

Research of the Relationship Between Color and Biochemical Properties of Buckwheat Groats

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Abstract: In the study a significant linear correlation is shown between x and y chromaticity coordinates of the color of buckwheat groats in CIE xyY diagram and the regression function $y = f(x)$ is given. A quantitative correlation is established between the change in color and the content of the main components of buckwheat groats biochemical complex (starch and proteins) and dextrin which occurs during hydrothermal processing of buckwheat grain. The results obtained allow assessing the quality of buckwheat groats by its color as well as open up the possibility of effective management of the groats production processes. The range of colors is determined in which the content of the studied components of buckwheat groats biochemical complex changes insignificantly, so, it may be used as a basis for rational choice of modes of hydrothermal processing of buckwheat grain.

Key words: Hydrothermal processing of grain, buckwheat groats, color, biochemical complex, protein, starch, dextrin, chromaticity coordinates

INTRODUCTION

Tough competition in the modern food market imposes stringent requirements for quality and food safety, all-round improvement of which is one of the main tasks of food production, including groats.

Hydrothermal processing is widely used to improve the technological properties of buckwheat grain, increasing the yield of groats as well as to improve its consumer properties, nutritional value and stability during storage.

Consumer quality of the groats is mainly determined by organoleptic characteristics-taste, color and odor which may greatly change during the hydrothermal processing of buckwheat grain. Among these indicators, color is not only consumer attraction and marketable appearance factor but is the only measurable one. Color is an external manifestation of the biochemical changes that occur in the grain when it is treated with moisture and heat.

Hydrothermal processing of buckwheat grain causes various quantitative changes in components of the biochemical complex of the groats. For protein complex which is the main in the evaluation of nutritional value of the product, various studies have shown contradictory results but most of them noted a decrease in protein

and some amino acids content during hydrothermal processing of buckwheat grain (Smirnov *et al.*, 1963; Yakovenko *et al.*, 1980; Knyazeva, 1997; Kaminsky *et al.*, 2000). According to, other studies (Pokrovsky, 1975) hydrothermal processing of grain has no significant impact on the amino acid composition of proteins, however, such treatment, held in harsh conditions, leads to a high degree of their denaturation, degradation and the formation of the solid residue which is not digestible by the human body (Kaminsky and Babich, 1999). Reduction in protein content by 2, 1-3, 3% in buckwheat grains noted during the steaming in production conditions (vapor pressure of 0.25 MPa, processing time 5 min) as well as during roasting on the heating surface with a temperature of 180°C for 10 min, followed by wetting by water with temperature 98°C up to 20% humidity, moistening for 1 h and steaming at atmospheric steam pressure for 6 min (Knyazeva, 1997; Kaminsky *et al.*, 2000).

Hydrothermal processing of buckwheat has a significant effect on its carbohydrate complex (Knyazeva, 1997). The starch is partially hydrolyzed and gelatinized with the formation of dextrans which leads to a decrease in its content in the groats (Krivolapov *et al.*, 1963; Popov and Dyk-Hoi, 1972; Kuzmina and Torzhinskaya, 1973; Melnikov, 1980).

Excessively rigid regimes of hydrothermal processing cause abundant formation of dextrans which degrade the groats consumer qualities, especially, taste (Kaminsky and Babich, 1999). No changes in the fiber content during hydrothermal processing were noted (Slepnyova, 1958).

It was found that hydrothermal processing of buckwheat has virtually no effect on the total lipids content but changes their group composition (Zalesskaya, 1976; Melnikov, 1980).

In assessing the consumer properties of buckwheat it was established that during steaming at 127°C of grain for 4-5 min it starts to get noticeable, darker color, less typical for unprocessed buckwheat grain (Kaminsky *et al.*, 2000).

Consumers prefer buckwheat groats mainly of bold brown or dark-brown color accompanied usually by delicious taste and flavor of roasted nuts. This determines the main aim of the hydrothermal processing of buckwheat-formation of a nice brown color tone on the surface. However, it should be noted that obtaining of dark brown color by the groats leads to impossibility for consumers to determine the degradation in quality of the groats before buying and cooking it.

In some researches amino acid composition of proteins is correlated with the buckwheat color, obtained during preset regimes of steaming (Maryin and Vereschagin, 2011), however, the method of visual determination of color used in this research is limited by the color names, set by researchers which makes the results nearly inapplicable for solving practical tasks of further improvement of groats production process. In the research of buckwheat groats production technology including roasting the correlation between the color and roasting regimes is also, noticed (Knyazeva, 1997) however, the color of the groats is again characterized by only name.

