DESCRIPTIVE EMPIRICAL MODEL OF INSTRUMENTAL HARDNESS CHANGES IN DRY-CURED *SEMIMEMBRANOSUS* AND *BICEPS FEMORIS* MUSCLES AS A FUNCTION OF WATER CONTENT, NACL AND PH

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Background

The dry-cured ham process involves a long drying period that produces a gradient in hardness in the product. Extreme superficial hardness could cause the crust formation, which is one of the most important problems in cured meat products. This problem is related to a high drying rate on the outer part while in the inner part there is a high moisture content. The diffusion rate of water from the inner zone does not compensate the high dehydration rate on the surface and consequently the surface hardens and forms a crust (Flores, 2001). The experimental relationship between hardness and water content has been reported by various authors (e.g. Virgili *et al*., 1995; Ruiz-Ramírez *et al*., 2003) but until now no attempt has been made to describe the effect of NaCl and pH on this relationship. According to Ruiz-Ramírez *et al*. (2003), the hardness-water content relationship can be described by an exponential model.

The effect of pH and NaCl content on the texture of dry-cured meat products have been examined in previous studies. Arnau *et al*. (1998) and Guerrero *et al*. (1999) established higher hardness for normal or low pH hams than for high pH hams. Whereas, Magraner *et al*. (2003) associated high pH levels with harder dry-cured hams. Low NaCl content was related with pastiness and softness in dry-cured ham (Arnau, 1991), while high NaCl content increases the shear force in dried fish products (Iseya *et al*., 1998).

Objectives

The aim of this study was to model the relationship between water content and hardness of dry-cured meat products considering the NaCl and pH effects.

Materials and methods

The experiment was undertaken using 18 hams. Half of the hams had a pH<5.7 and the rest a pH>6.2. The pH was measured on *Semimbranosus* (SM) muscle at 24-h post mortem (pH_{SM}) with a combined electrode (Ingold 406, Ingold, Urdof, Switzerland) attached to a portable pH-meter (Crison 507, Crison Instruments S. A, Barcelona, Spain). SM and *Biceps femoris* (BF) muscles were separated from the hams and manually rubbed with a dry salt-cured mixture of 0.5 g of KNO_3, 0.3 g of $NaNO_2$ and depending on treatment with 20, 50 and 80 g of NaCl per kg of muscle (8.19%, 16.67% and 21.29%) on a dry matter basis (DM) respectively. These muscles were individually packaged in bags of polyamide and polyethylene (SACOLIVA® permeability: 2.6 g H_20/m^2/day at 23 ºC/85%RH) and were horizontally placed in trays in a room at 2±2 ºC for 45 days. Thereafter nine samples from each muscle (N=324) were shaped as a parallelepiped (4x2x2 cm). The rest of the muscles were ground and packaged in metallic bags (SACOLIVA® permeability: < 1 mg H_20/m2/day, to 23 ºC/85%HR), and stored at 2±2 ºC until its posterior physicochemical analysis. Each parallelepiped was weighed in an analytical balance of 0.01 mg of precision (Mettler PE 300) and was dried in a drying tunnel at 3±2 ºC, 57.5±2.5% RH and 1m/s air speed, until desired levels of drying were reached. Levels of drying used corresponded to the range of water content 28,5- 59.7%. The dried samples were individually packed in plastic bags (20 µm polyamide / 70 µm polyethylene; water vapor permeability: 2.0 g/m^2/24h; SACOLIVA S.L.®, Castellar del Vallès, Barcelona) with a 70% nitrogen atmosphere and kept at 15±2ºC for a minimum of 30 days to allow homogenization of NaCl and water throughout the sample.

A texture Analyzer (Universal MTS Alliance model. RT/5, SEM, Barcelona, Spain) was used to determine hardness. Before carrying out texture analyses nitrogen-packed samples were kept for one hour at room temperature. The cores of the dry-cured loin slices were accurately carved with a scalpel into 10 x 10 x 10 mm (length x width x height) and triplicates were obtained. The samples were compressed to 50% of their original height. Force-time curves were recorded at crosshead speed of 1 mm/s. Hardness was defined by maximum peak force during the compression cycle.

The parallelepiped samples used for texture analysis were immediately cut up and water content was determined by drying at 103±2ºC until reaching constant weight (AOAC, 1990). Water content of the samples was expressed on a dry mater basis (DM) (X = kg H_2O / kg DM).
Sodium chloride content was determined by the Volhard method (ISO 1841-1: 1996), water content (AOAC, 1990) and pH (measured with a xerolyt penetration electrode Crison) were determined in the rest of the ground muscle.
Statistical analysis: All the statistical analyses were carried out with the SAS statistical package (SAS Institute, 1999). The relationships between hardness and water content on a dry mater basis (X) were studied through a non-linear regression analysis (PROC NLIN). The following model was used:

$$Y = aX^b \quad \textbf{(1)}$$

Where Y is the predicted hardness, a and b are the model parameters and X= water content on a dry mater basis.

