DEVELOPMENT OF A COLOURIMETRIC METHOD FOR QUALITY CONTROL OF SAUSAGE PRODUCTS PRODUCED USING CHITINOUS FOOD ADDITIVES

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Abstract

A crucial technological task that must be solved in the production of sausage products is to stabilize the product's red colour. In this paper, we propose a scheme to determine the most significant parameters of the quality of dry-cured sausages by their colour characteristics. For this purpose, colour digital images were obtained, which were further processed using two classical colour representation systems: RGB and xyY. We monitored changes in pH and the ratio of water to dry matter in meat products. These crucial sausage properties were changed by introducing chitin-containing supplements into their recipes, which allowed us to solve two tasks simultaneously. The first comprises, as already mentioned, changing the properties of sausages to obtain correlations with colour characteristics. The second is to enrich meat products with chitin complex for preventive purposes to improve people's nutrition. The construction of correlation dependencies using each coordinate separately in two colour systems showed that each system (RGB and xyY) has one colour channel with a maximum correlation coefficient. This is due to the colour features of sausages, which can be represented to the greatest extent with the help of only one colour coordinate in the considered colour representation systems (RGB and xyY). Using these colour coordinates will allow one to achieve maximum measurement accuracy. Thus, two tasks are being solved: the enrichment of food with dietary supplement and the development of a method to control their content.

Keywords: *dry-cured sausage, calcium, dietary supplement, 'Hizitel', quality control*

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1. Introduction

Dry-cured sausages are very popular among consumers. Raw materials for the production of sausage products are beef, pork and pork fat. For some types of sausages, offal, blood, poultry and rabbit meat can be used. The sausage is suitable for meat of any fatness and category, but manufacturers start with meat with a low fat content. High-quality sausage is made only from the best meat, from animals of a certain type, age and fatness. The desire of contemporaries to save time and effort is a prerequisite for the growth of the share of sausages in the human diet. Sausage products have a higher nutritional value than any other meat product. This can be explained by the fact that valuable nutritional tissues are not removed from the raw materials during production. Hence, sausages contain a high amount of protein and have a high nutritional value. Eggs, whole milk, cream, etc. are added to the production. These additives improve the taste and increase the nutritional value of the product. However, excessive introduction of various preservatives and dyes into sausages threatens health. That is why we must pay great attention to the production of sausages, to know how to make them of the highest quality. For this endeavour, we need to carefully analyse the product itself and the technology of its preparation, to monitor the quality of the final product.

Dangerous and common disorders in the human diet are a lack of dietary fibre and calcium. The ideal rate of dietary fibre consumption per day is 25–35 g, but most individuals only consume 10–12 g, which is 2–3 times less than the desired norm. A lack of dietary fibre leads to a slowdown in intestinal peristalsis, the development of stasis and dyskinesia; this is one of the causes of appendicitis, hemorrhoids, cases of intestinal obstruction and even colon cancer. Dietary fibre affects the motor function of the bile ducts, an action that is especially important for people with liver and bile tract diseases. Dietary fibre can be effectively incorporated into processed meat products as binders and fillers; it can significantly replace unhealthy fat components from products; and it can increase acceptability by improving nutritional components, pH, water retention, emulsion stability, sensory characteristics, etc. of finished products. Adding dietary fibre to meat products can increase product yield and therefore make the product more cost-effective [1].

Calcium is one of the most necessary elements; it affects bones, hair and nails. On average, a person needs 1,250 mg per day, but in reality most people only consume 200–500 mg, i.e. 2.3–3.6 times less than the recommended dose [2]. It is quite problematic to ensure the consumption of dietary fibre and calcium at the expense of conventional food, so the question of compensating for these indicators in the body is very relevant. One possible way to solve this problem is to create functional foods with a high content of calcium and dietary fiber.

The use of chitin supplements in the food industry is a relatively new, developing application. It is proposed to solve the problem of a shortage of dietary fibre by different methods, for example, by manufacturing a food product – fish balls – based on a combination of chopped fish meat from pollock and salmon belly, containing biologically active chitin mineral food additive ‘Hizitel’. Nutritional additives are obtained from processing shrimp shell waste. The influence of chitin mineral food additive on rheological properties of chopped fish and biological value of products based on it has been studied [3].

Chitosan has attracted increasing attention as a food preservative due to its universality, nontoxicity, biodegradability and biocompatibility. Chitosan shows antimicrobial activity: it disturbs the negatively charged cell membrane of microorganisms with its polycation structure. Chitosan characteristics, including molecular weight and degree of deacetylation

(DD), and other environmental conditions, including pH, temperature and related components, affect its activity. Given that the antimicrobial activity of chitosan is mainly based on ionic interactions with negatively charged components of the bacterial cell membrane, the food matrix can strongly influence the antimicrobial activity of chitosan. Despite its limited antimicrobial effectiveness, chitosan demonstrates both bactericidal and bacteriostatic effects in certain food products [4].

