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DIFFUSION AND DISMUTATION OF NITRITES IN PORK MEAT CURED BY INJECTION

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Introduction

Application of nitrite curing in industrial technologies required a change from the immersion technology to the injection one, due not only to the intensification of the process but also to the necessity of accurate dosing of the toxic substance. Nitrite injected into meat is reduced in the process of dismutation to nitric oxide which reacts with meat pigments and is oxidised to nitrate. In the professional literature there is no information on any successful test on the process of diffusion of nitrites and their changes after injection into meat, what results from the methodologic difficulties both in the analysis of nitrates and nitrites in very small samples as well as in the field of mathematic interpretation of the results.

Materials and methods

The tests were carried out on the pork *longissimus dorsi* muscle. From each muscle, two end sections about 4 cm long were cut as control samples as well as 5 sections, each 8 cm long, as test samples. Sample diameter was about 7 cm. The samples were placed in beakers, 10 - 12 cm high and of a diameter approximately equal to that of a muscle cross-section. For injections a medical syringe with a 4 cm long needle was used. In the central point of the cross-section, having the whole needle length inserted into meat, 1 cm^3 of brine containing 18 g NaCl and 135 mg $NaNO_2$ was injected. A surgeon stitch had been put on the muscle around the needle to held brine inside. The times of diffusion were 2, 5, 9, 15 and 24 hours and ambient temperature 4 - 6°C. After the predetermined time each portion of the muscle was thermally denaturated in a microwave oven. The samples were cut as follows: first each sample was cut crosswise, transversely to the cylinder axis at its mid-height. The red spot of cured meat on the cross-section was then contoured on a transparent foil. Then the samples were cut along the cylinder axis and perpendicularly to the epimysial (external) side of the sample and another contour was taken. Consecutive cuts were made in such a way that finally a horizontal central slice, 1 cm thick, and a vertical central slice, also 1 cm thick, were obtained. From those slices samples of a circular or semicircular shape of 0,8 cm diameter were cut using a cork-boring device. The samples represented fragments of meat layer on one level at a distance of 0,5; 1; 1,5; 2; 2,5 and 3 cm from the cylinder axis and vertical layers at a distance of 1 and 2 cm downwards from the cylinder centre. In the samples the contents of nitrates and nitrites were determined. Nitrites and nitrates were extracted according to the international standards [2, 3]. A quantitative detrmination was made by flow-injection analysis using the Tecator 5010 FIA-star System [4]. The colour reaction with Griess reagent was the basis of the analysis and nitrates were reduced to nitrites in a cadmium column.

Results

The contours of cured meat at muscle sample cross-sections showed more or less regular ellipses. At vertical sections the spots were less regular but always oblique in relation to cylinder axis. It means that the sampling procedure allowed for the determination of diffusion constant on the main muscle directions what, however, did not guarantee proper measuring of their maximum values. The comparison of the results of determination of the sum of nitrates and nitrites with the results of determination of nitrites only showed a specific distribution, dependent on the position of the sample in the muscle. In the centre, where the highest concentrations of nitrites were noted, a relative contents of nitrates was minimal, the further off the centre the higher concentration of nitrates was noted. Figure 1 shows exemplary concentrations distributions of the sum of nitrates and nitrites along the sample diameter and figure 2 - distributions of ratios of nitrites to the sum of nitrites and nitrates. The results marked with squares relate to the analysis after 2 hours and with triangles - after 24 hours of curing.

A significant variation of values of the ratio $NO_2'(NO_2' + NO_3')$ for meat samples taken from different carcasses was noted. It might possibly depend on variations of pH value and redox potential among meats.

Discussion

Analytical solution of a differential quadratic equation describing, according to Fick's law, the diffusion phenomenon, was in our case practically impossible. Also all the simplifying assumptions like uniformity of material and lack of substrate losses were unacceptable. First of all, moreover, the initial distribution of nitrite concentration (x_1, x_2, x_3, t) in the moment $t = 0$ was unknown. In such circumstances there was applied an interpretation method consisting in attributing to the phenomenon the arbitral solution in which the equalization of concentrations in any direction goes with another finite value of diffusion factor a_i and the distribution of concentrations is a normal distribution in the diffusion area. For three-dimensional space it means that points of equal concentration lie on the surface of an ellipsoid. In this connection a typical solution of a diffusion equation:

$$\frac{du}{dt} = a_i\left(\frac{d^2u}{dx^2{}_1} + \frac{d^2u}{dx^2{}_2} + \frac{d^2u}{dx^2{}_3}\right) \tag{1}$$

from the very assumption got a form:

$$u(x_1,x_2,x_3,t) = \frac{1}{(2\sqrt{\pi\cdot a_1\cdot a_2\cdot a_3})^3}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\exp\left[\left(-\frac{x_1^{\,2}}{4a_1t}\right)+\left(-\frac{x_2^{\,2}}{4a_2t}\right)+\left(-\frac{x_3^{\,2}}{4a_3t}\right)\right]dx_1dx_2dx_3 \tag{2}$$

where: u - concentration, x_1 x_2 x_3 - co-ordinates in three-dimensional space, t - time, a_1 a_2 a_3 - diffusion coefficients on the main axis of the ellipsoid.