Results and discussion

Figure 1 shows the relationship between hardness and water content (X) for all dry-cured samples. Experimental data indicate that for a range of X between 0.8 and 1.3 the hardness remains practically unchanged while for X<0.6 the hardness increases substantially. This substantial increase occurs at different values of X according to the product, i.e.: 0.8 in dry-cured loin (Ruiz-Ramírez, submitted) and 0.6 in dry-cured ham (Ruiz-Ramírez *et al*., 2003). In the present study, the substantial increase of the hardness is similar to the one observed in dry-cured ham. The different anatomical origin of the samples can explain the difference between ham and loin. Figure 2 (a) shows the predicted hardness by muscle. The BF and SM muscles presented similar hardness at each water content. Figure 2 (b) shows the predicted hardness according to pH measured in the muscle SM (pH_{SM}). The samples from hams with low pH_{SM} presented greater hardness than those from hams with high pH at X values from 0.6 to 1.3. But when X diminished below 0.6 the differences between samples from hams with different pH_{SM} were not significant (P>0.05). Nevertheless, at X>0.7, which corresponds to the inner part of the dry-cured ham, the samples from hams with low pH_{SM} presented greater hardness. The lowering of the meat pH closer to the isoelectric point of myosin, increases intermolecular linkages between negatively and positively charged groups, which would explain the greater hardness in the muscles with low pH. This result agrees with those reported by Arnau *et al*. (1998) and Guerrero *et al.* (1999), who found a higher hardness for low pH hams than for high pH hams at X values around 1.7.
The NaCl content also influenced the hardness of the muscles (Figure 3a and 3b). The muscles with higher NaCl content presented higher hardness for samples from hams with low pH_{SM}. These results are probably due to the fact that when high NaCl contents are used there is a compaction of myofibrillar structure (Shomer *et al*., 1987), which would increase the hardness. Similarly, Iseya (1998) found a higher hardness when the NaCl content was increased in dried fish products. The NaCl effect was different depending on the pH_{SM}. The NaCl effect was more evident in samples from hams with low pH_{SM} than in those from hams with high pH_{SM}, which presented similar hardness for NaCl content of 2% and 5% and higher for 8% in the range of X between 0.6 and 1.3. But when X diminished below 0.6 the significant differences between samples from hams with different NaCl content disappeared.
The behavior observed for the NaCl content was similar to that observed for pH, in the sense that when the X values diminished below 0.6, the differences among NaCl contents were lower. These results show that at X values below 0.6, which were achieved in the surface layer of dry-cured meats products, the hardness is more influenced by the water content than by NaCl or pH.
The estimates of parameters, the residual standard deviation (RMSE) and coefficient of determination (r^2) of the equation (1) obtained from the non-linear regression analysis for all dry-cured samples (general model), by muscle, pH_{SM} and NaCl content are showed in Table 1. The lowest RMSE for the model was for samples from hams with high pH_{SM} and 5% of NaCl and for samples from hams with low pH_{SM} and 2% NaCl content.

Conclusions

An exponential model was found appropriate for describing the relationship between hardness and water content (X). The hardness of the muscles was affected by the pH_{SM} and the NaCl content. As the NaCl content increases the hardness increases, especially at pH_{SM}<5.7. At X values lower than 0.6 the hardness is more influenced by water content than by NaCl content or pH.

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Table 1. Estimates of parameters from the non-linear regression of hardness versus water content on dry mater basis (X).

Dry-cured muscles		*a*	*b*	r^2	RMSE
General model		5.5119	-2.0985	0.82	3.70
pH	pH<5.7	6.0903	-1.9879	0.82	3.89
	pH>6.2	4.9980	-2.2022	0.84	3.41
NaCl pH_{SM}< 5.7	2%	4.4071	-2.1529	0.83	2.16
	5%	6.1547	-1.9141	0.86	3.29
	8%	8.7051	-1.5938	0.79	4.28
NaCl pH_{SM} > 6.2	2%	4.5340	-2.3245	0.73	4.08
	5%	4.3105	-2.4846	0.91	2.35
	8%	5.8779	-1.9775	0.87	3.52

a and *b* parameters of the model; r^2, coefficient of determination; RMSE, residual standard deviation.

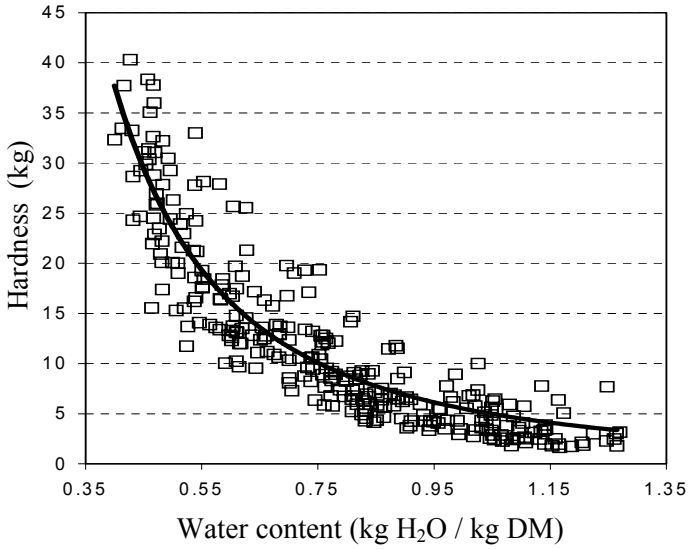

Figure 1. Hardness versus water content for overall samples. □ experimental hardness; — predicted hardness ($Y = aX^b$).