The influence of chitosan with a 95% degree of deacetylation (DD95) on spore germination, cell proliferation and heat resistance of *Clostridium perfringens* CCRC 10 648 and CCRC 13 019 was studied, and its use for pork sausages with reduced sodium nitrite content was evaluated. Chitosan DD95 reduced the concentration of sodium nitrite, which is necessary in pork sausages for colour retention [5].

Chitosan has various applications in the food industry. The crosslinking properties of chitosan have a beneficial effect on protein-carbohydrate interactions, which, in turn, improves the functional properties of meat products based on emulsion. A study was conducted to include hydrogel with different concentrations of chitosan (0%, 0.125%, 0.25%, 0.375% and 0.5%) in minced fish sausages (*Pangasianodon hypophthalmus*). Comparative analysis of the various functional properties of the obtained sausages showed that the inclusion of chitosan gel had a significant impact ($p < 0.05$) on the stability of the emulsion, gel strength, pH, yield during cooking, structural compactness, texture, colour and sensory attributes compared with the control. In addition, it can be concluded from the study that sausages with chitosan content of 0.25% (CS-2) have the best necessary functional and physicochemical properties and are considered an excellent ready-to-eat product [6].

Based on the abovementioned studies, we can say that the use of chitin supplements is a promising trend. This paper was devoted to studying the influence of the biologically active additive 'Calcium-D3-Hizitel' on dry-cured sausages. The results were used to construct correlated dependences between the colour parameters – including each individual channel – and sausage characteristics: pH, dry matter content and Hizitel concentration.

2. Materials and Methods

The object of this study was a dry-cured sausage, the recipe for which included meat: beef grade 1 (back, ham) and pork belly (flank, undercuts) in a 50/50 ratio, as well as sodium nitrite, dry marjoram, fresh garlic, black pepper and Armenian cognac to refine the aroma and taste.

The production technology of dry-cured sausage included the following stages: freezing raw meat for 3 h at -18°C and then grinding it (6–8 mm), followed by preparation of minced meat with the addition of salt, spices and cognac. Then maturation takes place within 24–36 h, filling the shells with minced mass followed by a 2–3-day precipitation (11-15°C, φ = 80%–85%) and drying for 5–7 days. (11–15°C, φ = 75%–85%). Dry-cured sausages were stored at 0–40°C until the onset of damage.

In seven samples of dry-cured sausages, chitin-containing additive Calcium-D3-Hizitel was introduced. The first control sample was not processed. The chemical composition and quality indicators of all eight sausage samples were studied according to their colour characteristics. The following biochemical parameters were determined daily for each sample: pH, water-retaining capacity, water-binding capacity and colour characteristics (brightness, saturation and colour tone).

pH was determined with a laboratory pH meter [7]. Before determining the pH of the meat, you need to prepare its aqueous extract: 10 g of minced meat is added to 100 mL

distilled water and allowed to infuse for 30 min, with periodic stirring. The extract is then is filtered through a paper or cotton filter and the pH value is determined in the filtrate.

The determination of the mass fraction of moisture and solids is based on drying the samples to a constant mass. The lamp was mounted on a tripod in an upright position. Ditches or boxes with the material to be dried were installed on asbestos cardboard, porcelain or clay tiles in the centre of the light circle cast off by the lamp. A portion of the crushed product (2 g), weighed accurate to the third decimal place, was mixed with twice (by weight) the amount of sand, transferred to the bottle and placed under the paw of infrared radiation. The first weighing of the weighing boxes was carried out after 1 h of drying; it was then weighed every 30 min. Before each weighing, the bottle was cooled in a desiccator for 30 min. Drying is carried out until the difference between the two weights does not go beyond the accuracy established for a given experiment. The total drying time should not exceed 6 h [8].

Determination of colour characteristics in RGB and xyY systems was carried out by obtaining colour digital images of surfaces and slices of sausages with their subsequent processing. The perception of colour by a person is very subjective, because in nature there are light waves of different frequencies, and the human eye perceives only a certain range of frequencies (visible light). Nevertheless, we perceive a set of waves, not each wave separately. The RGB system (an abbreviation of the English words red, green, blue) is a colour model that describes a way to encode a colour for reproduction using three primary colours. The choice of primary colours is determined by the peculiarities of the physiology of colour perception by the retina of the human eye. The xyY colour space model is quite clear and popular, because it is in the x and y coordinates that the colour gamut of the eye (locus or colour chart) is mainly represented, including all colours perceived by the human visual apparatus.