The research of quantitative correlation between buckwheat groats color and its biochemical properties can be promising for development of new methods of on line quality control of final product, further improvement of methods of control and management of technological process and facilitate the justification of choice of rational hydrothermal processing regimes.

In this regard and taking into account the importance of protein and starch in the biochemical complex of buckwheat groats and their significant variability during hydrothermal processing, the aim of the research was to establish quantitative correlation between the color of buckwheat groats and its proteins, starch and dextrans content.

MATERIALS AND METHODS

To get the maximum possible color range the groats was produced from different parties of buckwheat. The first one of them was not exposed to hydrothermal processing while the second one was exposed to heat treatment with temperature of heating surface 190°C for 4 min, then moistened in the damping machine with the temperature 95°C for 5 min and then softened for 1.5 h. Six more parties of grain were steamed in drum-type steamer unit (Streckel and Schrader KG, Germany) for 5 min with steam pressure 0.1, 0.2 and 0.3 MPa and for 7, 9 and 11 min with steam pressure 0.4, 0.5 and 0.6 MPa correspondingly. The grain was previously separated from contaminants and calibrated. Without hydrothermal processing it was husked straight away. The grain that went through hydrothermal processing was dried till moisture content not exceeding 13.5% cooled down and then husked. For all parties, the husked grain was calibrated, sorted and separated from contaminants.

Taking into account that quality of experimental research is heavily dependent on color uniformity, special attention was given to taking samples from different grain parties. Firstly, five samples of 0.15 kg were taken from different parts of tare using a sampler. From these samples, defected, rotten and grains with unusual color and extraneous bodies were selected out. Then individual samples were combined into general sample which was then examined.

The next step was the direct measurement of the numerical parameters of colors which were RGB-color components of each scanned face of grain which then were transmitted into suitable for the analysis "Two dimensional" color coordinates x and y of the diagram CIE xyY (CIE chromaticity diagram 1964 10° supplemental standard observer). These coordinates were distinguished in turn from spatial tristimulus values $X-Z$, accepted by CIE (Commission Internationale de l'Eclairage-International Commission on illumination) as the main characteristics of color. Methods of analytical calculations were based on the works of Wyszecki and Stiles (1982), Giorgianni and Madden (1998), Anonymous (1998) and Byvaltsev *et al.* (2001) and summarizing work of (Gerasimov and Burygina, 2002). Practical realization of digital method of x and y color coordinates determination was done using a computer and Hewlett-Packard® Scanjet 2300 flatbed scanner with optical resolution 600 dpi and color depth 24 bits on 5×5 pixel area in the middle of each of 3 faces at the vertex of the tetrahedron which can be assumed to be a form of a buckwheat grain. The face of a grain taken as the base of a tetrahedron which has small area and unstable convex surface was not scanned.

The grain was placed by each of the flat faces on the top of a flat glass dish, placed on the scanner glass (Konstantinov *et al.*, 2012).

To measure the influence of glass dish on the results 2 preliminary tests were conducted. Firstly, a white sheet of paper was placed on the scanner glass and scanned.

Then, the glass dish was placed on the scanner glass and a sheet of paper was put on its bottom. In both cases identical values of RGB-components the intensity were obtained-255 conventional units which proved the absence of the glass dish influence on the results of experiments.

The name of the color was determined using a color atlas Pantone®, a computer database of the value of RGB color components and widely used in practice names.

The grounds for need to determine the coordinates for all three faces of each grain was the assumption of the presence of a noticeable color variation within the same grains, especially, for a hydrothermal processed buckwheat which was confirmed by the results of preliminary measurements and visual inspection.

Obviously, measure of the dominant color (common background color) of the sample are the sample mean of the color coordinates \bar{x} and \bar{y} ; Measure of its homogeneity-selected variability indexes such as the standard deviation S_x , S_y and the coefficient of variation V_x and V_y , calculated from the known formulas (Sachs, 1968).

Sample was considered to be homogeneously colored if V_x and $V_y < 0.05$. The relative accuracy of calculations and was taken equal to $\Delta = 0.02$. When it turned out that $V < 0.05$, selected grains were returned and additional "Cleaning" of the sample was conducted by the method described above and grains were selected again to perform the necessary measurements and test the homogeneity of the sample. In most cases it was not required.

