DIFFUSION OF SODIUM CHLORIDE AND SODIUM NITRITE IN RAW MEAT MODEL SYSTEMS

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BACKGROUND: The quality and the shelf life of dry-cured raw meat products are highly influenced by the diffusion behavior of the curing additives, especially sodium chloride and sodium nitrite. Salt reduces the water activity and in this way prevents the development of undesired microorganisms. Nitrite gives cured meat products the typical colour. The penetration of salt into muscle tissue in principle obeyes the laws of diffusion. With this work the influence of meat treatment on the diffusion of sodium chloride in comparison to the curing agent sodium nitrite was investigated in two model meat systems - porous disk (meat slice) and meat cylinder -. That investigation was supplemented by salting and curing pork hams of different volumes such as M. long. dorsi, short cut hams (top side and part of leg) and bone-in hind legs.

OBJECTIVE: The production of raw ham is mainly based on empirically found knowledge until now. There are a lot of different curing technologies, but most of them are lacking a scientific basis. The difficulties of curing are seen first in the salting process, i.e. in reaching and distributing a defined amount of salt within a piece of meat, because salt penetration conforms to the laws of diffusion and is therefore depending on physico-chemical parameters (Palmia, 1991). Another problem is the addition of the proper amount of nitrite. The amount of nitrite should be as small as possible, but enough to form a stable cured colour in all parts of a ham. This is of special interest, if the German nitrite curing salt (99.5-99.6 % NaCl plus 0.5-0.4 % $NaNO_2$) is used for ham curing. The purpose of the experiments was to compare the salt diffusion in fresh and frozen/thawed meat and to compare the diffusion velocity of salt with that of nitrite, because nitrite is expected to be lost during penetration by reacting with the constituents of meat.

METHODS: All the investigations were carried out using defatted M. longissimus dorsi from pork, because of its relatively homogeneous texture. The muscle samples were either cut into 3 mm thick slices or meat cylinders of 150 mm in length. The slices were placed as a porous disk between the two chambers of a diffusion cell (J.B. GROS et al., 1984), which had been modified in two points: the screws, fixing the meat slice between the two parts of a frame, were sealed with o-rings at both sides of the frame and the low concentration tank (B) contained half the volume of the high concentration tank (A). Chamber (A) contained a 10 % solution of sodium chloride or nitrite curing salt (99.5-99.6 % NaCl plus 0.5-0.4 % $NaNO_2$). Chamber (B) was filled with destilled water. The salt solution was stirred with a magnetic bar at a temperature between 21 and 24 °C. The increase of salt ions in the low concentration tank was measured after different periods of time within 24 hours. The meat cylinders were prepared as follows: the cuts were wrapped tightly with four layers of plastic foil and then stuffed into an elastic net. Thus a more or less one-dimensional diffusion from only the cranial and caudal cut was forced. The curing room temperature was about 5°C. The curing brine contained 10 or 15 % nitrite curing salt. Chemical evaluations including pH, sodium chloride, residual nitrite and nitrate were conducted at 1, 2, 4, 7, 10, 14 and 28 days after cure application. For this reason the cylinder was cut into 8 slices (10 mm thick) starting from the first cut.

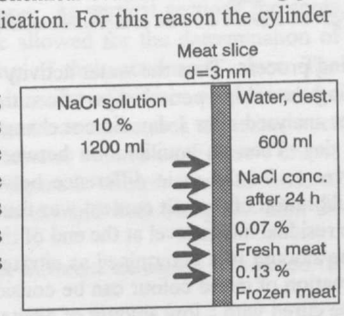

Fig.1: Illustration of diffusion velocity in a diffusion cell

Parallel to these model systems ham cuts from fresh and frozen/thawed raw material were cured according to a modified usual curing technology, which is characterized by a mechanical salting process. The analyses included the determination of sodium chloride and nitrite, nitrate and water content as well as the measurement of pH and water activity. The hams were devided into a surface and a core section. Chloride was determined by the method by Volhard and with 'Spectroquant 14755' (Merck), resp. Nitrite was analysed photometrically using Griess-agent, and nitrate was reduced with an enzym to nitrite. Sodium was determined with an ion sensitive electrode (KÜHNE, 1986). The measurement of the aw-value was done as by RÖDEL et al., 1989.