The method of obtaining colour coordinates in RGB and xyY systems included the following sequence of actions. For each sample, colour digital images were obtained via a specialized vision system using a highly stable lighting system. Prior to the measurements, the technical vision system was set up for the operation of the image registration system, as well as energy and colourimetric calibration to eliminate uneven illumination of the analysis zone and chromatic distortions of the utilized optical system of the lens. During mathematical processing of the obtained surface images and sections of the samples, the colour coordinates of the most represented colour shade in the RGB system were obtained. These colour coordinates were converted to the coordinates of the xyY colour space, considering the spectral sensitivity curves of the vision system and the spectral radiation curve of the backlight. Based on the obtained results, correlation dependences were constructed between the pH and the dry matter/water content in raw sausages, as well as between the values of individual colour coordinates and the pH values and the dry matter or water content in sausages [9–11].

3. Results and Discussion

Dry-cured sausage is very popular among consumers because it has original organoleptic properties and because it is a high-quality, biologically complete meat product with a rich set of useful substances. This type of sausage refers to meat products with a long shelf life, which makes it easier to transport and sell. Dry-cured sausage has a high nutritional and biological value, and it can be easily enriched with dietary supplement; hence, the product is of special interest. Over the past decade, there has been a steady trend for meat products with improved composition. Reducing fat, cholesterol, salt and nitrite, as well as improving the fatty acid profile and including bioactive

compounds, is increasing worldwide. When processing crustaceans for food purposes, about 50%–80% of the material is shell waste, which makes it possible to organize industrial production of calcium-enriched preparations. JSC 'GIPRORYBFLOT' (Saint Petersburg, Russia) developed an electrochemical technology for processing solid waste and obtained a new product of a unique composition – Hizitel, which is a chitin – mineral complex of the shell. Hizitel is an absolutely natural composite product consisting of chitin polysaccharide-dietary fibre (20%–40%) and minerals (60%–80%, depending on the type of raw material), which are part of crustacean shells [12].

In the body, Hizitel does not accumulate, cause an astringent sensation in the mouth or dissolve in the gastrointestinal tract, unlike chitosan, so it does not penetrate the walls of the gastrointestinal tract, and also normalizes increased acidity. Hizitel has no negative influence on the processes of digestion and assimilation of food. It should also be noted that Hizitel, which is a scaly powder with a low bulk weight, is not soluble in water, and therefore is not very convenient for direct consumption.

Dried sausage (see recipe in section 2) was enriched with the biologically active calcium food additive Calcium-D3-Hizitel. Hizitel was obtained by electrochemical method according to the method described in patent № 94013408 of the Russian Federation [13]. Eight dry-cured sausage samples were produced and studied. The samples differed from each other in concentrations of this food additive: 1, Control (without addition of Hizitel); No. 2, 0.5%; No. 3, 1%; No. 4, 1.5%; No. 5, 2.0%; No. 6, 2.5%; No. 7, 5%; and No. 8, 10%. Fig. 1 shows dry-cured sausages with different concentrations of the additive.

For sausages, colour is formed as a result of the decomposition of sodium nitrite ($NaNO_2$) to nitric oxide (NO) and the interaction of the latter with myoglobin with the formation of nitrosomyoglobin. Chitin affects the sausage's pH. In turn, the pH affects the decomposition of $NaNO_2$ to NO because certain products from the reduction of $NaNO_2$ from ammonia (NH_3) to NO_2 will predominately determine the pH during $NaNO_2$ decomposition. In addition, pH also affects the interaction of NO with myoglobin

Figure 1. Dry-cured sausages with different concentrations of Calcium-D_3-Hizitel additive. The sample number is indicated by the tag.

and the formation of nitrosomyoglobin, which, in this case, is the main pigment in the sausage because there is no heat treatment. To a lesser extent, chitin affects colour as a result of the very fact of an increase in its content in sausage, because chitin is not red.

White colour can be decomposed into three components: red (R), green (G) and blue (B). Depending on the colour of the analysed surface, the ratio of these three components will change. For the red surface, the red component is predominant.

Colourimetric measurements of sausages were carried out immediately after completion of the entire sausage production technology, including the longest stage of production – drying, because this point is of particular interest for quality control. Experiments were conducted to determine the pH and the amount of dry matter for all sausage samples, i.e. for each Calcium-D3-Hizitel concentration [2].