In order to ensure the accuracy of the experiment it was necessary to determine the sample size n which is calculated by the Eq. 1:

$$n = \frac{V^2}{\Delta^2} \times t_{a,k}^2 \quad (1)$$

Where:

$t_{a,k}$ = Student criterion at a significance level of $\alpha = 0.05$ and the number of degrees of freedom

k = $n-1$, determined from tables

As V was taken the largest of the two calculated values of V_x and V_y that is, $V = \max \{V_x, V_y\}$. Given that a priori V_x and V_y were not known, determination of the total

number of measurements was carried out by successive approximation to the required accuracy Δ while for the convenience of us Eq. 1 was used as:

$$\Delta = \frac{V}{\sqrt{n}} \times t_{a,k} \quad (2)$$

First, the measurements of x and y coordinates for the 10 randomly selected grains were conducted that is for the sample volume $n_1 = 30$, V_1 was calculated and $t_{a,k}$ criteria defined for the n_1-1 degrees of freedom. If it turned out that the calculated Δ_1 exceeded the required, the sample size and the number of grains involved were increased and the computational procedure was repeated. Sample size if necessary was increased until the condition of $\Delta \leq 0.02$ was met.

After these measurements conclusions were drawn about the color of the composite sample, the degree of its homogeneity and samples were taken for determination of moisture content in accordance with GOST 26312.7-88, content of protein nitrogen using Bernstein for method and protein content according to GOST 10846-91, starch content using Ewers for polarimetric method according to, GOST10845-98 and for determination of dextrin content using technique developed by Popov and Shanenko. Grains to be investigated had humidity of 11.8-12.5% and the same dimensions (tailings 2.4×20 mm).

RESULTS AND DISCUSSION

According to the materials of the research (Konstantinov and Rumyantsev, 2013) a significant linear correlation was established between the color coordinates x and y with a correlation coefficient $r_{xy} = 0.764_{0.05}^{0.12}$, adequately described by a linear regression:

$$y = 0.37x + 0.22 \quad (3)$$

The resulting linear statistical model of color coordinates correlation proved useful for further interpretation of research results. It should be noted that the relative difference between the actual values of the individual average y color coordinates and calculated from the regression Eq. 3 did not exceed 1.5%. Such deviations have little effect on the shift in the color evaluation.

The influence of color of buckwheat on the content of protein starch and dextrin in it is shown in Fig. 1 where each experimental point corresponds to the average content of the component in the biochemical composition of cereals and color coordinates x . Using Eq. 3 to each

such value of x in line you can cast y coordinate while you can also, take advantage of the construction of additional axes from Oy (not shown).

Obtained in this way slightly shifted estimate of the grains color is represented in the form of colored stripes with the conventional boundaries forming an analogy to a discrete spectrum of grains color which provides visual information in addition to the names of colors.

The form of the location of data points assumes bending of a certain degree. Given this, an approximation of experimental data was produced by the third degree polynomials using a known method of least squares which is implemented in the program Microsoft® Office Excel 2003. The degree of approximation of the experimental and theoretical values of output parameters was high ($R^2 = 0.95-0.99$ for all cases).

It is evident that the hydrolysis of starch to dextrins begins largely manifested on acquisition grains intense brown color when $x \approx 0.400$. Further darkening of the brown color, accompanied by an increase in x is characterized by a significant increase in the content of dextrins. It should be noted that the nonlinear changes of the dextrins content in groats throughout discrete spectrum of color is always accompanied by a tendency to increase of this indicator with the acquisition of the increasingly dark coloration.

The least intensive increase in the content of dextrins groats occurs in its acquisition of the first, slightly expressed, brown shades (burly wood, light-brown). These colors are characteristic for groats, produced at low modes of hydrothermal processing and are in practice, inadequate both from a technological and from a culinary point of view (Melnikov, 1980).

Simultaneously with the growth of dextrins content in groats with the darkening of its color almost monotonous decrease in starch content is observed till the acquisition of wood-brown and brown color with $x \approx 0.410$. With the further darkening of groats color to dark brown and dark with a brown shade with $x = 0.445$, decrease in the starch content becomes more rapid.

The changes in the content of protein in groats, depending on its color are to a large extent similar to the behavior of the starch content in it. The essential difference here is mainly in quantities.

