Phosphate crystals in raw cured ham

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SUMMARY: The storage of raw cured ham at refrigeration temperature causes sometimes the formation of translucent crystals in the muscles after some days. Crystals composition was analyzed and consist of $Na_2PO_4H.7H_2O$ and $Na_2PO_4H.12H_2O$. The crystals dissolve in the crystallization water as the temperature increases. High NaCl and phosphate concentrations, low humidity level and high pH in the muscle favour the formation of these crystals when the ham is stored at refrigeration temperatures. A high relative humidity facilitates the formation of phosphate crystals in the outer part of the ham. The P_2O_5/protein relationship diminishes during the process, specially during the salting (due to water exudation) and postsalting period (due to crystallisation in the outer part of the ham). The P_2O_5/humidity relationship is always higher in the drier areas.

INTRODUCTION: During the storage of raw cured hams, some crystals sometimes appear in the muscle, on the cut surface and on the outer part of the ham during the postsalting period. This phenomenon has not yet been described in raw cured hams but it is known that this occurs in white ham, showing many big crystals of ortophosphates in the flesh (Rozier and Durand, 1969). In fermented sausages crystals of Na_2PO_4H have been found when temperature diminishes to 3-5 ^0C (Ghinelli, 1977). In canned tuna phosphates form unwanted crystals of struvite ($Mg(NH_4)PO_4.6H_2O$), formed from the naturally occurring phosphates in the fish, and may look like broken glass (Van Wazer, 1971). The objective of this research was to determine the composition of this kind of crystals, the factors that could influence the presence of them and the evolution of P_2O_5 during the aging process in different parts of the ham.

MATERIAL AND METHODS: **Measurement of pH:** 10 g of muscle were homogenized with 90 ml of destilled water with an Ultraturrax homogenizer. The pH was measured immediately after homogenization. **Measurement of the presence of crystals at different temperatures:** 15 pieces coming from five different hams were vacuum packaged and stored at three different intervals of temperature (1-3 ^0C, 8-10 ^0C and 15-18 ^0C) for 15 days. **Raw cured ham fabrication:** 48 hams were cured with 0,4 g of nitrate and 10 g of salt per Kg of green ham for 24 hours, then they were covered with salt one day per Kg of raw ham at 3-5 ^0C. After the salting period hams were washed and hung at 3-5 ^0C for 30 days. The ageing period was carried out for 5 months at temperatures ranging from 5 ^0C at the begining to 30 ^0C at the end of the process. Nine parts of the hams were sampled at 0, 18, 122 and 207 days. 1, gluteus medius; 2, adductor; 3, rectus femoris; 4, vastus medialis and vastus intermedius; 5, vastus externus; 6, shank; 7, Gastrocnemius; 8, Semitendinosus; 9, gracilis. In order to evaluate the effect of the pH in phosphate precipitation, 14 hams (7 with low pH (group 2) and 7 with high pH (group 1) in Semimembranosus muscle) were cured for 15 days with 40 g of salt and 0,4 g of nitrate per kg of ham, then the hams were washed and hung for 30 days at 3-5 ^0C. At the end of this period 2 mm of dry cured ham were removed and the pH and P_2O_5 was analysed. **Na, K, Ca, Mg, P_2O_5 analysis:** The crystals of six hams were dried at 103 $\pm$ 2 ^0C for

24 hours and then analyzed by atomic absorption (VARIAN AA 1275). P_2O_5 was analyzed after the Molybdat-Vanadat method (Pulls, 1961). **X-ray diffraction:** X-ray diffraction diagram was carried out according to the method of crystalline powder, radiation Kα of the Cu λ = 1,5405, by comparison with the Joint Committee of Powder Difraction Standards. **Statistic analysis:** Data were analysed by variance analysis (General Linear Models Procedure). Mean separation was accomplished using Bonferroni test (S.A.S., 1987).