Studies have shown that as the pH shifts to the alkaline region, the dry matter content decreases and the proportion of water increases. This phenomenon is due to a deviation from the isoelectric point and an increase in the negative charge on the carboxyl groups and a decrease in the positive charge on the amino groups that are part of the side chains of some amino acids. As a result, the total negative charge increases, which leads to an increase in the hydration of proteins and peptides. The drying conditions in this situation deteriorate, and more water is stored in the sausages at a fixed drying time provided by the technology. However, as it shifts to the alkaline region, the increase in humidity gradually decreases, which is due to the exhaustion of the possibilities for increasing the hydration of protein-peptide structures. Therefore, the change in the ratio of dry matter and water in sausages is nonlinear, tending to reach the limit as the pH shifts to the alkaline side. In this case, the approximation coefficient R^2 has the maximum value for the R channel of the RGB system (Figs. 2–7); the R^2 is markedly less for G and especially B.

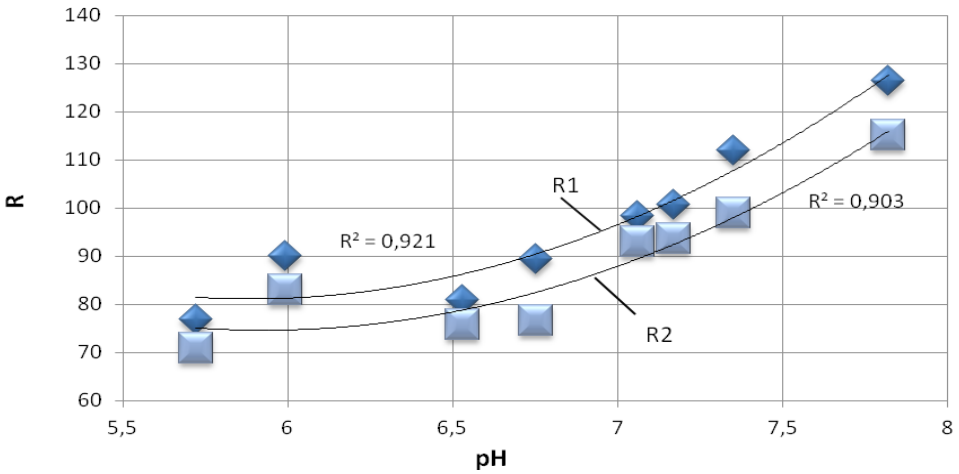

Figure 2. The dependence of the parameter R (red) on the pH value, where the R1 line represents points from the surface and the R2 line represents points taken from the cut

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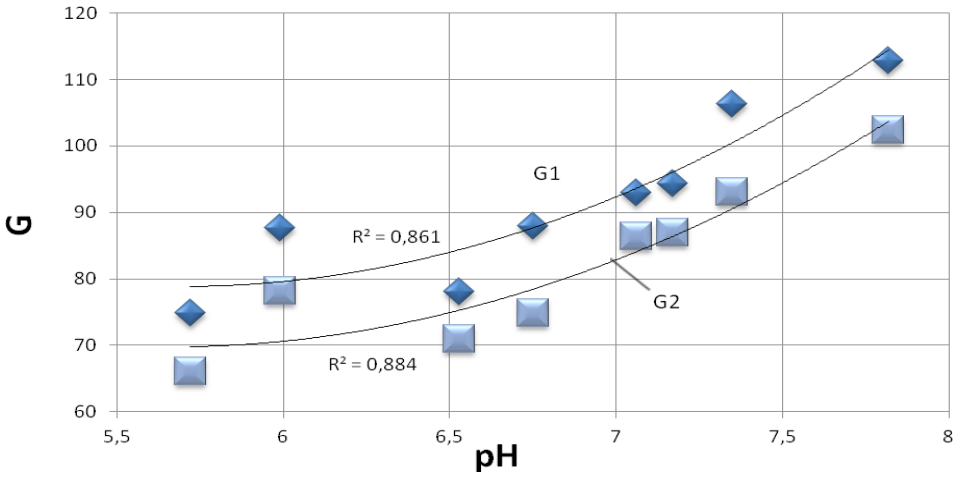

Figure 3. The dependence of the parameter G (green) on the pH value, where the G1 line represents points from the surface and the G2 line represents points taken from the cut.

