Pomegranate seed and peel powders are suitable for the production of pectin, oil, proteins and as biologically active additives for food enrichment.

Knowledge of the chemical composition and thermal changes of powders allows to control the technological regimes, yield and quality of the final product. As a result of the studies, the chemical composition and thermal properties of a finely dispersed pomegranate peel and seed powder subjected to heat treatment by X-ray diffractometry, IR-, EPR spectroscopy and thermal analysis (TG/DTG/DSC) have been carried out.

X-ray diffractometry showed that the crystal structures present in the original samples, when heated in air at 110 °C for 30 min. are destroyed and in all cases the samples pass into the amorphous state, a noticeable difference is found in the position and intensity of the observed bands in the spectra in the initial and heat-treated samples.

IR spectroscopy data show that drying the samples at 105 °C in air for 30 min leads to a significant change in the chemical composition of the powders. EPR spectroscopy showed the presence of paramagnetism in the samples and identified organic radicals and paramagnetic centers from Fe3+ ions. The features of the change in the chemical composition during drying of samples, which are characteristic of drying processes, namely, are the result by dehydration, dehydroxylation and denaturation of protein compounds that make up this process, have been established.

Temperature intervals (54.2–147.9 and 71.7–95.4 °C, 147.9–343.7 and 343.7–466 °C) associated with changes in the composition of organic compounds, contained in the powders were determined

Keywords: *pomegranate peel, pomegranate seed, thermolysis, IR-spectroscopy, EPR-spectroscopy, diffractogram, thermal analysis, temperature characteristic, thermal effect, food production*

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CHEMICAL COMPOSITION, THERMAL STABILITY OF POMEGRANATE PEEL AND SEED POWDERS AND THEIR APPLICATION IN FOOD PRODUCTION

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1. Introduction

In the food industry, namely in the juice, canning, oil and fat, wine, dairy and other industries, after processing the main raw materials at enterprises, a significant amount of secondary raw materials remains suitable for use for additional processing in order to obtain food compositions, additives and biologically active components. The latter are necessary not only to increase raw materials, but also to expand the range of food products, improve traditional technology and create new technologies in production [1, 2]. Pomegranate industrial processing extracts some of the hydrolysable tannins present in the fruit rind [3]. Studies have been carried out [4] where the process of extracting oil from melon seeds in a screw oil press is considered by the method of planning a full-factor experiment.

Thus, secondary products (waste) of the fruits of promising cultivated and wild food and medicinal plants, such as pomegranate and grape berries, licorice roots, etc., are rich in structure-forming gel-forming polysaccharides, protein, fat and biologically active substances, which, require compliance certain technological modes, knowledge of the thermophysical and thermoanalytical characteristics of the above components in the form of industrial preparations,

especially in the form of a powder. The use of raw materials and preparations in this form is necessary and appropriate for multi-purpose use, to create flexible technologies for the development of new types of products. Thus, the presence of industrial waste (secondary raw materials) from traditional and non-traditional types of raw materials in the form of a powder requires the study of their properties before and after processing, after obtaining fatty products, pectin, protein preparations, starch, food concentrates, etc. Under thermal exposure, fruits, vegetables and other plant materials and products of their processing undergo significant physical and chemical changes associated with their hydration and dehydration, dehydroxylation (water release), denaturation and splitting (destruction) of organic components. Thermal analysis methods such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) [5] in combination with IR spectroscopy, and EPR spectroscopy X-ray diffractometry, atomic absorption and emission spectroscopy, chromato-mass spectrometry can be effectively used to obtain information about the composition, kinetics and mechanism of thermolysis of food products [6, 7].

In this regard, the scientific topics for the study and use of recycled raw materials are always relevant.

Therefore, the study of industrial food waste (secondary raw materials) from traditional and non-traditional types of raw materials, such products requires the study of their properties before and after processing, after obtaining fatty products, pectin, protein preparations, starch, food powders deserves attention. A better understanding of the effect of temperature on properties of the main raw materials and processed secondary raw materials, the products of processing of the latter allows food manufacturers to optimize processing conditions and improve the quality of the final product [8, 9].

As it is possible to see, the topics of problems related to the study of the chemical composition and the influence of temperature processing conditions on the properties of secondary raw materials using modern physical methods are always relevant. Based on this, the characterization of the chemical constituents and thermal changes in the composition of powders obtained from industrial pomace, namely peel and seeds, using modern methods of X-ray diffractometry, IR and EPR spectroscopy, as well as thermal analysis methods, is timely and necessary. In this aspect, the topic of developing the issue of studying the chemical composition and thermal properties of garnet powders depending on the temperature intervals during drying is relevant, has practical and theoretical significance.

2. Literature review and problem statement

The studies related to the study and use of pomegranate peel and seed powders in recent years have mainly concerned the determination of the content and changes in bioactive components in various aspects, namely, depending on the type (method) of extraction and drying, the preservation of antioxidant and technological (water-retaining, emulsifying etc.) properties.

There are studies where pumpkin seed flour, konjac and low-gluten wheat powder were used as the base material, and maltitol was added as a sweetener to make healthy cookies that are high in protein, dietary fiber and low in sugar [10].

Other studies have determined the physicochemical and functional properties of pomegranate peel powder and seeds, where differences have been established between water-retaining, oil-retaining and emulsifying abilities [11].

In an article [12] studying the antioxidant activity of pomegranate peel powder and pomegranate seed powder with the determination of total phenol content, it was concluded that they can find several applications as functional food ingredients due to their antioxidant properties.

In addition to these works, a study was conducted with pomegranate peel, in terms of finding a replacement for the use of synthetic preservatives in meat product formulations in addition to imparting functional properties to finished products [13].

The effect of various drying methods and solvents for extraction on the extraction of the main biologically active compounds from modified peel powders of two types of pomegranate, which can be used in the food and pharmaceutical industries at high temperatures, was studied [14].

An interesting work was carried out with the separation of parts of the fruits (epicarp, mesocarp and stalk) of pomegranate in the temperature range of 7–45 °C, where their thermophysical properties were determined, which did not differ significantly [15].

A pomegranate juice pomace extract obtained by direct extraction with the participation of the peel was studied, where a powder from this pomace was obtained, which can become a functional ingredient in food products [16].

It has been shown that pomegranate peel and seed powder, having a rich chemical composition, simultaneously contains a profile of essential amino acids, including lysine, isoleucine and sulfur-containing amino acids, a high content of polyphenols should be directed to the technology of production and food preservation [17].

However, in them, the study of the thermal properties of these powders is complex in relation to the change in the chemical composition, temperature characteristics and thermal effects, and mass loss was not considered. In addition, in all of them, in addition to instruments and methods, various chemical reagents and others were used that were not economical.

