail network: sample №1—Aston OJSC; sample №2—OJSC ‘Efko’; sample №3—LLC ‘Bunge CIS’, sample №4—LLC ‘Blago’. Sunflower oils were kept in a thermostat at a temperature of 20°C and 50°C and at 120°C for 5 hours for their oxidation.

The quality control of vegetable oil by the example of sunflower oil was carried out under the production conditions of OJSC Efko.

The determination of the electrophysical parameters of vegetable oils was carried out using a comprehensive analysis system (CAS) (figure1). CAS includes: 1—ultra-thermostat type LOIP LT–108; 2—a stainless steel heat exchanger connected with a thermostat for pumping a liquid heat carrier (water). A shielded glass beaker with an analyzed product and a sensor element is immersed in a stainless steel heat exchanger; 3—three-electrode capacitive sensor DP; 4—thermometer; 5—an auxiliary device for connecting the DP sensor to immittance meter E7–20 through coaxial cable connections (radio frequency cables) with a length of not more than 2 m; 6—immittance meter E7–20; 7—a metal screen without contact with the analyzed sample; 8—a glass cup made of heat-resistant
glass, the outer surface of which is covered with a thin metal screen that does not have galvanic contact with oil.

Figure 1. Comprehensive analysis system of electrophysical indicators of vegetable oils.

The electrical conductivity (G, S m⁻¹) was determined in vegetable oils at various frequencies of electromagnetic oscillations (F, kHz) in the range from 35 kHz to 100 kHz. The studies were performed in triplicate at two temperatures (22°C and 50°C). The results of observations of electrophysical indicators at various sinusoidal frequencies of electromagnetic waves were displayed on the screen of the E7–20 immittance meter and recorded in a computer. The intersection point of the curves obtained at different temperatures of vegetable oil was considered as an identification indicator (hereinafter identification frequency).

The peroxide value of vegetable oils has been determined according to ISO 27107:2008 ‘Animal and vegetable fats and oils. Determination of peroxide value’. The acid value of vegetable oils has been determined according to ISO 660:2009.

3. Results and Discussion
The method of analyzing the composition and quality of vegetable oils is based on the effect of the ability of liquids placed in an electromagnetic field to maintain constant their ability to conduct electric current—electrical conductivity (G, S m⁻¹) at a frequency of electromagnetic oscillations that is completely defined for each liquid (F, kHz) [21]. For further studies, it was assumed that this point is determined by the identification frequency (Fᵢ, kHz) and the identification specific conductivity (Gᵢ, S m⁻¹), and can serve to characterize the composition and quality of vegetable oil.

In sunflower oils with different temperatures, the electrical conductivity was determined at different frequencies of electromagnetic waves. According to the obtained data, curves were constructed (figure 2). For all samples of sunflower oil, the curve at 20°C intersected with the curve at 50°C.

The discovered fact of the conservation of the value of the identification electrical conductivity of vegetable oils at various temperatures and identification frequencies of oscillations indicates the formation of special supramolecular structures in the liquid under the action of a high-frequency electromagnetic field, in which strictly equal but opposite in direction of increment two types of characteristic active currents are instantaneously compensated. One of the types of active currents is
due to the amount of movement of the so-called ‘free’ charges (charge transfer current from electrode to electrode). Another type of current is due to the amount of motion (oscillations) of the ‘connected’ charges. It can be called bias current or orientational current. After the termination of the high-frequency electromagnetic field, these structures cease to exist [21].

Figure 2. The dependence of the electrical conductivity of sunflower oils on the frequency of oscillations of the electromagnetic field at two temperatures: --- at a temperature of 22°C; - - - at a temperature of 50°C.

Despite the fact that the studied oils were of the same type—refined sunflower oil, which has almost the same fatty acid composition, the identification points (figure 2) significantly differed in their coordinates. To check the influence of the quality of sunflower oil on the coordinates of the identification point, quality indicators were determined—acid value (AV) and peroxide value (PV) (table 1). AV is determined by the content of free fatty acids, PV—characterizes the content of primary oxidation products (peroxides).
Table 1. Quality indicators and identification electrophysical indicators of sunflower oil samples.

| Sample    | AV, mg KOH g⁻¹ | PV, µE kg⁻¹ | F₁, kHz | G₁, S·m⁻¹ |
|-----------|----------------|-------------|---------|-----------|
| Sample №1 | 5.9            | 9.8         | 95.0    | 33.3      |
| Sample №2 | 0.97           | 1.72        | 38.0    | 0.2       |
| Sample №3 | 1.5            | 3.80        | 56.0    | 12.0      |
| Sample №4 | 0.7            | 2.75        | 42.5    | 4.8       |

With an increase in the content of polar compounds in a particular sample of sunflower oil, not only F₁ but also G₁ naturally increase, that is, the identification point shifts to the right upward along the curve. With increasing values of AV and PV of sunflower oil, there is a tendency to increase the values of its identification frequency. This can be explained by the fact that with an increase in the content of polar compounds in particular vegetable oil, F₁, but also G₁, naturally increases.

In order to verify this assumption, the specific electrophysical characteristics of fresh oil were determined even after forced oxidation at a temperature of 120°C for 5 hours (figure 3) with simultaneous determination of AV and PV.