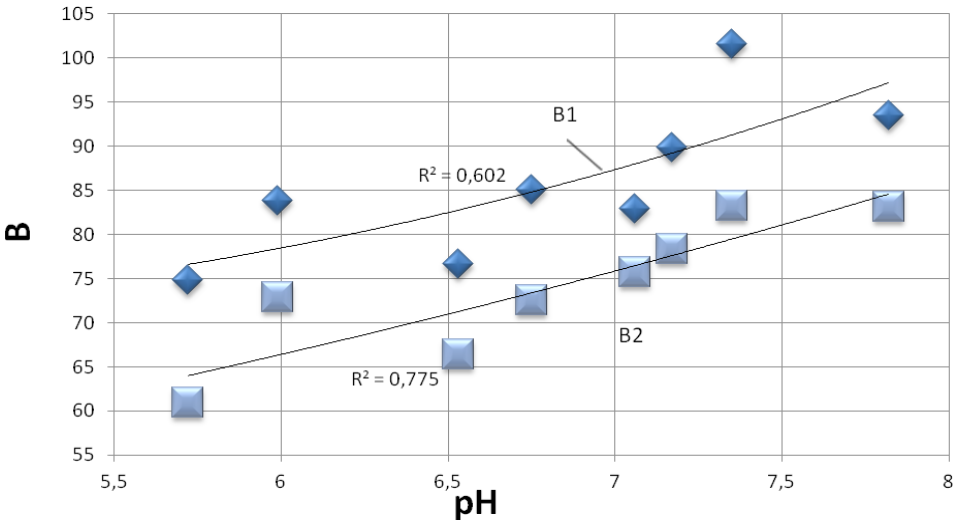

Figure 4. The dependence of parameter B (blue) on the pH value, where the B1 line represents points from the surface and the B2 line represents points taken from the cut.

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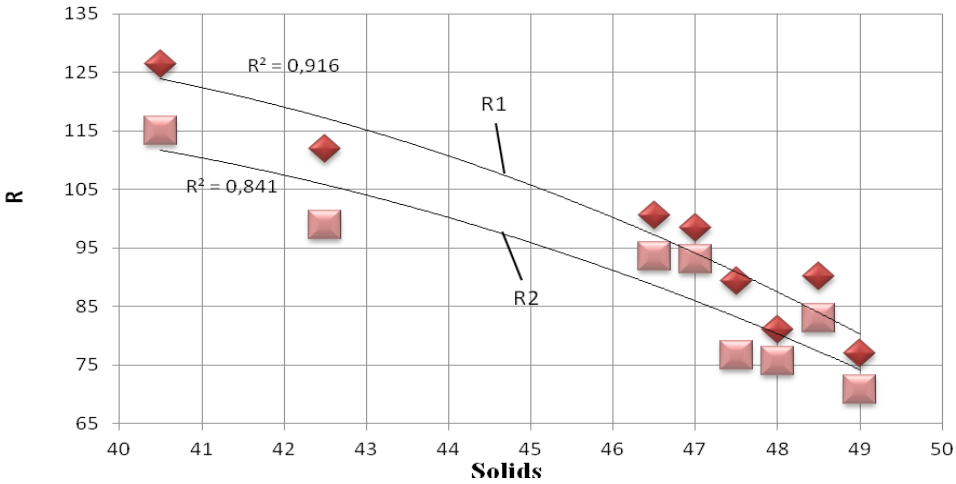

Figure 5. The dependence of the parameter R (red) on the amount of solids, where the R1 line represents points from the surface and the R2 line represents points taken from the cut.

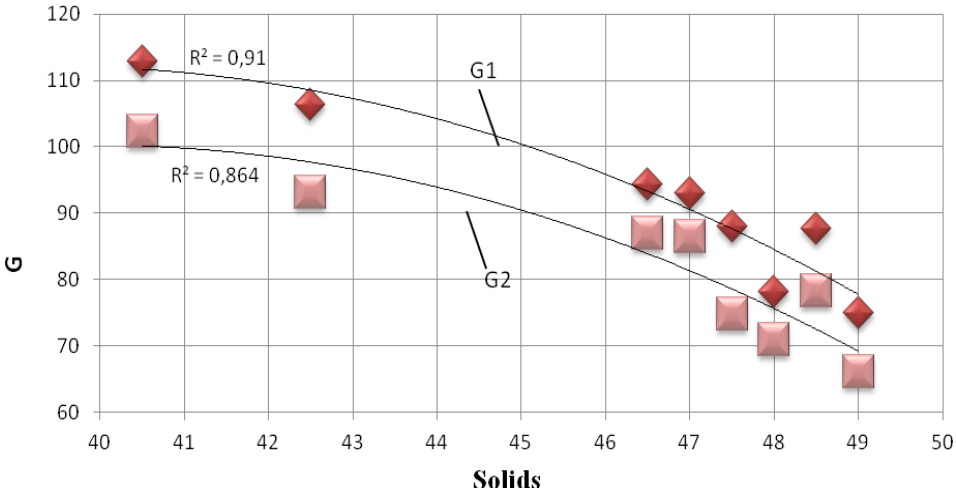

Figure 6. The dependence of the parameter G (green) on the amount of solids, where the G1 line represents points from the surface and the G2 line represents points taken from the cut.