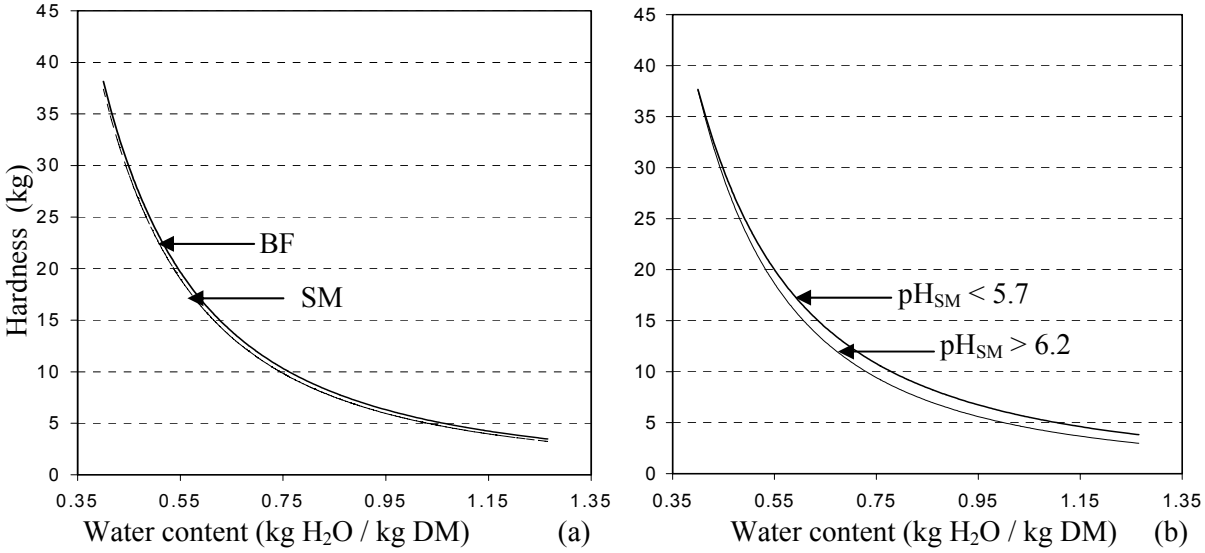

Figure 2. Predicted hardness versus water content by muscle (a) and by pH_{SM} (b) in dry-cured muscles.

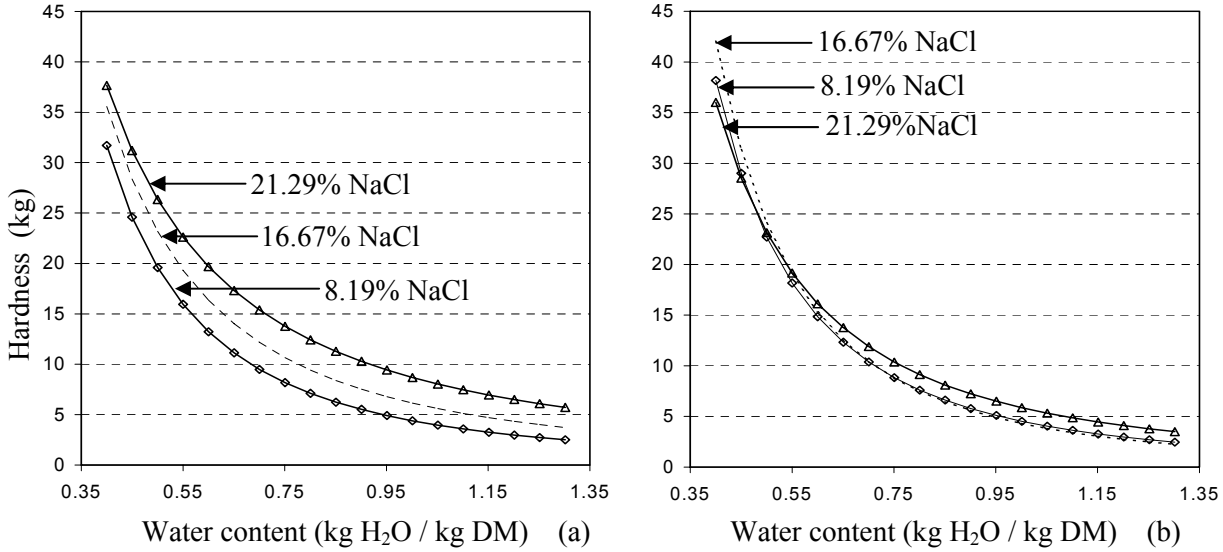

Figure 3. Predicted hardness versus water content by NaCl content in dry-cured muscles with $pH_{SM} < 5.7$ (a) and $pH_{SM} > 6.2$ (b).