![Figure 3. The dependence of electrical conductivity on the frequency of oscillations of the electromagnetic field of sunflower oils, depending on the degree of oxidation.](image_url)

It was found that a change in PV (µE kg⁻¹) from 1.30 in oil before oxidation to 8.82 in an oxidized oil sample leads to a change in the values of F₁, kHz from 56 to 84.9. To assess the effect of free fatty acids (AV) on the change in the identification frequency and electrical conductivity of vegetable oil, experiments were conducted with refined sunflower oil, AV of which was changed by adding free palmitic acid. Based on the obtained experimental data, the dependencies of F₁ on the values of AV and PV were constructed (figure 4).

The dependencies of the identification frequency (F₁) on AV and PV were linear with correlation coefficients (R²) of 0.9728 and 0.9682, respectively. Identified dependencies can be very important in creating an operational diagnostics of the quality of oils at all stages of its production and storage. Operational and accurate control of vegetable oils during processing and storage according to the degree of oxidation has risen particularly sharply lately.
Figure 4. Dependencies of the identification frequency (F₁, kHz) of refined sunflower oil samples on quality indicators: a) — AV, mg KOH g⁻¹; b) — PV, µE kg⁻¹.

In the process of industrial cleaning (refining), vegetable oils are subjected to intense exposure using concentrated phosphoric acid, alkali solutions, special acidic adsorbents, high temperatures (up to 250...260°C), and hot steam. Because of these effects, a neutral taste and the absence of a specific smell of vegetable oils are achieved; their safety for the consumer and stabilization during storage is ensured. However, such active effects on vegetable oil change the ratio of the products of oxidation and hydrolysis at individual stages of the process, leading to the destruction of primary products and the accumulation of secondary oxidation products. As a result, the relationship between the content of the polar decay products and the electrophysical parameters of vegetable oils is significantly violated. For example, in the process of alkaline neutralization of vegetable oils, along with the removal of the bulk of free fatty acids in the form of soap, an undesirable partial saponification of the oil occurs with the formation of additional amounts of mono- and diglycerides, which accelerate the processes of further oxidation and lead to an increase in PV [8, 22].

Removal of peroxide compounds occurs at the stage of bleaching oil with bleaching clays; therefore, we have chosen this production stage to confirm the effect of the amount of free fatty acids and peroxide compounds to study the effect on electrophysical parameters (table 2).

Table 2. The limits of the main indicators established at the stages of the technological process of refining sunflower oil under the production conditions.

| Process stage                   | The limits of electrophysical indicators | The limits of the content of polar compounds |
|---------------------------------|------------------------------------------|-------------------------------------------|
|                                 | F₁, kHz                                  | G₁, S·m⁻¹                                  | AV, mg KOH g⁻¹ | PV, µE kg⁻¹ |
| Crude oil                       | 77.0…95.4                               | 28.0…33.6                                  | 1.5…6.0       | 7.0…10.0   |
| Oil after alkaline neutralization | 54.2…78.9                               | 11.4…28.4                                  | 0.4…2.5       | 3.0…8.5    |
| Oil after whitening             | 37.6…59.6                               | 9.4…16.6                                  | 0.2…2.0       | 2.0…6.0    |

After alkaline refining, the identification frequency decreases by 1.2–1.4 times, the identification conductivity by 1.2–1.3 times, after bleaching, and these indicators decrease further the identification frequency by an additional 1.3–1.4 and the identification conductivity by 1.2–1.6 times. The features of the course of refining processes can explain this at these stages.

Crude sunflower oil may contain free fatty acids and oxidation products in a wide range depending on its initial quality. At the same time, their electrophysical indicators are within well-defined limits. Alkaline neutralization leads to the removal of free fatty acids, which confirms a decrease in AV values of 3–4 times, but the binding and removal of peroxides occur to a lesser extent. The possible
formation of mono— and diglycerides at this stage can accelerate further oxidation processes. The less the oil contains free fatty acids and peroxides after alkaline neutralization, the lower the $F_1$ and $G_1$ values.

Before the bleaching operation using bleaching clays, the first task is to decompose and further remove the oxidation products. In addition, whitening further removes free fatty acids. This is important because free fatty acids are the most easily oxidized components of vegetable oils and their high content can lead to an increase in oxidation products during storage. In addition, the bleaching removes the residual content of phospholipids and soaps. All that leads to a decrease in the acid and peroxide numbers in the oil and their complete discoloration.

4. Conclusions
Vegetable oil is a complex food system in which oxidation products that are toxic to humans can form during production, storage and sale. The quality and safety of vegetable oils is controlled by chemical methods that do not allow the automation of this process and the accumulation of data in digital format.

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The experimental studies carried out on the example of one of the most easily oxidized oils, sunflower oil, showed that to control the quality of vegetable oil in digital format, specific electrophysical indicators—specific conductivity depending on the frequency of electromagnetic field oscillations can be used. It was established that, regardless of temperature, the oil has an identification frequency, which shifts only depending on its initial quality, associated with the content of free fatty acids and oxidation products.

At certain stages of the technological process (neutralization and bleaching), specific electrophysical indicators differ significantly and can be used for production control of the quality and safety of vegetable oil, which will increase efficiency and adapt processes to suit the needs of customers.

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