For each sample of dry-cured sausage, colourimetric characteristics were determined in the xyY system, for which colour digital images were obtained with preset and colourimetric calibration of the image registration system. After mathematical processing of the data, considering the spectral curves of the sensitivity of the technical vision system and the spectral curve of the radiation of the backlight, the colour coordinates x, y and Y were obtained for all the studied dried sausage samples.

On the basis of the obtained results, correlation dependences between pH and the content of dry substances/water in dry-cured sausages, as well as between the values in

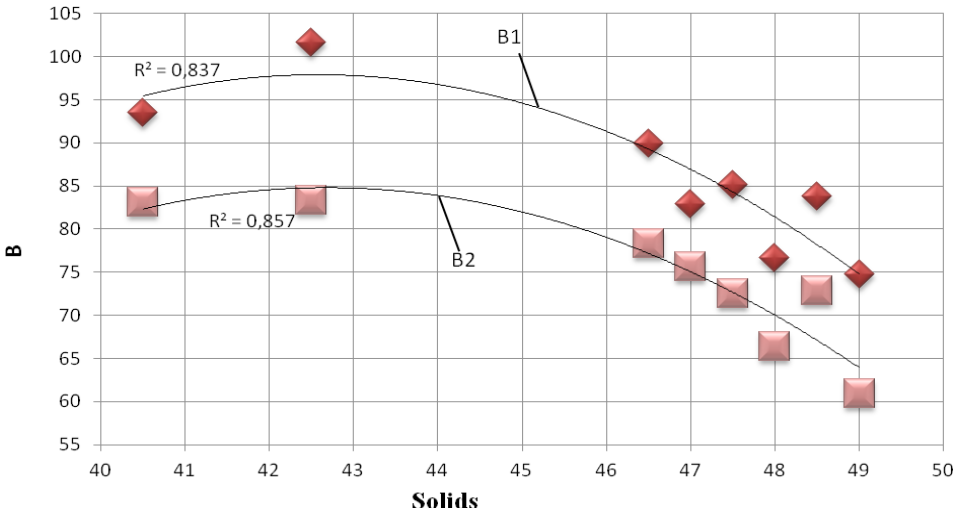

Figure 7. The dependence of parameter B (blue) on the amount of solids, where the B1 line represents points from the surface and the B2 line represents points taken from the cut.

individual x, y and Y colour coordinates and pH and the content of dry substances/water in sausages, were determined. For parameters x and Y, the point spread at the respective dependencies is significantly higher, as confirmed by the R^2, which is close to 0.4. Given these findings, we recommend using parameter Y from the xyY colour system for practical purposes. The Y characteristic for the surface and cut of the sausage is the most reliable because R^2 is 0.9–0.95 (Figs. 8–13). Using this system, we can determine with a high degree of reliability the pH value, and for dry substances the spread of points is significantly higher, which does not allow the dependence of the xyY parameters on the dry substance content for their determination.

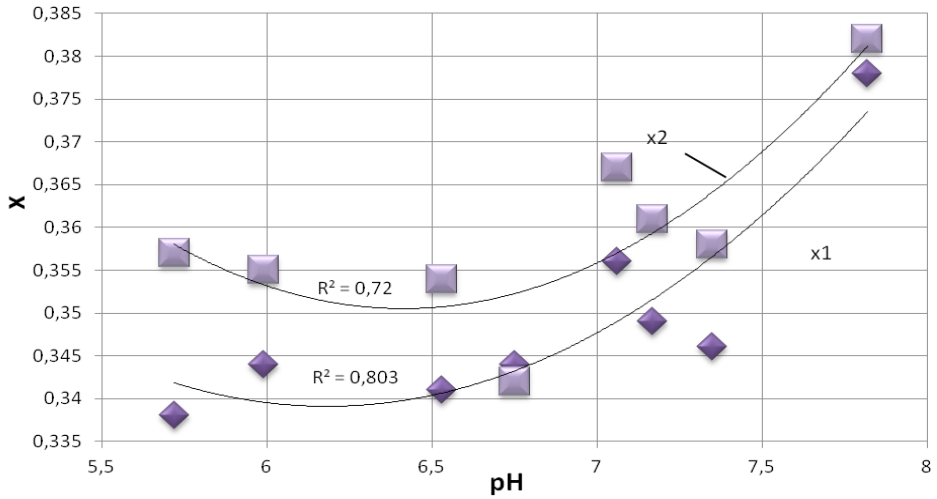

Figure 8. The dependence of the parameter x on the pH, where the X1 line represents points from the surface and the X2 line represents points taken from the cut.