A complex of experimental studies [18] was carried out to establish the effect of the mixing time of the components of nanocomposite materials on their thermal conductivity, heat capacity and density.

Due to the peculiarities of the composition and the multicomponent nature of products, incl. vegetable raw materials, it is necessary to combine a fairly wide range of methods, and in this case, in each case, analytical studies are required to some extent. The polymorphism of five new fat mixtures was studied by differential scanning calorimetry and X-ray diffraction [5]. Using the EPR method, one can determine the number of radicals, evaluate the mechanisms of redox chemical reactions in food products, the antioxidant capacity, stability and shelf life of food products [6, 7]. mentioned in the introduction. For example, the method of differential thermal analysis using a device for synchronous thermal analysis using the methods of differential scanning calorimetry (DSC) and non-isothermal kinetics, examines the state of moisture in the developed products [19, 20]. Since the dehydration process occurs in samples in a smaller temperature range, it is possible to determine the humidity – weakly and/or strongly bound water according to from experimental curves obtained by thermogravimetry,

thermal effects characterizing the dehydration process. A quantitative assessment of the ratios of moisture fractions with different bonds is determined from experimental curves obtained by thermogravimetry. In this case, the ranges of endothermic effects are determined, indicating a stepwise removal of moisture, in accordance with the forms and energy of its connection with the biopolymers of experimental samples. All this indicates the presence of bound forms of moisture by biopolymers of plant materials.

The data obtained make it possible to predict an increase in the shelf life of the studied systems, an improvement in their consumer properties and the preservation of the biopotential of all prescription components in them.

The thermogravimetry (TG) method provides control of the change in the mass of the test sample when heating or cooling in the temperature range corresponding to the phase transformations of moisture in the sample.

EPR spectrometry is a direct, highly efficient method for detecting free radicals and transition metal ions in food and biological systems. Free radicals can appear in many foods during processing.

EPR spectrometry can also be used to detect free radicals in products exposed to gamma and microwave radiation [6, 7].

An analysis of the literature on the study of plant waste from the food industry shows that despite numerous studies on the factors that determine the quality of secondary raw materials, they are often scattered due to the limited use of analysis methods, which does not fully reveal the picture of the internal change of the studied samples during processing.

Studies of raw waste in its natural state in the form of powders only after drying in a gentle mode open up new possibilities for their multi-purpose use.

A comprehensive diffraction, spectroscopic and thermoanalytical study using modern instruments and methods allows to actually trace in detail the state and properties of the studied powders in their natural form before they are used in production.

It is this approach, in our opinion, that is expedient for studying powders from the peel and seeds of pomegranate fruits from pomace under industrial conditions as an additional raw material for technological purposes.

However, despite the significance of such studies, in fact, secondary raw materials are studied by scientists after a certain change in their structure and composition due to preliminary preparation for analysis. Naturally, this will affect the results of the obtained data. In addition, the use of physicochemical or physical methods separately in the study of one or another secondary raw material does not allow a wider range to characterize their chemical composition and properties before the stage of use in food production.

To these it is possible to add the fact that at currently, there is no methodology for the rapid assessment of the technical properties of vegetable powders in terms of their structural-mechanical and thermo-analytical characteristics, taking into account their granulometric, chemical composition due to the type of feedstock or processed products.

As a rule, vegetable powders are a two-phase system of the "solid phase – gas" (TG) type, their properties are primarily determined by the size of dispersed particles and their chemical composition. Since the interaction of structure-forming elements is determined by the chemical nature of the surface of particles of the solid (dispersed) phase, which has a significant impact on the formation of structures in composite systems, the determination of the physicochemical (structural) and thermal characteristics of powders is essential in the developed technologies. At the same time, the study of the change in humidity for this purpose is also very important.

At the same time, many issues related to changes in raw materials and processed products specifically for each production, especially for powdered products, have not been sufficiently studied, they require the determination of the general chemical composition, their characteristics, and temperature processing conditions.

Taking into account the relevance of the use of food powders from vegetable raw materials, including those obtained from industrial pomace of pomegranate fruits, this paper investigates the issues of thermolysis of fine pomegranate peel and seed powders by thermal analysis methods in combination with IR and EPR spectroscopy and X-ray diffractometry.

It should be noted that the research on the application of thermal analysis methods, spectroscopy and X-ray diffractometry to the processed products of Azerbaijani pomegranate is limited in the literature. The use of thermal analysis methods for local raw materials was carried out by us only once in Germany with the participation of German scientists from the Institute of Food Technologies and Food Chemistry at the Technical University of Berlin, where the expediency of using industrial pomace from pomegranate fruits for the production of oil and pectin in industrial conditions is substantiated [21].

3. The aim and objectives of research

The aim of the study is the investigation of the chemical composition and the process of thermolysis of fine powders of pomegranate peel and seeds by thermal analysis in combination with the methods of X-ray diffractometry, IR-, EPR spectroscopy and use the results of this research in preparation of foods with these additives.

To achieve this aim, the following objectives are accomplished:

– the phase transformations of the structure of pomegranate seeds and peel powders as a function of the temperature and the time of drying were studied;

– the humidity and percentage loss in the tested samples of dry powders depending on the heating temperature were o determined;

– the effect of temperature on the pomegranate peel thermolysis process was studied.

4. Materials and methods of research

The object of these studies is the pomegranate peel and seeds which is prepared in the form of fine in the laboratories of the Department of Food Technology of the Azerbaijan State University of Economics from the raw materials of industrial enterprises "AZ-GRANATA" harvest of 2020 (pomegranate pomace: peels and seeds) using convective drying at a temperature 25–30 °C under normal room conditions. For comparison, dry seeds are also prepared at home from the fruits of sweet and sour pomegranate purchased at the "Safastore" supermarket in Baku.

It was suggested that the influence of heat treatment on the composition and mechanism of destruction of these

samples allows to develop the technologies of the using the additives in the food industry.

Dried samples of pomegranate peel and seeds from pomegranate pomace were ground to a powder in laboratory conditions. Photos from dry industrial samples of peel and seeds, as well as the studied powders from them are presented in Fig. 1.

Fig. 1. Samples from industrial pomace of pomegranate fruits: *a* – dry peels of pomegranate fruits from industrial pomace; *b* – dry seeds from industrial pomace of pomegranate fruits; *c* – powder from pomegranate fruit peels; *d* – powder from pomegranate seeds

The X-ray diffraction patterns, electron paramagnetic resonance and infrared spectra were recorded at room temperature using an X-ray diffractometer XRD TD 3500, China, an infrared FT-IR Alfa, EPR EMX-micro spectrometers, Bruker, Germany. Thermal analysis (TG, DTG, and DSC) of the samples was carried out using a thermal analyzer STA 409C, NETZSCH, Germany, with a temperature rise rate of 10 °C/min. the weight of the samples is approximately 16 mg [22].

