Reduction Potential of Meat, Depending on the Curing Composition

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Abstract— In formation of high quality of food products and their stability during storage, reduction reactions are important, their development can be estimated by measuring the reduction potential (ORP). The ORP value of meat products depends on many factors, including the nature of conjugated redox pairs, temperature, concentration of pro- and antioxidants. The objective was to study the process of preservation of meat with different pigment contents (pork, poultry) by curing compositions with low sodium content and their effect on the ORP of cured material, the rate of lipid and protein oxidation. The results indicate that the process of curing raw meat, both with sodium chloride and compounds with a low sodium content, is accompanied by a decrease in the ORP, which helps to stabilize the processes of pigment oxidation. A decrease in the amount of sodium chloride in the curing mixture composition contributes to inhibition of oxidative changes in lipids of the studied raw materials.

Keywords—reduction potential, pH, sodium chloride, meat pigments, lipid oxidation, curing compositions, meat curing.

I. INTRODUCTION

Formation of properties of biological systems, which include food products, redox is of great importance, the degree of electron activity characterizes the redox potential (ORP).

Development of redox processes in biological systems has its own characteristics, which is due to the action of not only oxygen and its active forms, but also the transformation products of lipids, proteins and enzymes, including those with antioxidant activity. The result of combined redox reactions is the redistribution of electrons in the molecules, a change in their structure due to the non-hydrolytic cleavage of individual bonds, the formation of new ones, isomerization of the carbon skeleton, etc. [1]. The ORP is used as a measure of processes such as glycolysis, oxidative phosphorylation and dehydrogenase oxidation of fatty acids [2].

The growth rate of microorganisms depends on the ORP value. Moreover, the range of potential values, at which we observe intensive growth of microorganisms, varies depending on their relationship to oxygen. According to the current classification, aerobic microorganisms actively grow at the ORP of +500 to +300 mV; facultative anaerobes +300 to −100 mV; and anaerobic from +100 to less than −250 mV [3]. The addition of ascorbic acid and a decrease in the ORP can cause anaerobic bacteria growth in the presence of oxygen, and, conversely, it is possible to cause aerobes growth under anaerobic conditions, increasing the ORP of the medium [4]. Morris, J.G. et al. put forward several hypotheses about the effect of the ORP and oxygen on the anaerobic microorganisms’ growth, according to one of which, anaerobes are able to actively grow and multiply in environments with a low reduction potential from minus 150 to minus 400 mV at pH 7.0 and in the presence of free oxygen [5].

In meat systems, the ORP value and the microorganisms’ growth rate are influenced by such processes as grinding and mixing of raw materials with the use of oxygen, various food additives, curing and heat treatment. For example, anaerobic Clostridium perfringens can grow at an ORP close to +200 mV, but in the presence of high concentrations of salt, the growth range increases [1].

In order to study the ionic composition of various conjugated redox pairs in inorganic systems we can use redox electrodes based on an inert metal — platinum. An exchange of electrons occurs through platinum between the reduced and oxidized forms in conjugated redox pairs.

To characterize the redox properties of biological conjugated pairs, instead of the standard values of the potentials E, which correspond to pH 0 or pH 14, normal values of the reduction potentials E, measured at 1 M concentration of the components and at pH 7.0 and at a constant temperature of 37 °C, are used.

In general, natural conjugated redox pairs of meat, including pigments, antioxidants have potentials in the range of -0.42 V to +0.82 V, characterizing the electrochemical stability of water [2].

Under these conditions, the potential value of hydrogen electrode E (2H+/H2) = -0.42V, and the ratio between the values of the normal and standard recovery potentials: E = E-0.42.

The ORP value is affected not only by the nature of conjugated redox pair and temperature, but also by the ratio of oxidized and reduced forms in solution activities.

The ORP value can be associated, with chemical transformations in the product, i.e. with the stability of food system, on the one hand, and with the concentration of components capable of receiving or giving away electron, on the other.