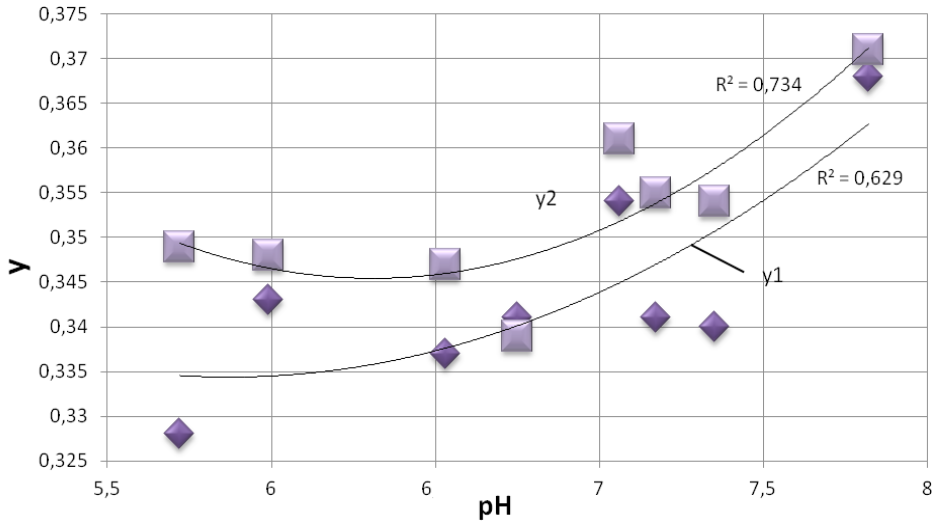

Figure 9. The dependence of the parameter y on the pH, where the y1 line represents points from the surface and the y2 line represents points taken from the cut.

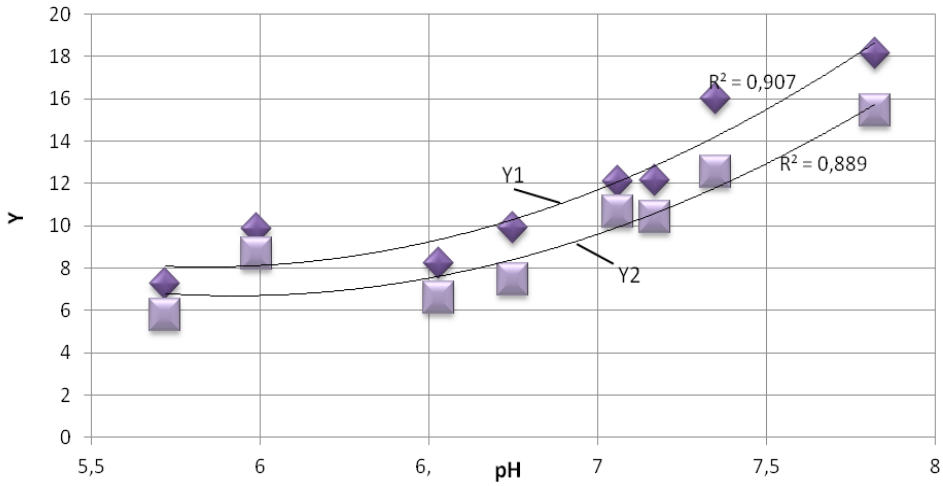

Figure 10. The dependence of the parameter y on the pH, where the Y1 line represents points from the surface and the y2 line represents points taken from the cut.

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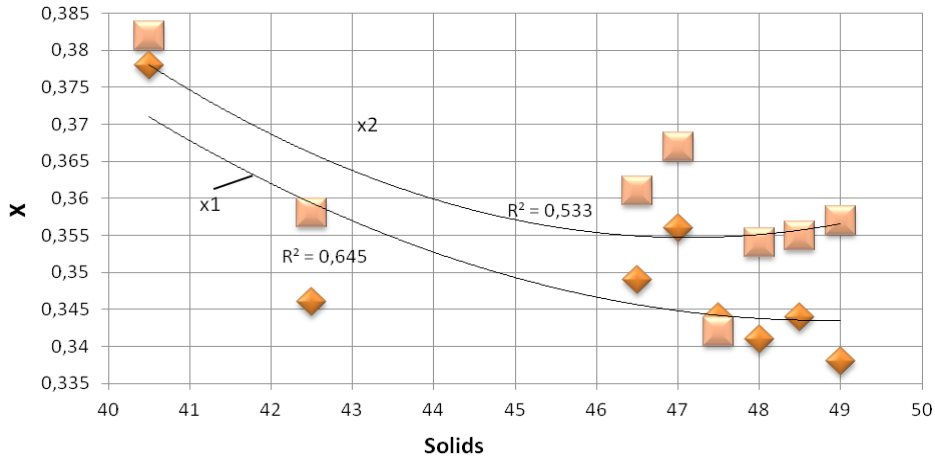

Figure 11. The dependence of the parameter x on the amount of solids, where the x1 line represents points from the surface and the x2 line represents points taken from the cut.