RESULTS and DISCUSION: The percentage of Na and P_2O_5, give a Na/P molar relationship of 1,92, and suggest that the composition of the crystals was mainly Na_2PO_4H (table 1). The X-ray diffraction diagram confirmed the crystals were made up by Na_2PO_4H. Two specimen of Na_2PO_4H were found: the majority specimen was $Na_2PO_4H.7H_2O$ (Reference index 10.191) and the minority one was $Na_2PO_4H.12H_2O$ (Reference index 11.657). Both crystals belong to the monoclinic system. In the range of pH for dry cured ham (5,5-6,5) ortophosphate normally exist in solution as $NaPO_4H_2$. The influence of the different storage temperatures in phosphate crystals formation was studied. Crystals only appear in ham slices stored at 1-3 ^0C and the size increases during the storage. After the 5th day the crystals had increased to 1-2 mm. The reason could be that solubility of orthophosphate decreases together with the temperature and Na_2PO_4H solubility decreases more quickly than $NaPO_4H_2$ (Mark, et al. 1975). When the temperature increases, the solubility of the Na_2PO_4H raises and the crystals dissolve in the crystallization water. Na_2PO_4H and $NaPO_4H_2$ dissociate in aqueous solution in PO_4H^{-2} + 2 Na^+ and $PO_4H_2^-$ + Na^+, but in the ham the presence of the Na^+ cation from NaCl added will shift the former equilibrium more strongly towards the non dissociate form than in the later equilibrium, according to the "Le Châtelier" principle. DFD hams showed more crystals and phosphate in the surface during the post-salting period than the lower pH hams. The same was observed at the end of the process in DFD hams packaged in vacuum or modified atmosphere. The concentration of PO_4H^{-2} increases in meat with a high pH value, thus, the formation of Na_2PO_4H crystals would be favoured. During the postsalting period phosphate crystals are formed in the outer part of the ham, specially when the room humidity is high, because it would facilitate the dissolution of the phosphates, and the low temperature and high salt concentration would facilitate the precipitation. The results of the concentration of P_2O_5 obtained are similar to the results of Flores et al. (1985), they found 5100 ppm of P_2O_5 at twelve month in slowly maturated hams and 6400 in rapid maturated hams. In the salting period the P_2O_5/protein relationship diminishes in the muscular zones in contact with salt (zones 6, 9). In the postsalting period the P_2O_5/protein diminishes except in Semitendinosus and Gracilis muscles, this could be justified by the precipitation of the phosphate in the outer part of the ham. In the gracilis muscle the P_2O_5/protein increases due to the migration of the phosphate from the neighbouring muscles and would justify the increase of pH during the postsalting period. The migration in the shank (6) is more difficult because this muscle is anatomically isolated from the rest of the ham by tendons and the joint. The P_2O_5/protein relationship does not change in Semitendinosus muscle, because is an intern muscle in the ham. The P_2O_5/humidity ratio is higher in the drier areas (1, 2, 3, 4 and 9) and lower in the more humid ones. The equilibrium in the concentration of phosphates between different parts of the ham does not occur during the aging

process.

CONCLUSIONS: The translucent crystals consist of $Na_2PO_4H.7H_2O$ and $Na_2PO_4.12H_2O$. High NaCl and phosphate concentration, low humidity level and high pH in the muscle favours the formation of these crystals when the ham is stored at refrigeration temperatures. A high room humidity facilitate the formation of phosphate crystals in the outer part of the ham. The P_2O_5/protein ratio diminishes during the process and the P_2O_5/humidity relationship is higher in the drier areas.

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Table 1. Percentage of Na, K, Ca, Mg and P_2O_5 in the crystals dried at 103 ± 2 0C.