5. Results and discussion of the study of the chemical composition and thermal changes of pomegranate peel and seed powders

5. 1. Effect of heat treatment on the X-ray patterns, EPR and IR spectra of the pomegranate peel and seeds powders

Fig. 2, 3 show powder diffraction patterns from pomegranate seeds and peels: fresh (Fig. 2) and after drying at 105 °C for 30 minutes (Fig. 3).

Comparison of the diffraction patterns shown in Fig. 2, 3 shows that the crystal structures present in the initial samples when heated in air at 110 °C for 30 min. are destroyed and in all cases the samples pass into the amorphous state. The process proceeds by dehydration, dehydroxylation of the sample, and possible denaturation of protein compounds, obviously with a change in the chemical composition.

EPR data. The original samples of garnet powders of various origins have similar EPR spectra (Fig. 4).

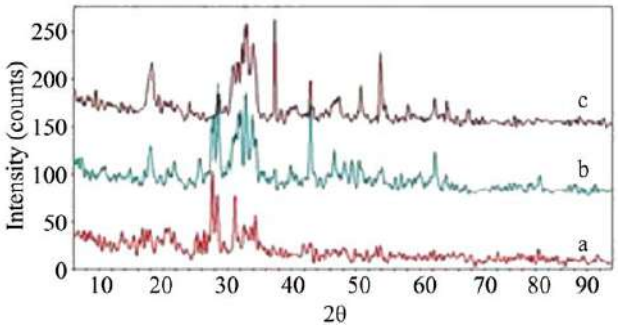

Fig. 2. Powder diffraction patterns from pomegranate seeds and peel: *a* – seeds from fruits (from the supermarket) of sweet and sour pomegranate; *b* – seeds from industrial pomace; *c* – pomegranate peels from pomace of industry

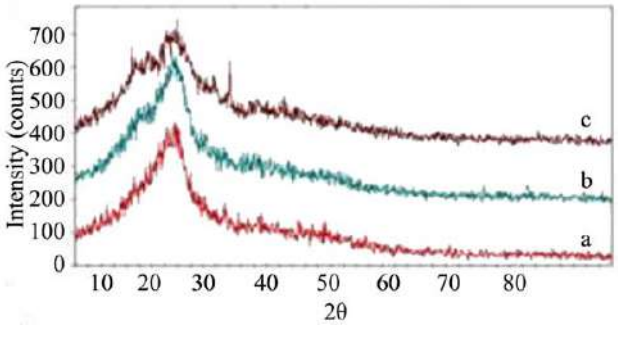

Fig. 3. Diffractograms of powders of pomegranate seeds and peels after drying at 105 °C for 30 minutes: *a* – pomegranate seeds; *b* – pomegranate seeds from industry; *c* – pomegranate peels

Recording conditions: HF amplitude of magnetic field modulation 10.00 Gs, microwave power 2.242 mW, microwave source frequency 9.784 GHz, field center 3000 Gs, temperature 298 K Fig. 4.

The presence of EPR spectra, first of all, indicates that the samples under study have paramagnetic properties. The EPR spectra of the initial samples of both seeds and barks are characterized by two types of signals. The first is wide, branched, and the second is narrow, almost isotropic. The first belongs to iron ions Fe^{3+} with different ligand environment and structure, and the second belongs to an organic radical (g=2.0034 ΔH=0.9 mT), most likely, phenoxy radicals (2.003–2.004) present in natural lignin. The concentration of these free radicals in these samples is ~10^{17} spins per gram of sample. The EPR spectra shows a line in the g=4.3 region due to the high-spin state of Fe^{3+} ions ($3d^5$ is an electronic state with a total electron spin of S=5/2) located in octahedral or tetrahedral positions with orthorhombic symmetry. Similar spectra are observed in low-symmetry iron-containing mineral matrices – in glasses, as well as clay minerals, etc. For these samples, signals with g=2.28 and 2.93 are also detected, which can also be attributed to Fe^{3+} ions in the magnetically concentrated phase. Thermal annealing of the samples in air for 30 min. at 300 °C leads to significant changes in the EPR spectra. So, in this case, the samples are carbonized with the formation of a significant amount of paramagnetic carbon structures and, most likely, superparamagnetic/ferromagnetic iron oxide/hydroxide formations ($g^1_{ave}=2.0$, ΔH=700–800 mT; $g^2_{ave}=2.3$, ΔH=300–400 mT).