RESULTS and DISCUSSION: The experiments with the diffusion cell showed, that the diffusion of salt ions through a meat slice is a very slowly running process (fig. 1), that the diffuson of salt is accelerated, when frozen/thawed meat is used (fig.2) and that nitrite penetration is retarded, because of its reaction with the various constituents of meat during the diffusion process (fig. 3).
Figure 1 and 2 illustrate, that even under favourable conditions (stirring of the salt solution at temperatures about 22 °C; double volume of concentrated solution compared to that of the receiving tank) it takes about 24 hours to increase the amount of salt ions in the water tank to a level, which is approximately corresponding to a 0.1 % solution. Thus it can be assumed, that the salt diffusion under practical curing conditions will last much longer because of the low curing temperature and the use of naturally grown meat, which consists not only of muscle, but also of fat and connective tissue. From figure 2 it can be concluded, that the diffusion process in meat is influenced by the treatment of the meat before curing. So the salt ions can penetrate faster and more continually through a meat, that was frozen and thawed before curing, than through fresh meat. While the increase of chloride ions in tank (B) amounted to 0.84 mmol/l·h with frozen/thawed meat the corresponding value with fresh meat was only 0.65 mmol/l·h. This effect may be caused by the destruction of the muscle cells, which leads to an increase of the extracellular liquid phase.

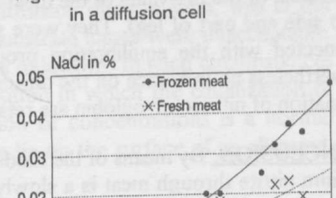

Fig.2: NaCl diffusion in fresh and frozen meat

15 tests were carried out with a 10 % sodium nitrite solution to compare the diffusion behavior of the nitrite anion with that of the sodium kation. Figure 3 indicates the increase of both kation and anion within 9 hours after starting the diffusion process. During the first 4 to 5 hours nitrite ions penetrated slower than sodium ions. Afterwards the amount of both ion types measured in mmol in the receiving tank was the same. Thus it can be concluded, that a small part of the nitrite anion has reacted with myoglobin and/or other constituents of the meat. However, it should be mentioned, that the loss of nitrite is very low.

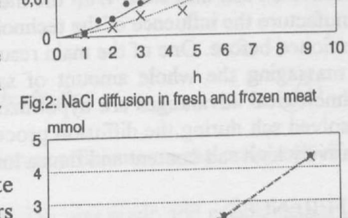

Fig.3: Diffusion of sodium and nitrite ions through a meat disk

From the investigation with meat cylinders nearly the same results as with the meat slices can be drawn. First it could be found, that the increase of salt concentration c in meat in dependence on the diffusion distance s can be described by a reciprocal, exponential equation. That means, the concentration curve slops down to a zero level within a relatively short distance. Regardless of the applied technology (brine or dry curing) it was found, that the salt concentration decreased from about 12 % at s = 1 cm to 0.3 % at s = 5 cm even after ten days of curing (fig. 4). These curves are also valid for nitrite. For this reason one can conclude, that the amount of nitrite, which is used up by reacting with other substances, has no significant influence on its diffusion process in meat pieces. The diffusion is mainly determined by the meat constitution itself. The increase of salt concentration in a meat cylinder in dependence on time was found to follow a linear function. Figure 5 shows the develpoment of the salt concentration at two diffusion distances (1 and 4 cm) related to the first cut. Additionally the concentration-time-courses in the meat at different cure concentrations (25 % with dry curing, 15 and 10 % with brine curing) are compared. The cure concentration has a significant influence on the slope of the concentration curves, although this influence decreases with a rising diffusion distance. Apart from time and distance the influence of the pH-value of the meat on the salt diffusion was investigated. Figure 6 demonstrates exemplarily the salt diffusion in dependence on pH and distance at 10 and 21 days after the begin of curing. It was found, that there hardly exists a relation between diffusion velocity and pH. This is especially true to advanced curing time and diffusion distances over 5 cm.

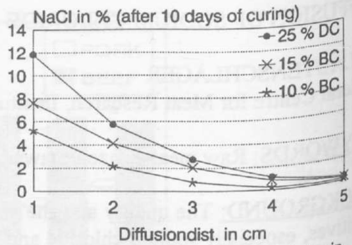

Fig.4: Diffusion of salt in a meat cylinder in dependence on applied salt concentration

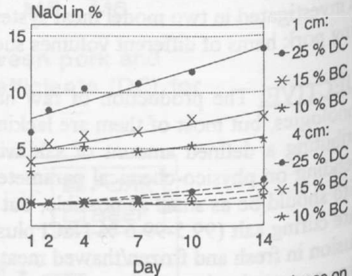

Fig.5: Increase of salt conc. in dependence on time at a diff. distance of 1 and 4 cm