Na	P_2O_5	K	Ca	Mg
30,5 ± 1,6	50,3 ± 3,6	0,2	0,013	0,027

Table 2. Effect of pH on phosphate precipitates at the end of the postsalting period

Group	$pH1^x$	$pH2^y$	$P_2O_5{}^y$ (%)
1	$6,81^a$ ± 0,12	$7,76^a$ ± 0,11	$2,29^a$ ± 0,19
2	$5,86^b$ ± 0,17	$7,10^b$ ± 0,14	$1,37^b$ ± 0,21

x: pH measured in the gracilis muscle 24 h. post-mortem. y: pH and P_2O_5 in a 2 mm thick layer around the ham.

Table 3. Concentration of $(P_2O_5/humidity)x100^x$ (%) during the process at different muscles of the ham.

Muscle	Aging time (days)			
	0	18	122	207
1	0,65 ± 0,05	$0,72^{abc}$ ± 0,09	$0,95^{b}$ ± 0,07	$1,27^{bc}$ ± 0,10
2	0,65 ± 0,08	$0,74^{ab}$ ± 0,05	$0,94^{b}$ ± 0,15	$1,37^{b}$ ± 0,21
3	0,61 ± 0,05	$0,75^{a}$ ± 0,04	$0,86^{b}$ ± 0,08	$1,17^{bc}$ ± 0,11
4	0,60 ± 0,05	$0,68^{abcd}$ ± 0,10	$0,82^{bc}$ ± 0,09	$1,10^{bc}$ ± 0,12
5	0,63 ± 0,05	$0,70^{abcd}$ ± 0,05	$0,75^{b}$ ± 0,06	$1,01^{bc}$ ± 0,07
6	0,59 ± 0,04	$0,64^{cd}$ ± 0,04	$0,64^{b}$ ± 0,08	$0,81^{c}$ ± 0,10
7	0,57 ± 0,06	$0,64^{cd}$ ± 0,02	$0,66^{b}$ ± 0,06	$0,88^{bc}$ ± 0,12
8	0,65 ± 0,06	$0,64^{bcd}$ ± 0,08	$0,82^{b}$ ± 0,06	$1,23^{bc}$ ± 0,09
9	0,65 ± 0,07	$0,61^{d}$ ± 0,07	$2,52^{a}$ ± 0,60	$3,69^{a}$ ± 0,92

a-d: Means within a column with the different superscripts are significantly different ($P<0,05$). x: mean value of 12 hams ± standard deviation.

Table 4. Concentration of $P_2O_5x100/protein^x$ (%) during the process at different muscles of the ham.

Muscle	Aging time (days)			
	0	18	122	207
1	2,25 ± 0,18	$2,17^{ab}$ ± 0,32	$1,88^{b}$ ± 0,13	$1,77^{bc}$ ± 0,14
2	2,21 ± 0,23	$2,08^{ab}$ ± 0,14	$1,78^{b}$ ± 0,24	$1,64^{bc}$ ± 0,16
3	2,28 ± 0,21	$2,30^{a}$ ± 0,22	$1,94^{ab}$ ± 0,21	$1,82^{b}$ ± 0,15
4	2,38 ± 0,15	$2,28^{a}$ ± 0,33	$1,90^{ab}$ ± 0,20	$1,72^{bc}$ ± 0,16
5	2,12 ± 0,27	$2,27^{a}$ ± 0,21	$1,90^{ab}$ ± 0,09	$2,00^{b}$ ± 0,20
6	2,30 ± 0,41	$1,89^{bc}$ ± 0,14	$1,48^{c}$ ± 0,14	$1,40^{c}$ ± 0,26
7	2,10 ± 0,11	$2,08^{ab}$ ± 0,13	$1,71^{bc}$ ± 0,19	$1,72^{bc}$ ± 0,19
8	2,28 ± 0,21	$2,23^{ab}$ ± 0,27	$2,18^{a}$ ± 0,10	$2,37^{a}$ ± 0,22
9	2,23 ± 0,25	$1,73^{c}$ ± 0,16	$1,93^{ab}$ ± 0,31	$1,81^{b}$ ± 0,45

a-c: Means within a column with different superscript are significantly different ($P<0,05$). x: mean value of 12 hams ± standard deviation.