The redox potential of meat varies depending on the pH, the amount of hemeproteins and lipid oxidation products, the
enzymatic activity in muscles, the duration of autolysis, as well as the level of microbial contamination, the type and method of packaging, the partial pressure of oxygen in the storage medium, as well as the composition product and the presence of additional ingredients (ascorbic acid, sodium nitrite, reducing sugars, the level of cation oxidation, ionic strength, etc.) [1, 6].

Works on the effect of heat treatment of meat products on the redox potential value are acknowledged. It was found that low ORP values in raw meat are due to the presence of active respiratory enzyme systems; meat raw materials after heat treatment are characterized by a higher value of this indicator [7].

Measurement of the redox potential of meat and meat products opens up great opportunities in assessing the impact of technological parameters and processing methods on the nature and intensity of changes in the properties of raw materials and products during maturing, processing and storage.

One of the most significant technological processes is the raw meat curing with addition of sodium chloride. The prooxidant effect of sodium chloride is due to its effect on the integrity of cell membranes and faster interaction with proteins and lipids, a decrease in the catalytic activity of antioxidant enzymes and the formation of metmyoglobin, which accelerates the oxidation process. The presence of impurities in salts, such as salts of iron and copper, can have an additional prooxidant effect [8]. Puolanne and Halonen revealed a specific mechanism of the prooxidant effect of salt on muscle proteins [9]. These facts indicate that curing of raw materials strengthens the tendency to oxidation.

The objective is to study effects of curing compositions with a partial replacement of sodium chloride on the of redox direction in the process of curing raw meat raw.

II. MATERIALS AND METHODS

A. Sample Preparation

Traditionally, salt (sodium chloride) is used for curing raw meat, which is a vital source of sodium for the human body. At the same time, excessive sodium intake increases the risk of developing cardiovascular diseases. In accordance with the recommendations of the World Health Organization, the recommended rate of sodium intake is 5 g of salt per day.

The amount of sodium chloride added to most meat products varies from 1.7% to 4%. Considering that the negative effect of salt on the human body lies in the cumulative effect, a decrease in the salt amount, and, consequently, sodium, fully complies with modern trends of healthy nutrition.

In this regard, for the raw meat curing we used table salt (K) and a curing mixture (70% sodium chloride + 15% potassium chloride + 15% calcium chloride) – (A).

Cooled raw materials were used for the curing – chicken meat (thigh fillet), pork (the longissimus muscle). Cooled poultry and pork were crushed to a particle size of 2-3 mm and mixed with the studied curing ingredients – salt and curing mixture. The level of introduction of dry curing compositions is 3% by weight of raw materials.

Raw meat mixed with curing ingredients was kept for 48 hours at a temperature of (4 ± 2) °C. Determination of the redox potential, pH, amount of pigments and thiobarbituric acid (TBA) number was carried out after 48 hours of curing.

B. Determining pH

Active acidity (pH) is a potentiometric method based on measuring the electromotive force of an element consisting of a silver chloride electrode and a reference electrode with a known potential value.

C. Determining reduction potential (ORP)

The ORP was determined using an ionomer with a platinum electrode, and a silver chloride electrode as a reference electrode. A platinum electrode was tightly placed in a sample of chopped meat (100 g) and measurements were performed 2 minutes after immersion [10].

D. Determining total pigment content

Content of the total pigment amount in the samples of raw meat was determined by the method [11], based on extraction of meat pigments with an aqueous solution of acetone and subsequent measurement of the optical density of the extract on a spectrophotometer of a PE-5400UF spectrophotometer (ECROSHIM, Russia) at a wavelength of 640 nm with respect to hydrochloric acid acetone.

E. Determining metmyoglobin content

The content of metmyoglobin was determined by the method of Krzywicki et al. [12], based on the extraction of pigments with subsequent measurement of the optical density of the solution at wavelengths of 525, 545, 565, 572 nm.

F. Determining thiobarbituric acid (TBA) number

The thiobarbituric acid number was determined by the Tarladgis distillation method [13] using thiobarbituric acid.

G. Statistical processing

For each type of raw meat, the results were obtained on 5 series of measurements, checked for homogeneity; the measurement repeatability of each of the indicators within the series is threefold. Data processing was carried out by standard methods of mathematical statistics. The measurement results are presented as mean ± SD (standard deviation) at a confidence level of p <0.05.