Compared with light cream colored groats (groats from the grain without hydrothermal processing) dextrin content increased from 0.71-11.95% for groats of dark with brown shade color. With the same colors of borders of the spectrum, the starch content decreased from 74.7-57.5% and the protein content decreased from 16.8-11.8% for groats of dark with brown shade color. The starch content decreased by an amount greater than the increase in the

content of dextrin. The difference in the first case, 6.0% is comparable with the level of reduction of the protein (5.0%).

The interval in the groats colors from light-brown to brown with some darkening ($x = 0.365-0.410$) for which changes in the biochemical components of the complex can be considered insignificant which is consistent with other studies (Maryin and Vereshchagin, 2011) aimed at studying the change of fractional composition of buckwheat protein which meet regulatory requirements for color.

It is clear from the presented discrete color range of hydrothermally processed buckwheat grains that brown is its main color tone which saturation, hue and lightness can vary in wide limits with different parameters of hydrothermal processing. It can be intense brown, light cream or dark with barely noticeable brown shade which creates premises for tangible perception of unevenness in the color of buckwheat grain surface with certain methods of hydrothermal processing, especially with high-temperature contact heating method. It is obvious that unevenness in coloring will be more expressed, the more inferior the hydrothermal processing method is. At the same time, the biochemical complex of the grain becomes heterogeneous.

The color of grain thus can be considered to be such a criterion which allows monitoring parameters of hydrothermal processing and provide reasoning for the choice of one or another method of hydrothermal processing with regard to the quality of groats they allow to achieve.

Development of express methods of buckwheat grain color evaluation would not only solve the problem of its separation (removal of impurities, damaged grains, etc.) which is already implied in modern groats production but also to operatively manage the technological process and quality of groats within the certain limits.

Using the achieved results it is possible to reasonably limit the use of any method of hydrothermal processing of buckwheat using color as a criterion, also to provide the basis for development of control of hydrothermal processing, quality management of final product and indirect operative approximate methods of analysis of biochemical complex of grain which can be used in practice.

The results show that acquisition by buckwheat groats of brown color with the given color coordinates can be considered not only optimal in terms of pleasantness of perception but also as a characteristic of negative biochemical processes which intensify with further darkening of the color and decrease in culinary properties with the whitening of the color (Fig. 1).

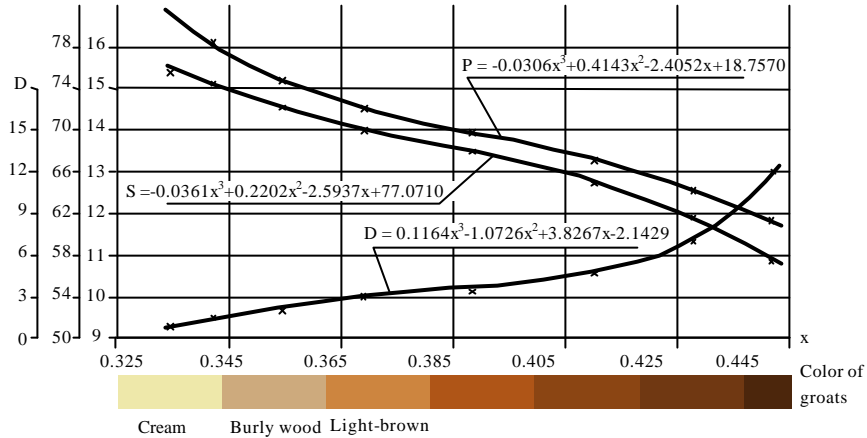


Fig. 1: Protein content (P), Starch content (S), Dextrins content (D) in buckwheat groats % correlated with color

CONCLUSION

A significant correlation between x and y color coordinates is established with the correlation coefficient $r_{xy} = 0.764^{+0.12}_{-0.05}$. Quantitative correlation between x and y color coordinates is defined by the formula $y = 0.37x + 0.22$.

Quantitative correlation is established between the change of color of groats and the content of main components of biochemical complex of groats-proteins, starch and dextrins which is defined by the approximating third degree polynomials. In these polynomials on of the color coordinates in color diagram CIE xyY (x coordinate) is taken as an argument while the other on is calculated using regression equation.

It is found that the buckwheat groats color range with color coordinates from $x = 0.365$ and $y = 0.355$ to $x = 0.410$ and $y = 0.372$ can be taken as the most rational for the choice of hydrothermal processing regimes. The obtained data can be used for the quality management of final product and production control of buckwheat groats.

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