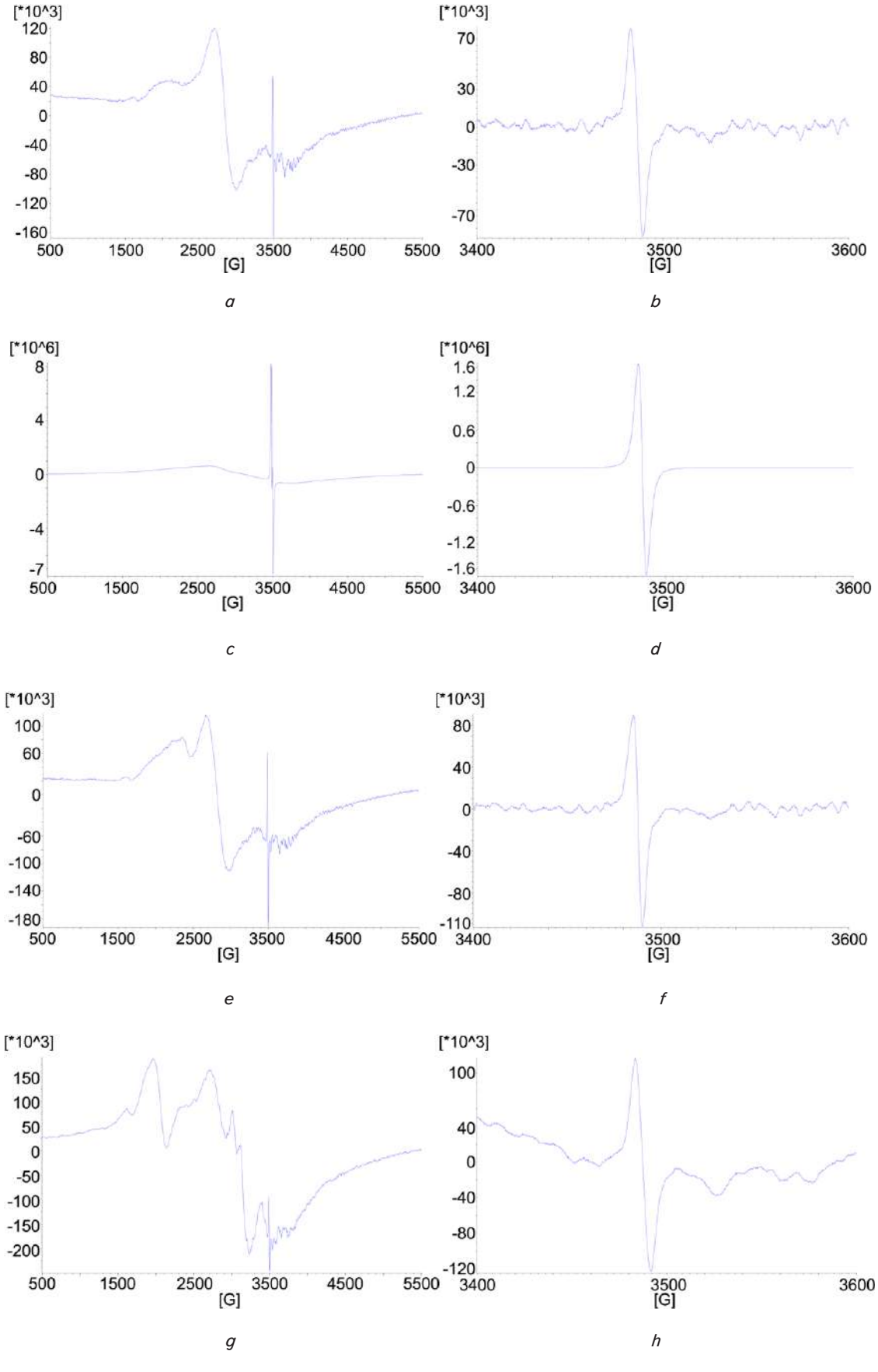

Fig. 4. Electron paramagnetic resonance spectra recorded at room temperature of the initial and heat-treated in air at 105 °C pomegranate powders of different origin: *a*, *b* — fresh; *c*, *d* — heat-treated in air at 300 °C, 30 min. Homemade seed samples; *e*, *f* – fresh samples of pomegranate seeds from industrial pomace; *g*, *h* — pomegranate peels (squeeze from the industry)

Note that the values of the g-factor (2.003–2.004) and the line width ΔH (0.6–0.9 mT) of organic radicals in the studied samples are typical for humic substances with oxygen functional groups, characterized by a significant delocalization of the unpaired electron on fragments with conjugated double bonds. During the natural carbonization of organic residues or, for example, its pyrolysis, the destruction of C–H, C–O bonds and the formation of condensed carbon rings occur, on the defects of which new carbon free radicals with a lower value of the g factor and EPR linewidth are formed. The EPR lines of carbon radicals of this type were recorded in the EPR spectra of all the studied samples. In the latter case, thermal annealing led to a sharp increase in the concentration of carbon radicals. The shape of the carbon radical line in the initial samples is almost purely Lorentzian function, while in the annealed samples, its inhomogeneous broadening is noticeable. The broadening of the carbon radical line in EPR spectra occurs as a result of the dipole-dipole interaction of unpaired electrons with protons, and the Lorentzian shape of the line indicates the aromatic nature of the structure of organic matter, delocalization of electrons, and averaging of its interactions with local fields of a large number of protons [11]. A detailed analysis of the carbon radical line in the original samples shows that the lines are well described by the Voigt function at a ratio of the widths of the Lorentzian and Gaussian forms equal to 0.8. It can also be approximated by the sum of a narrower Lorentzian and a broader Gaussian component with close g-factors in a 2:1 ratio of integral contributions.

FT-IR data. In the IR spectra in the region of 3800–2600 cm^{-1}, the frequencies of stretching vibrations of OH groups included in inter – and intramolecular hydrogen bonds, as well as CH_2 and CH_3 groups, usually appear. In the region of 1800–1200 cm^{-1}, the characteristic frequencies of the stretching vibrations of –C=O and –C=C– groups, bending vibrations of methyl and methylene groups, and also OH groups are mainly manifested. The maximum absorption peaks of the studied initial garnet samples are found in the frequency range 1100–1000 cm^{-1}. These bands may be due to fluctuations associated with the C–O–H group of some phenolic compounds (for example, primary and secondary alcohols), which are present in large quantities in berries and fruits of plants, incl. grenade. It should be noted that phenolic compounds are one of the numerous classes of secondary plant compounds that determine their biological value. The presence of phenolic compounds is also associated with absorption bands caused by stretching vibrations of free OH groups (frequencies 3670–3580 cm^{-1}), intra- and intermolecular H-bonds in dimers and polymers (frequencies 3400–3200 cm^{-1}), vibrations associated with C–O–H group: R–O–H (frequencies 1450–1250 cm^{-1}, 750–650 cm^{-1}), primary alcohols (frequencies 1075–1000; 1350–1260 cm^{-1}), secondary alcohols (frequencies 1125 –1030; 1350–1260 cm^{-1}), tertiary alcohols (frequencies 1170–1100; 1410–1310 cm^{-1}), phenols (frequencies 1270–1140; 1410–1310 cm^{-1}), vibrations of carboxylic acid groups: stretching vibrations of groups -COOH (frequencies 1760; 1725–1700 cm^{-1}), polygalacturonic acid with free OH groups (frequencies 3350–3500 cm^{-1}), bound OH groups (frequencies 3300–2500 cm^{-1}), these acids with any OH groups (frequencies 995–890 cm^{-1}), vibrations of C–O bonds (frequencies 1320–1210 cm^{-1}); C–O–C vibrations in aromatic acid esters (frequencies 1300–1250 cm^{-1}). The presence of carbohydrates is evidenced by bands due to stretching vibrations of CH_2 groups at a frequency of ~2937 cm^{-1}.

Fig. 5 shows the IR spectra recorded at room temperature of the initial garnet powders of various origins dried in air at 105 °C for 30 min.