III. RESULTS AND DISCUSSION

The process of curing raw meat materials is accompanied by a change in its functional, technological and consumer properties, a change in the state of the protein and lipid fraction. The direction of all these changes can be estimated, including the magnitude of the ORP.

According to the obtained data, the ORP value for the initial cooled raw material is 124.3 mV for pork and 60.6 mV for poultry. The obtained results should be explained by a number of significant factors, among which, in our opinion, the ion ions Fe^2+ and Fe^3+ which are part of heme pigments, which content meat is minimal in poultry and 1.86 times less than in pork (Table 1).

The pH value of pork is lower than the pH of poultry meat at 0.95 units. The results are consistent with the available data that there is an inverse relationship between pH and the ORP [14].
It was found that curing with table salt (sample K) and subsequent exposure for 48 hours leads to an increase in ORP. So, in pork with table salt (sample K), the ORP value decreased by 8.5% relative to unsalted raw materials, in a similar sample of poultry meat – by 8.0%. The introduction of sodium chloride in raw meat leads to an increase in the pH of the medium in the studied samples, which is consistent with the known dependencies.

The obtained ORP values are consistent with the dynamics of the pH of the raw material during the salting process [7, 14].

The pH value affects the redox direction, so with an increase in pH and a decrease in redox potential, favorable conditions are created for the reduction reactions.

This type of reaction occurring during curing is the conversion of meat pigments, that is, myoglobin.

Curing sodium chloride leads to an increase in the amount of metmyoglobin in meat raw materials on the background of a constant content of total pigments. It was found that the amount of metmyoglobin in pork after 48 hours of curing increased relative to unsalted raw materials by 31.0% and by 35.4% for poultry meat.

When replacing 30% sodium chloride with a mixture of potassium chloride and calcium chloride in a 1:1 ratio, the following dependences of the studied parameters were obtained. After 48 hours of salting, the pH of salted pork and poultry meat increased, but turned out to be lower than the values of similar samples with table salt by 0.13 units and 0.15 units, respectively. The results should be explained by an increase in the concentration of potassium and calcium ions in the studied curing composition.

As a result of lowering the pH, there is a slight decrease in redox potential. Thus, the decrease in redox potential in sample A from pork relative to sample K was 2.8%, from poultry meat – 8.8%, respectively.

The decrease in redox potential in the experimental samples creates favorable conditions for the stabilization of heme pigments, since the oxidation rate of myoglobin decreases at a lower value of the potential, which ensures the preservation of the pink-red color that is typical for the initial raw material. This is due to the fact that in the presence of potassium chloride and calcium chloride, which exhibit the properties of weak reducing agents, there is a decrease in the concentration of Fe3+ ions and an increase in the number of Fe2+ ions, accompanied by a decrease in redox potential. A certain role in stabilization of the initial color can be played by carboxymyoglobin, the formation of which is promoted by a decrease in TBA number [6].

Experimental data indicate a decrease in the amount of metmyoglobin in meat samples treated with compositions with a low content of sodium chloride. The amount of metmyoglobin in pork (sample A) decreased by 9.7%, in comparison with the control sample, and in poultry meat – by 9.4%. The results are consistent with a visual assessment of the prototypes – the color was regarded as more attractive.

The obtained experimental data are confirmed by the studies of James R. Claus, Holownia K. et al., they found that the addition of 1% of sodium chloride during turkey curing helps to reduce the redox potential and create favorable reducing conditions for the pink color formation in the boiled turkey breast, as a result of preservation of myoglobin in native form [15, 16].

Similar results were obtained by Jong Youn Jeong [17], indicating that an increase in the concentration of sodium chloride from 1% to 3% during curing of chicken breast and subsequent exposure for 3 days helps to reduce the ORP, preventing the oxidation of myoglobin.

Ismail Hesham et al. report that curing turkey meat with 2.5% sodium chloride contributed to a decrease in the ORP, while the curing duration did not affect the change in the studied parameter [18]. Research of Morris J.G. [19] indicates that an increase in salt concentration during curing of herring contributes to an increase in the ORP values.