For the examination of the results received with the model systems different kinds of raw hams were produced according to usual technologies. The most important finding is, that the diffusion of the salt ions in meat is mainly determined by the following aspects: meat constitution (fat and connective tissue, bones), relation of muscle surface to ham volume and salting technology, that is the input of the required amount of salt into the surface layer within a short period of time. With the production of hams from M. long. dorsi ('Lachsschinken') it was found, that there is only little influence of freezing on the diffusion, if a tumbler was used for the salting procedure. The courses of the concentration curves determined in the surface and the core section, resp., are shown in figure 7. The ham cuts were cured over a period of 14 days at 5 °C. Due to the treatment of the meat (fresh or frozen/thawed) only slight differences can be seen, but if usual brine curing (fig. 8) is compared with mechanical salting, a remarkable difference of the salt content, especially in the surface section was reached. Meat pieces, which were salted mechanically (e.g. with a tumbler), contain a relatively high amount of salt in their surface layer from the beginning of the curing process. Thus the water activity of the ham is reduced to a value, that is able to prevent microbial spoilage during the salting period. Apart from this, attention should be payed to the fact, that the salt content in the surface layer analysed after 1 day did not change during the 14 days of salting. That of the core increased steadily up to the 7th day. Then an equilibration between surface and core salt concentration was reached. This point obviously proves to be the main difference between usual and tumble salting, because with usual brine curing no entire equilibration of the salt content was found even after 13 days of curing.

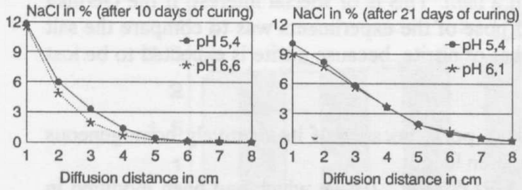

Fig.6: NaCl-diffusion in dependence on the pH of meat

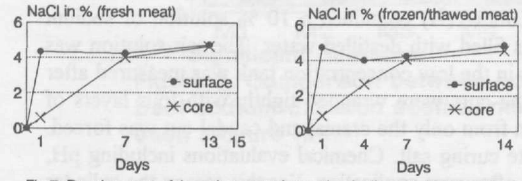

Fig.7: Development of the salt content in mechanically salted M.long.dorsi

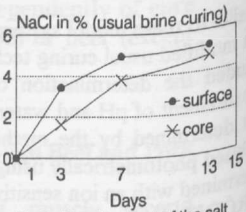

Fig.8: Development of the salt content in M.long.dorsi

The residual nitrite level at the end of the 14 days curing period amounted to more than 40 ppm. Approximately the same amount was determined as nitrate, which was formed by the oxidation of added nitrite. At the same time the formation of cured colour can be considered as completed. Problems may arise, if bone-in hams of big volume are to be cured with a low amount of nitrite curing salt mixture.
The effect of the pH-value of the meat on the diffusion of the curing salts was studied with deboned short cut hams (top side and part of leg). They were salted with a tumbler (moving time was 90 min.). This procedure was followed immediately by drying connected with the equilibration process of the salt. 50 % of the raw material had DFD-properties, that means pH-values over 6.1. Nevertheless no influence on the diffusion behavior of the salt ions could be found. It is assumed, that only the drying process as well as the formation of nitroso myoglobin are retarded by that pH level.

CONCLUSION: By means of the model meat systems 'porous disk' and 'meat cylinder' it was shown, that the diffusion of sodium chloride and sodium nitrite through meat is a slowly running process, which is mainly affected by the constitution of the meat and by its treatment before curing (e.g. freezing). Other factors such as brine concentration and convection, pH value of the meat and temperature have no remarkable influence on salt diffusion. With the meat slice a nitrite loss during the first period of the diffusion was proved. As shown with practical ham manufacture the influence of the technology together with the tissue composition of the ham seems to predominate the influence of the factors mentioned before. One of the main results of all investigations is the experience, that the salting process in meat can be accelerated by rubbing or massaging the whole amount of salt, expected or desired in the final product, into the muscular part of its surface. The following technological advantages are hypothized: a) the salt ions don't have to pass any boundary layers between different phases or states of the dissolved salt during the diffusion process, b) the meat surface, which is particularly succeptible to microbiological contamination, contains a relatively high salt content and thus a low a_w-value. Both factors protect the meat from spoilage.

REFERENCES:

GROS, J.B., C.G. DUSSAP and N. GONZALES-MENDEZ (1984): Solute diffusivities in meat - a review. Engineering and Food S. 287.
KÜHNE, D. (1986): Analyse von Kochsalz und Natrium in Fleischerzeugnissen. Fleischwirtschaft **66**, 1433-1436.
PALMIA, F. and BOLLA, E. (1991). Salt diffusion in dry cured ham. Proceedings of 37th ICoMST, II:918-921.
RÖDEL, W. et al. (1989): Neues Verfahren zur Bestimmung der Wasseraktivität in Fleischerzeugnissen. Fleischwirtschaft **69**, 1396-1399.