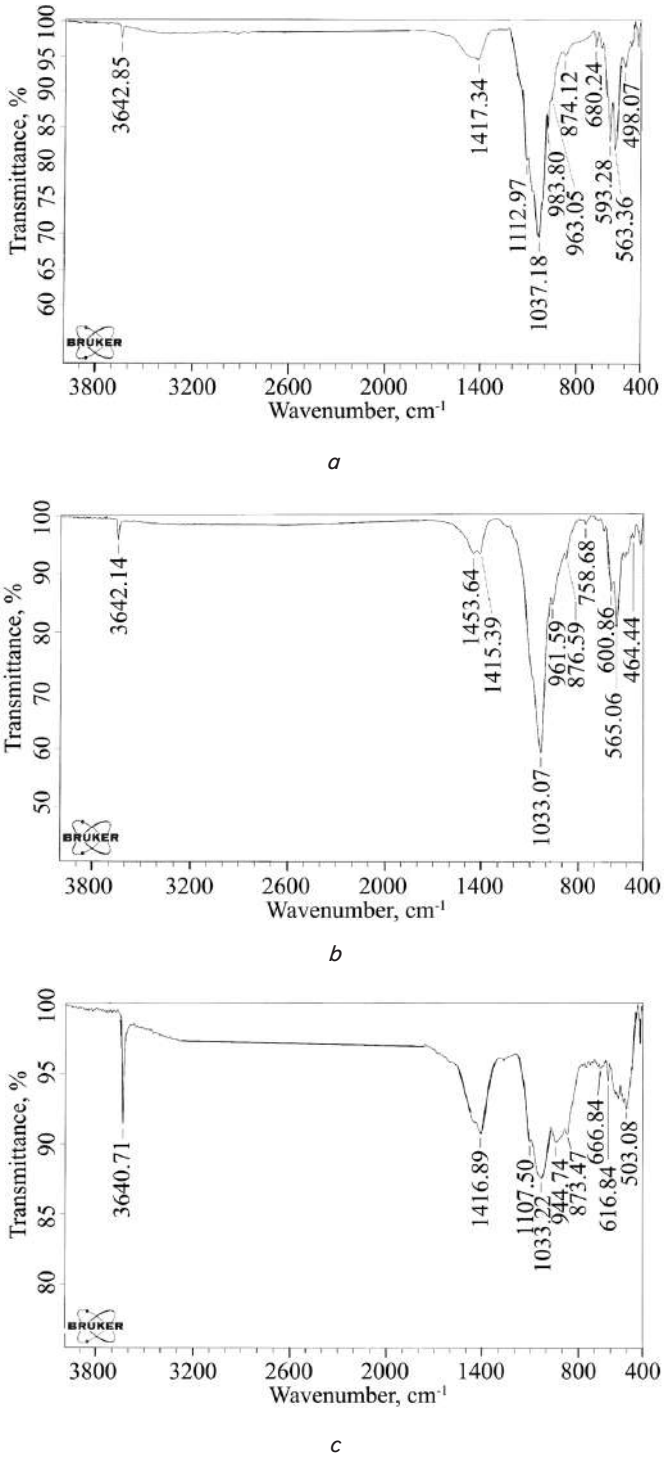

Fig. 5. Infrared spectroscopy spectra recorded at room temperature of initial garnet powders of various origins: *a* – seeds prepared at home, i. e. seeds from purchased fruits; *b* – pomegranate seeds from industrial pomace; *c* – pomegranate peels from industry, dried at 105 °C for 30 minutes

As can be seen from Fig. 5, drying of samples at 105 °C in air for 30 min. leads to a significant change in the chemical composition of garnet powders in all three cases. At the same time, there is also a noticeable difference in the position and intensity of the observed bands. So, in the region (3641±2 cm^{-1}) for all three samples, very narrow bands appear, namely at 3642.85 cm^{-1}, 3642.14 cm^{-1} and 3640.71 cm^{-1} for samples, respectively. These bands are characteristic of compounds with an OH group that are not associated with hydrogen bonds with other groups. Let's note that for these samples there are practically no bands characteristic of associated hydroxyl groups; OH groups linked together by intermolecular hydrogen bonds. There is also a noticeable difference in the position and intensity of the bands observed in the frequency range 1500–900 cm^{-1}.

5. 2. Determination of humidity and loss on ignition of powders from pomegranate seeds and peels

Humidity was determined by drying powder samples at 105 °C in air for 4 hours, loss on ignition was determined by holding powder samples in a muffle furnace at 850 °C for 4 hours, and the result of analysis was recalculated for samples dried at 105 °C. Moisture measurements (by mass in %) for samples of seeds from fruits (from the supermarket) of sweet and sour pomegranate – 5.57 %, seeds from industrial pomace – 5.78 % and pomegranate peel from industrial pomace – 8.82 % and losses (by weight in %) during calcination in air of the studied garnet powders, respectively, – 98.56 %, for the first, 98.74 % – for the second and 97.44 % – for the third.

5. 3. Temperature characteristics and thermal effects of the pomegranate peel thermolysis process

TG/DTG/DSC curves and data of pomegranate peel are given in Fig. 6–8 and Tables 1–3.

The DSC curve (Fig. 6–8) shows a broad and complex endothermic peak centered at 155 °C with a shoulder at 210 °C. This complex endothermic peak includes the processes of water evaporation, melting, dihydroxylation, decarboxylation, most likely, pectin, other polysaccharides, protein structures contained in the pomegranate peel.

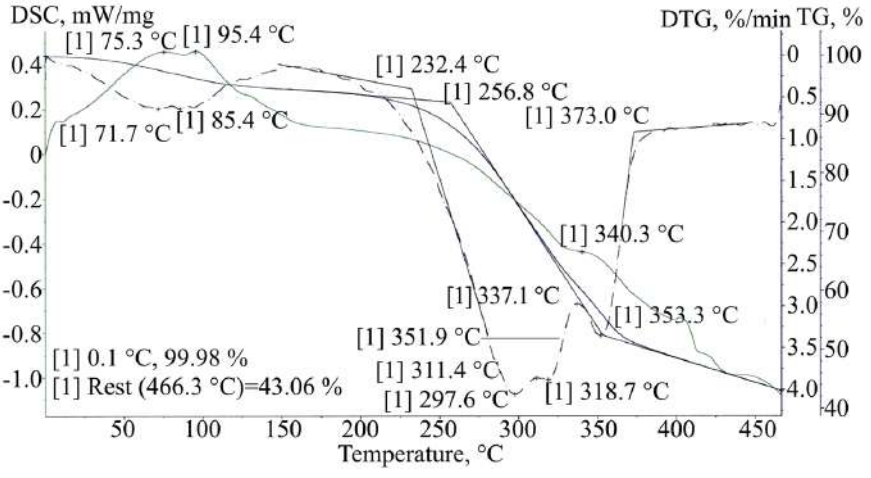

Fig. 6. TG/DTG/DSC curves of pomegranate peel powder: first region (54.2–147.9 °C)