The process of curing affects not only the formation of the functional and technological properties of raw meat, but also provokes the oxidation of lipids, which leads to poor quality.

The intensity of the oxidation processes was evaluated by the value of the thiobarbiturite (TBA) number, which characterizes the amount of malonic aldehyde formed. According to the obtained data (table 1), curing with sodium chloride provokes lipid oxidation processes in both pork and poultry (samples K). It was found that the value of TBA number relative to unsalted raw materials increased by 14.9% and 11.3% for pork and poultry, respectively.

An unambiguous explanation of the effect of sodium chloride on lipid oxidation mechanism does not exist today. One of the possible reasons is the violation of the integrity of cell membranes in the presence of sodium chloride, which makes lipids available to oxidation catalysts. Another reason is the participation of salt in the conversion of myoglobin to metmyoglobin, which is a prooxidant factor. Another possible

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**TABLE I. INFLUENCE OF CURING CONDITIONS ON PROPERTIES OF RAW MEAT MATERIALS (P < 0.05)**

| Sample          | pH      | ORP, mV  | Pigment amount, mg/100g | TBA number, mgMA/kg |
|-----------------|---------|----------|-------------------------|---------------------|
| Pork meat (longissimus muscle) |
| raw (n=15)      | 5.35±0.03abc | 124.3±3.31abc | 108.3±0.15abc | 50.1±0.10abc | 0.15±0.08bc |
| raw +K (n=15)   | 5.60±0.04bc | 113.7±12.39bc | 108.9±0.30bc | 65.8±1.17bc | 0.362±0.06bc |
| raw + A (n=15)  | 5.47±0.06bc | 110.5±2.04bc | 109.4±0.26bc | 59.4±0.12bc | 0.322±0.09bc |
| Poultry meat (thigh fillet) |
| raw (n=15)      | 6.30±0.20abc | 60.6±1.21abc | 58.2±0.11abc | 23.4±0.13abc | 0.167±0.04abc |
| raw +K (n=15)   | 6.54±0.05abc | 55.7±1.48abc | 59.6±0.12abc | 31.7±0.10abc | 0.186±0.05abc |
| raw + A (n=15)  | 6.39±0.02abc | 50.8±1.62abc | 58.7±0.14abc | 28.7±0.12abc | 0.179±0.03abc |

K – table salt
A – curing mixture (70% sodium chloride + 15% potassium chloride + 15% calcium chloride)

The a-c values in the columns are significantly different (p < 0.05)
reason is the ability of salt to reduce the activity of antioxidant enzymes such as catalase, peroxidase and glutathione peroxidase [20, 21].

When curing pork and poultry with a potassium chloride and calcium chloride mixture instead of sodium chloride, a decrease in the TBA number was revealed. When curing meat with a low sodium chloride mixture (samples A), the TBA value decreased relative to the control sample for pork by 11.0% and poultry meat by 3.8%. The results can be explained by a decrease in the amount of sodium ions that can displace iron ions from heme-proteins, on the one hand, and, by a decrease in the number of chlorine ions in curing compositions that act on lipids as an oxidizing agent, on the other hand.

The rate of lipid oxidation is affected by the change in redox potential. It is known [5] that an increase in the ORP of raw meat after curing contributes to an increase in the amount of metmyoglobin and, as a result, intensifies the processes of lipid oxidation, which is expressed in the TBA value increase.

The obtained experimental data indicate that the process of curing meat raw materials is accompanied by an intensification of oxidation processes, against the background of a decrease in redox potential. At the same time, a decrease in the amount of sodium chloride helps to stabilize the amount of sodium chloride, thus reducing the ORP. The results can be explained by the fact that the determining factors, affecting the intensity of the lipid fraction oxidation, are the type of raw material – its fatty acid composition, the presence of food additives, including sodium chloride, and to a lesser extent – the ORP.

IV. CONCLUSION

An analysis of the experimental results suggests that replacing 30% sodium chloride with a KCl+CaCl2 mixture in a 1:1 ratio during curing helps to reduce the ORP in raw meat materials. In turn, this leads to the oxidation processes inhibition of the lipid fraction and pigments and to an improvement of meat color.

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