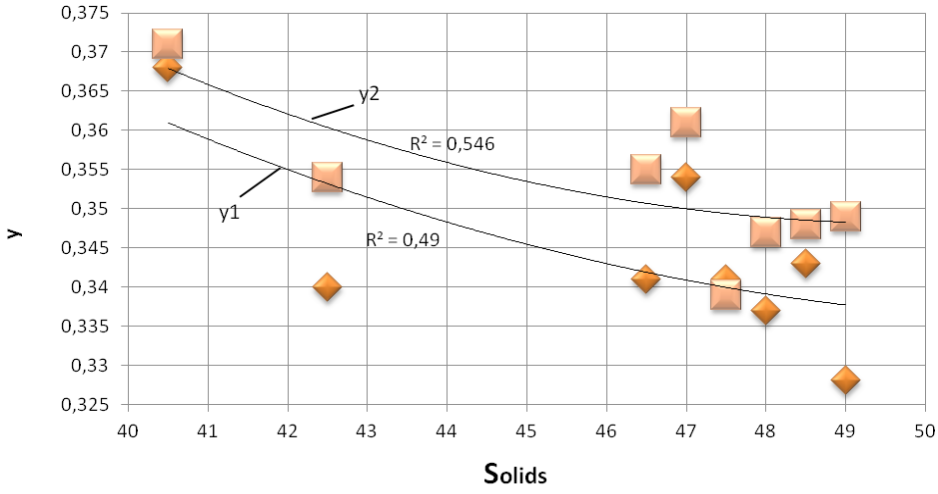

Figure 12. Dependence of the parameter y on the amount of solids, where the y1 line represents points from the surface and the y2 line represents points taken from the cut.

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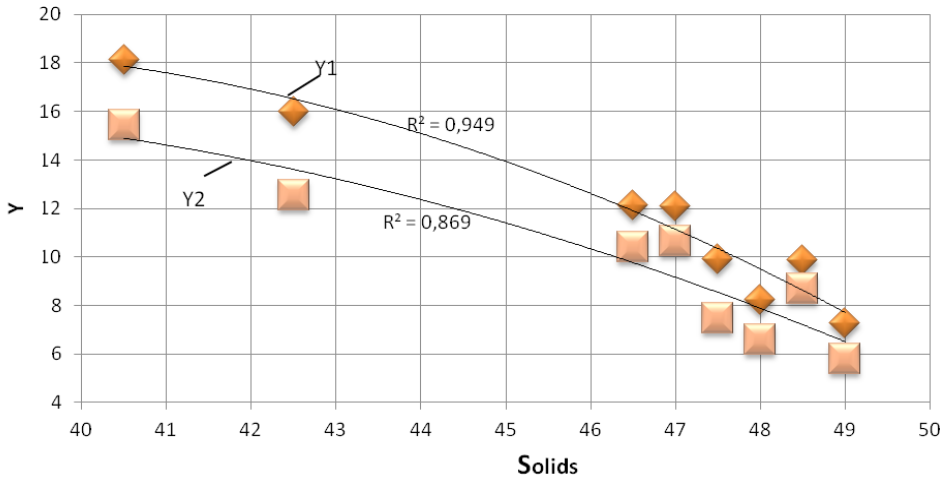

Figure 13. The dependence of the parameter Y on the amount of solids, where the Y1 line represents points from the surface and the Y2 line represents points taken from the cut.

4. Conclusions

The results revealed that the RGB and xyY colour systems have their own specificity in the course of building correlation dependencies between colour parameters and characteristics (pH, dry matter and food additive concentration). For the RGB system, the best results (namely, the highest R^2 value for the corresponding dependencies) are obtained using the R channel. For the xyY system, the best results are obtained using the Y channel, and the worst results are obtained using the x and y channels. All parameters give qualitative results in terms of their statistical processing. The conducted research opens an opportunity to control quickly and reliably the correct sausage production technology and ensure the quality of finished products by values of parameters in colour channels RGB and xyY under conditions of preliminary reception of correlation dependence for the given kind of meat products. The use of the Calcium-D3-Hizitel supplement in dry-cured sausage with a long shelf life cannot exceed 1%, as calcium content in the additive affects pH. To extend the shelf life, it is necessary to use vacuum packaging or a modified gas medium.

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