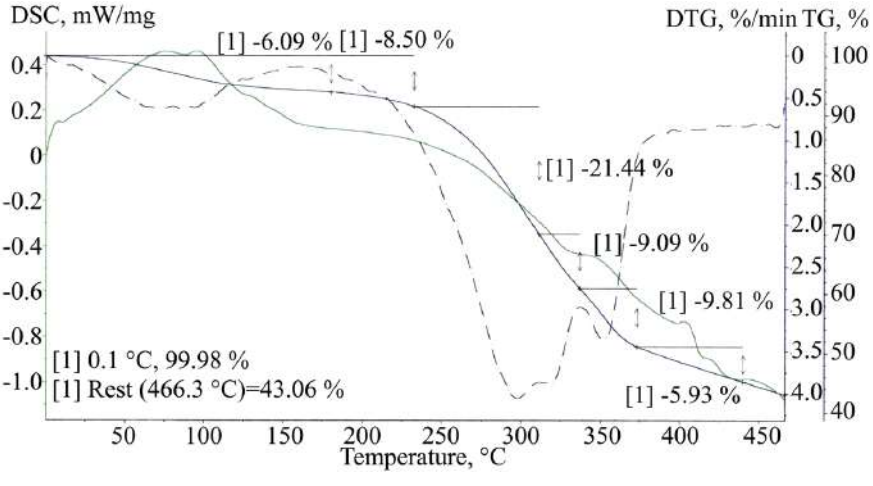

Fig. 7. TG/DTG/DSC curves of pomegranate peel powder: second region (147.9–343.7 °C)

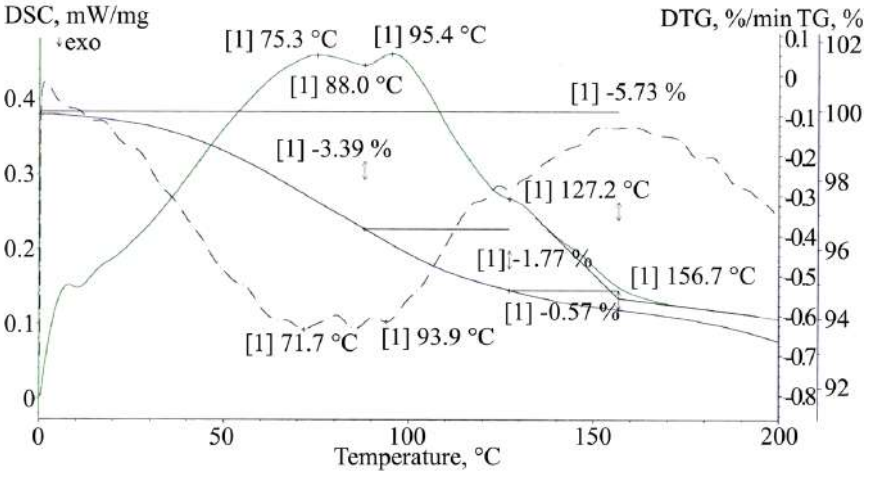

Fig. 8. TG/DTG/DSC curves of pomegranate peel powder: third region (343.7–466.3 °C)

Table 1

TG/DTG Data of pomegranate peel

Parameter	Result	Range (min)	Range (max)
Turning point	340.3 °C	322.4 °C	349.8 °C
Peaks	75.3 °C	54.2 °C	86.9 °C
Peaks	95.4 °C	89.2 °C	109.0 °C
Onset (DTG)	232.4 °C	147.9 °C	306.4 °C
Onset	256.8 °C	154.0 °C	310.2 °C
Final temperature (DTG)	373.0 °C	343.7 °C	445.8 °C
Final temperature	353.3 °C	281.2 °C	455.7 °C
Peak (DTG)	297.6 °C	282.0 °C	305.6 °C
Peak (DTG)	318.7 °C	312.4 °C	326.9 °C
Peak (DTG)	351.9 °C	346.7 °C	364.4 °C
Peak (DTG)	337.1 °C	331.5 °C	349.8 °C
Peak (DTG)	311.4 °C	299.5 °C	314.0 °C
Peak (DTG)	71.7 °C	52.7 °C	80.8 °C
Peak (DTG)	85.4 °C	80.8 °C	112.8 °C
TG	99.98 %	0.1 °C	–
Residual mass	43.06 %	466.3 °C	–

Table 2

TG Data of pomegranate peel

Parameter	Result	Range (min)	Range (max)
Mass loss	–6.09 %	0.1 °C	180.0 °C
Mass loss	–8.50 %	0.1 °C	232.4 °C
Mass loss	–21.44 %	232.4 °C	311.4 °C
Mass loss	–9.09 %	311.4 °C	337.1 °C
Mass loss	–9.81 %	337.1 °C	373.0 °C
Mass loss	–5.93 %	373.0 °C	440.0 °C
TG	99.98 %	0.1 °C	–
Residual mass	43.06 %	466.3 °C	–

Table 3

DTG Data of pomegranate peel

Parameter	Result	Range (min)	Range (max)
Final temperature	156.7 °C	125.2 °C	194.8 °C
Turning point	127.2 °C	115.0 °C	138.9 °C
Peak	75.3 °C	50.0 °C	85.0 °C
Peak	88.0 °C	85.0 °C	94.4 °C
Peak	95.4 °C	90.8 °C	108.8 °C
Mass loss	–3.39 %	0.1 °C	88.0 °C
Mass loss	–1.77 %	88.0 °C	127.2 °C
Mass loss	–0.57 %	127.2 °C	156.7 °C
Mass loss	–5.73 %	0.1 °C	156.7 °C
Peak (DTG)	71.7 °C	50.0 °C	80.7 °C
Peak (DTG)	93.9 °C	89.9 °C	106.2 °C

6. Discussion of the results of the study of the chemical composition and thermal changes of pomegranate peel and seed powders

Comparison of X-ray diffraction patterns showed that when the samples are heated in air at 110 °C for 30 min, their crystal structure is destroyed and they pass into an amorphous state. This is achieved through dehydration, dehydroxylation and possible denaturation of protein compounds in their chemical composition.

The EPR spectra recorded at room temperature of the initial and heat-treated in air at 110 °C powders of garnets of various origins indicate the presence of paramagnetic properties in the studied samples (Fig. 4, *a–h*). This is due to the different ligand environment of Fe^{3+} iron ions and the presence of organic (phenoxy) radicals, most likely in natural lignins. Thermal annealing of samples in air for 30 min at 300 °C leads to a significant increase in the content of carbon radicals, which is typical for humic substances. The broadening of the line of the carbon radical in the EPR spectra indicates the aromatic nature of the structure of organic substances in them.