In order to determine numerical values of the diffusion coefficients, a network of a normal distribution was made and concentration values for different values x_i and time t were marked on it. The concentration values were recalculated to an undimensional parameter $F(x)$ being the ratio of the concentration u_x in any place x of the axis to the maximum concentration u_{max} in the place $x = 0$, divided by 2. In the normal dystribution network the experimental points lie on a straight line what confirmed the normal distribution of the concentration.

From the figures the standard deviation values of the given distribution S_x were graphically determined. It was dimensional (in cm) and according to the equation (2) it should depend on a diffusion constant a_i and the time of curing t for the chosen direction of diffusion:

$$S_{xi} = 2\sqrt{\pi \cdot a_i \cdot t} \qquad (3)$$

Thus we should obtain an equation $S_{xi} = f(\sqrt{t})$ in the form of a straight line crossing the beginning of the co-ordinate system.

For the example shown the calculated coefficient of diffusion in the horizontal direction determined by the cross-section of muscle was $a_1 = 7{,}5 \cdot 10^{-8}$ cm^2 sek^{-1}. For the diffusion along the vertical axis of a muscle the diffusion coefficient was $a_2 = 18 \cdot 10^{-8}$ cm^2 sek^{-1}. The nitrite diffusion coefficient in the pork *longissimus dorsi* muscle determined by Fox [1] was $13 \cdot 10^{-7}$ cm^2 sek^{-1}, so it was 10 times higher than those determined in the present work. The difference results, most likely, from entirely different conditions of the experiments. The model conditions of the experiments carried out by Fox did not represent those which took place inside muscle tissue after brine injection.

Conclusions

1. Propagation rate of the front of nitrite and nitrate diffusion in injected muscle was proportional to the square root of time what means that the process went according to the Fick's diffusion law.
2. Concentrations of nitrates and nitrites in the diffusion area during the process of equalizing of concentrations were roughly of a normal distribution.
3. Diffusion rate depended on the direction of muscle fibres. The differences in the diffusion coefficient values might be substantial, even to 2 - 3 times.
4. The highest contribution of nitrates to the sum of nitrites and nitrates was observed in the front of the diffusion what most probably resulted from the loss of nitrites reduced to nitric oxide which reacted with hem pigments.
5. Values of diffusion coefficient calculated for the experimental data were 10 times higher than those given by Fox [1]. It might result from the entire dissimilarity of the experiments carried out by this author in the course of which, due to the permanent excess of nitrites, their loss resulting from the reduction and oxidation could be unnoticeable.

At present the works aimed at elucidation of the mechanisms of the observed phenomena and especially the influence of pH value and redox potential on the rate of change of nitrites into nitrates as well as influence of brine concentration and amount of injected brine on the process rate, are carried on.

Literature

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Fig.1. Distribution of concentration of the sum of nitrites and nitrates along the sample diameter

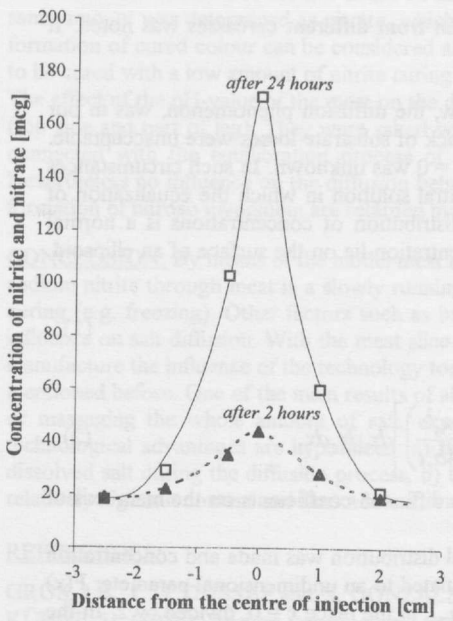

Fig. 2. Distribution of the ratio of nitrites to the sum of nitrites and nitrates along the sample diameter