As for the IR spectra recorded at room temperature of the original and heat-treated in air at 105 °C garnet powders of various origins, they show that, depending on the size of the regions (frequency 2800–2600 cm^{-1}, ranges 1800–1200 cm^{-1}, 1100–1000 cm^{-1}, etc.) show the frequencies of stretching vibrations of OH groups, CH_2 and CH_3 groups in hydrogen bonds; in groups – C=O and –C=C–, C–O–H associated with some phenolic compounds. The latter are one of the numerous classes of secondary plant compounds that determine their antioxidant properties and biological value. The absorption bands in these spectra with stretching vibrations of OH groups, C–O–H, R–O–H groups, primary and secondary alcohols, phenols, carboxylic acids, with the – COOH group of polygalacturonic acid, etc. simultaneously indicate the presence in the composition of not only phenolic compounds, but also pectin polysaccharides, aromatic acid esters and others that are present and (or) formed under the action of heat treatment during drying of pomegranate powder samples. In short, the analysis of IR spectra confirms the richness of the chemical composition of pomegranate peel and pit powders, suitable for the production of food additives and biologically active components important for functional nutrition.

As can be seen from the given thermograms, three regions are clearly distinguished (54.2–147.9 °C; 147.9–343.7 °C; 343.7–466.3 °C) with weight loss during the thermal decomposition of pomegranate crust powders. In the first region (54.2–147.9 °C), a weight loss of ~8.5 % is observed. It can be divided into two stages of water release – 6.09 % in the first and 2.41 % in the second stages. The second (147.9–343.7 °C) and third (343.7–466.3 °C) regions are characterized by a more complex mechanism of thermal decomposition of the powder, including the stages of dihydroxylation, decarboxylation and, possibly, carburization. The total weight loss of the sample at the final temperature of powder decomposition (~466 °C) is ~57 %.

The temperature characteristics and thermal effects of the garnet crust thermolysis process show that the first thermal endoeffect of the transformation, i.e. the first thermal endoeffect (71.7 (T_1)–85.4. (T_2) °C) corresponds to – 214.3 J/g and the second thermal endoeffect (297.6 (T_1)–318.7 (T_2) °C) corresponds to – 19.2 J/g (T_1 is the temperature of the beginning of the thermal effect, T_2 is the temperature of the peak of the thermal effect. Thermal heating of samples is accompanied by endoeffects in the range of 54.2–147.9 °C and at 297.6–318.7 °C. Both observed effects are accompanied by a loss of sample weight – 6.09 % in the range of 54–86.9 °C) and 2.41 in the range of (89.2–109.0 °C). The first minimum on the DSC curves, observed in the temperature range from 54.2 to 147.9 °C, is the result of evaporation of water bound to macromolecules by hydrogen bonds and partial denaturation of proteins that make up the pomegranate peel, practically match [21]. The TGA

curves show three general areas of weight loss (54.2–147.9; 147.9–343.7; 343.7–466.3 °C). The thermograms also show that with increasing temperature when the powders are heated above 165 °C, the DSC curves indicate the presence of an exothermic effect. The second minimum on the DSC curves, starting at 297.6 °C, also coincides with the sample mass loss and, apparently, reflects the reactions of intra- and intermolecular dehydration and decarboxylation of organic components occurring in the garnet crust [22]. The thermal effect of this stage is 19.3 J/g. The temperature range of 54.2–147.9 °C is of the greatest interest in the processes of heat treatment of food products. The weight loss of samples in this temperature range occurs as a result of the removal of water molecules associated with protein structures, pectin, organic components – proteins, carbohydrates. At this stage, water molecules linked by hydrogen bonds are removed from the sample, the content of which in the sample is 2.41 %. The temperature range of 71.7–95.4 °C can be characterized by the area of denaturation of the protein components of the pomegranate peel, accompanied by the removal of water molecules strongly associated with protein structures. Thermograms of pomegranate peel powder make it possible to identify no more than 6 areas of sample weight reduction 6.09; 8.50; 21.44; 9.09; 9.81; 5.93 % with end temperature for each section 180.0; 232.4; 311.4; 337.1; 466.3 °C, respectively. The obtained results suggest two types of water molecules in the structure of the pomegranate peel – "free" and "bound" water molecules. The removal of the former from the pomegranate peel powder occurs when heated to 72 °C, a further increase in temperature leads to dehydration and denaturation of protein structures (Fig. 6–8).

The results of these studies of the chemical composition and thermal properties of pomegranate powders depending on the temperature and drying time must be taken into account when preparing food products with these additives.

7. Conclusions

1. X-ray diffraction revealed the presence of crystalline phases in the initial powders and their destruction during treatment at 105 °C in air for 30 min. with the transition of the sample to the amorphous state. The use of IR spectroscopy made it possible to identify functional groups in the composition of both the initial and dried garnet powders at 105 °C and establish the change in their chemical composition upon drying at 105 °C for 30 minutes, and determine the nature of the change. It is shown that the obtained individual IR spectra and spectral characteristics (the intensity of the absorption band and the area under the spectral absorption curve) are strictly specific for each sample and are apparently due to their morphological features of the structure and chemical composition. The use of the EPR spectroscopy method indicates the presence of paramagnetism in the samples and identify carbon radical and paramagnetic centers from iron ions in the studied samples.

2. Humidity at 105 °C in air for 4 hours of seed samples from fruits (from the supermarket) is: sweet and sour pomegranate – 5.57 %, seeds from technical pomace – 5.78 %, pomegranate peel from technical pomace – 8.82 %. Losses during calcination by holding powder samples in a muffle furnace at 850 °C for 4 hours of the studied garnet powders are, respectively, 98.56 %; 98.74 %; 97.44 %.

3. The temperature characteristics and thermal effects of the pomegranate peel thermolysis process showed that the first thermal endoeffect (71.7 (T_1)–85.4 (T_2) °C) corresponds to 214.3 J/g, and the second thermal endoeffect (297.6 (T_1)–318.7(T_2) °C) corresponds to –19.2 J/g (T_1 is the temperature of the onset of the thermal effect, T_2 is the temperature of the peak of the thermal effect). As the temperature rises above 165 °C, the DSC curves indicate the presence of an exothermic effect. Thermograms of pomegranate peel powder revealed no more than 6 areas of sample weight reduction 6.09; 8.50; 21.44; 9.09; 9.81; 5.93 % at the final temperature of each section 180.0; 232.4; 311.4; 337.1; 466.3 °C respectively.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Manuscript has no associated data.

References

1. Brench, A. A. i insh. (2016). Tekhnalogiya vytvorchasci i realizacyi harchovyh praduktaў. Minsk: Infarmaciyny centr Minfina, 399.
2. Kurbanov, H. H., Gadimova, N. S., Akhundov, N. A. (2017). The content of lipids (oils) from industrial pomace seeds of pomegranate fruit. Pishchevaya promyshlennost', 5, 28–31. Available at: https://cyberleninka.ru/article/n/soderzhanie-lipidov-masla-iz-semyan-promyshlennyh-vyzhimok-plodov-granata
3. Gil, M. I., Tomás-Barberán, F. A., Hess-Pierce, B., Holcroft, D. M., Kader, A. A. (2000). Antioxidant Activity of Pomegranate Juice and Its Relationship with Phenolic Composition and Processing. Journal of Agricultural and Food Chemistry, 48 (10), 4581–4589. doi: https://doi.org/10.1021/jf000404a
4. Kairbayeva, A., Tlevlessova, D., Imanbayev, A., Mukhamadiyeva, K., Mateyev, Y. (2022). Determining optimal technological modes for pressing oil from melon seeds to justify rational engineering and structural solutions. Eastern-European Journal of Enterprise Technologies, 2 (11 (116)), 12–22. doi: https://doi.org/10.15587/1729-4061.2022.255731
5. Szydlowskaczerniak, A., Karlovits, G., Lach, M., Szlyk, E. (2005). X-ray diffraction and differential scanning calorimetry studies of β′ → β transitions in fat mixtures. Food Chemistry, 92 (1), 133–141. doi: https://doi.org/10.1016/j.foodchem.2004.07.010

6. Podkopaev, D. O. (2010). Metod EPR-spektrometrii dlya issledovaniya biologicheskih ob"ektov i produktov pitaniya. Pishchevaya promyshlennost', 7, 33–34.
7. Drouza, C., Spanou, S., D. Keramidas, A. (2019). EPR Methods Applied on Food Analysis. Topics From EPR Research. doi: https://doi.org/10.5772/intechopen.79844
8. Franca, A. S., Nollet, L. M. L. (Eds.) (2017). Spectroscopic Methods in Food Analysis. CRC Press, 664. doi: https://doi.org/10.1201/9781315152769
9. Hird, S. J., Lau, B. P.-Y., Schuhmacher, R., Krska, R. (2014). Liquid chromatography-mass spectrometry for the determination of chemical contaminants in food. TrAC Trends in Analytical Chemistry, 59, 59–72. doi: https://doi.org/10.1016/j.trac.2014.04.005
10. Gao, D., Helikh, A., Duan, Z., Liu, Y., Shang, F. (2022). Development of pumpkin seed meal biscuits. Eastern-European Journal of Enterprise Technologies, 2 (11 (116)), 36–42. doi: https://doi.org/10.15587/1729-4061.2022.254940
11. Jalal, H., Pal, M. A., Ahmad, S. R., Rather, M., Andrabi, M., Hamdani, S. (2018). Physico-chemical and functional properties of pomegranate peel and seed powder. The Pharma Innovation Journal, 7(4): 1127–1131. Available at: https://www.thepharmajournal.com/archives/2018/vol7issue4/PartR/7-4-101-663.pdf
12. Jalal, H., Pal, M. A., Hamdani, H., Rovida, M., Khan, N. N. (2018). Antioxidant activity of pomegranate peel and seed powder extracts. Journal of Pharmacognosy and Phytochemistry, 7 (5), 992–997. Available at: https://www.phytojournal.com/archives/2018.v7.i5.5677/antioxidant-activity-of-pomegranate-peel-and-seed-powder-extracts
13. Gullón, P., Astray, G., Gullón, B., Tomasevic, I., Lorenzo, J. M. (2020). Pomegranate Peel as Suitable Source of High-Added Value Bioactives: Tailored Functionalized Meat Products. Molecules, 25 (12), 2859. doi: https://doi.org/10.3390/molecules25122859
14. Kumar, N., Pratibha, Neeraj, Sami, R., Khojah, E., Aljahani, A. H., Al-Mushhin, A. A. M. (2022). Effects of drying methods and solvent extraction on quantification of major bioactive compounds in pomegranate peel waste using HPLC. Scientific Reports, 12 (1). doi: https://doi.org/10.1038/s41598-022-11881-7
15. Mukama, M., Ambaw, A., Opara, U. L. (2018). Thermal properties of whole and tissue parts of pomegranate (Punica granatum) fruit. Journal of Food Measurement and Characterization, 13 (2), 901–910. doi: https://doi.org/10.1007/s11694-018-0004-1
16. Viuda-Martos, M., Ruiz-Navajas, Y., Martin-S nchez, A., S nchez-Zapata, E., Fern ndez-L pez, J., Sendra, E. et al. (2012). Chemical, physico-chemical and functional properties of pomegranate (Punica granatum L.) bagasses powder co-product. Journal of Food Engineering, 110 (2), 220–224. doi: https://doi.org/10.1016/j.jfoodeng.2011.05.029
17. Rowayshed, G., Salama, A., Abul-Fadl, M., Akila-Hamza, S., Emad, A. M. (2013). Nutritional and chemical evaluation for pomegranate (Punica granatum L.) fruit peel and seeds powders by products. Middle East Journal of Applied Sciences, 3 (4), 169–179. Available at: https://www.curresweb.com/mejas/mejas/2013/169-179.pdf
18. Fialko, N., Dinzhos, R., Sherenkovskii, J., Meranova, N., Prokopov, V., Babak, V. et al. (2022). Influence on the thermophysical properties of nanocomposites of the duration of mixing of components in the polymer melt. Eastern-European Journal of Enterprise Technologies, 2 (5 (116)), 25–30. doi: https://doi.org/10.15587/1729-4061.2022.255830
19. Kaletunc, G. (Ed.) (2009). Calorimetry in Food Processing: Analysis and Design of Food Systems. Wiley, 412. Available at: https://www.wiley.com/en-us/Calorimetry+in+Food+Processing%3A+Analysis+and+Design+of+Food+Systems-p-9780813814834
20. Hatzakis, E. (2019). Nuclear Magnetic Resonance (NMR) Spectroscopy in Food Science: A Comprehensive Review. Comprehensive Reviews in Food Science and Food Safety, 18 (1), 189–220. doi: https://doi.org/10.1111/1541-4337.12408
21. Gurbanov, N., Gloyna, D., Kunzek, H. (2005). Herstellung und Charakterisierung von Pektin zellstrukturiertem Material aus Granatapfel-Trestern. Obst-Gemüse und Kartoffelverarbeitung 90, 3, 10–17.
22. Gurbanov, N., Gloyna, D., Senge, B., Kunzek, H. (2005). Zur Gewinnung, Zusammensetzung und zu den Eigenschaften von Salep-Pulver aus getrockneten Knollen wildwachsender Orchideen. Obst-Gemüze und Kartoffelverarbeitung 90, 2, 30–36.