Meat marination in organic acid-containing solutions : most influent process parameters on mass transfer and evolution of physicochemical characteristics

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Abstract

Food additives such as sodium chloride, alone or in combination with phosphates and polyphosphates, and some organic acids, are used as functional ingredients for improving the sanitary quality and organoleptic characteristics of meat. This paper deals with the migration of organic acids in turkey muscle and the various effects on the cured meat characteristics (e.g. pH, swelling). It also offers new perspectives in pH prediction during marination process.

Keywords: Meat, marination, acidification, mass transfer, swelling

1. Introduction

Meat marination is a treatment which consists in impregnating the product in varied functional ingredients, intended to improve the food qualities or to extend the shelf-life. The common ingredients used are salt, aromatic substances, acidic substances (vinegar, lemon juice) or alkaline substances like polyphosphates. The objectives aimed by this treatment are the prolongation of the shelf-life by improvement of the sanitary quality, the tenderizing, the improvement or the modification of the taste and the increase in weight yield [1]. The pieces of raw meat are treated by immersion or by spraying. In the case of using a standardized solution for pickling (water + salt + acid), the principal physico-chemical modifications observed are a fall of the pH, related to the impregnation in acid, as well as a salt gain. The impact are a destruction of part of the microbial flora, an increase in the water holding capacity and a tenderizing effect by opening of the proteinic structure, which can result in a swelling [1, 2]. It should be noted that the pH of the meat does not reach that of the solution, because of the buffering capacity of the meat due to the presence of various molecules present in the meat. The buffering capacity of post-rigor meat is mainly due to non-proteic substances. Of these, 45% is due to phosphates, 16% and 10% are due to the dipeptides, carnosine and anserine respectively as well as lactic acid (pK_a 3.9) and β- and γ-carboxyl groups [3, 4]. This work deals with the migration kinetics of the acid and water in turkey meat cubes *(Pectoralis major)* soaked in a water-acetic acid solution until equilibrium status. The effect on swelling was studied and attention was also given to the different chemical constituents present in the meat due to the dissociation of the acid, in order to propose tools of pH prediction at equilibrium state.

2. Material and methods

2.1 Material and marination conditions.

Post-rigor turkey meat (*Meleagris gallopavo*) was bought in butchery. The fillets (*Pectoralis major*) used for the tests were placed in vacuum bags each of 200 g of meat. A deep-freezing at -50°C in air pulsated machine (Facis - France) was applied, before the meat was stored at -18°C until their use.
The frozen fillets were defrosted for 24 h at 4°C. In order to facilitate slicing, the meat was exposed to a -50°C air flow in pulsated machine (Facis) for 3 minutes in order to harden the surface. The fillets were cut transversally into pieces of approximately 1 cm thick using a ham slicer (Italiana macchi 370). Cubes of 1cm^3 diameter were prepared for the experiments.

The soaking solutions used contain acetic acid (prepared from glacial 100%, Merck, Germany) at 0.03; 0.24 and 1.03 mol/kg of water respectively. All the experiments were made at room temperature. The soaking solutions were prepared with deionized water.
20 g of meat samples were soaked in 300 ml glass jars for 15 min., 30 min., 1 hr., 3 hrs. and 6 hrs. The system was maintained in agitation at 160 rpm (Heidolph Promax 2020). After soaking periods, the cubes were drained for about 5 sec. with towelling paper to drying the surface and than reweighed. Measurements were made to determine the pH, titratable acidity and water content. For each soaking solution three repetitions were made, as well as for every measurement.

2.2 Analytical analysis
The water content (WC) is determined by gravimetric method. It is measured by a difference in weight after 24 hrs. drying in an oven at 104°C. After gravimetric method the titratable acidity is withdrawn from the apparent water content, because of the volatilization of the acetic acid during drying.
Titratable acidity was measured by titration and by HPLC.
For the acid analysis by HPLC or titration, an extraction of the acids in the meat was first carried out. the samples of marinated meat were diluted in distilled water. The mixture was agitated for 2 hours with an agitator (Heidolph Promax 2020) at 160 rpm. A centrifugation was then carried out during 10 minutes at 5000 rpm using a Beckman GS-6R.
A HPLC column of type aminex HPX-87H Carbohydrate was used. The mobile phase was H_2SO_4 5mmol. The spectrophotometer was set at a wavelength of 210 Nm (UV). The concentrations are expressed in g/l and then reported in mass of acid for 100 g of meat.
For the determination of titratable acidity, a titration was made on 15 ml of the water-extract with 0.1 N NaOH. An automatic titrator (Titroline 96 – Schott - Germany) was used. The values obtained for titratable acidity were used to calculate the concentration of acetic acid in the marinaded turkey meat at different acetic acid concentrations of the marinades. The titratable acidity is expressed in meqH^+/100 g of meat.
The pH of the meat was measured using a pH meter (WTW - Inolab pH Level 2). Measurement was carried out using an electrode specially designed for solids like the meat. The measurement of the pH was taken directly on the meat after mincing the cubes. The pH measure was repeated three times.

3. Results and discussions
Figure 1 shows the time-course of pH and acid gain for turkey fillets soaked in acetic acid.

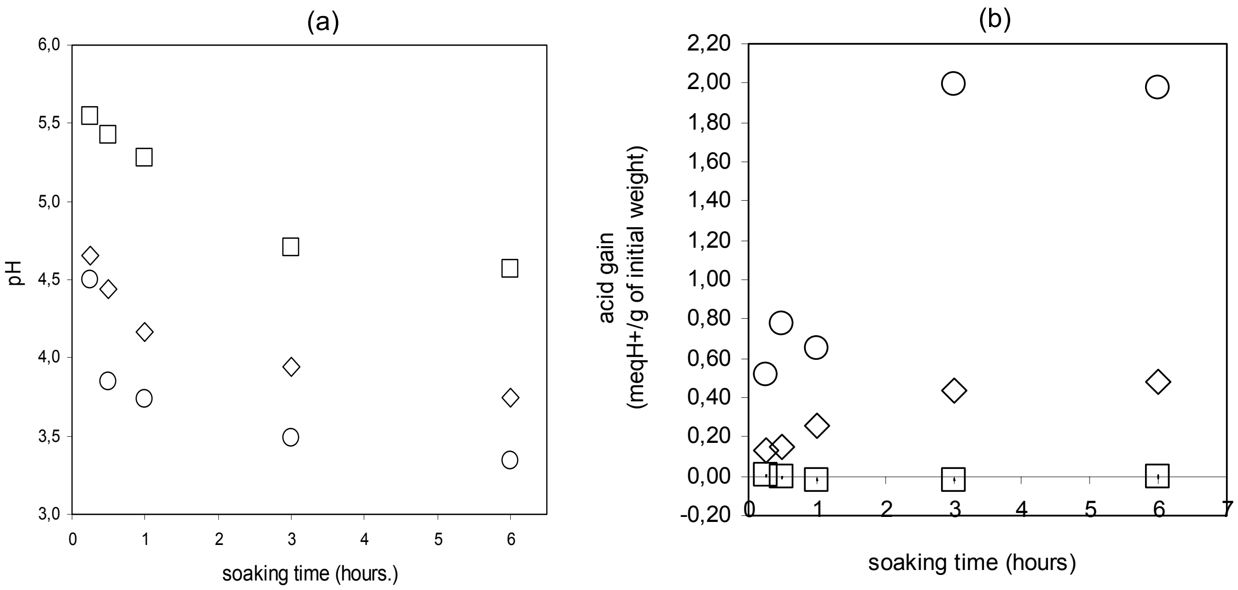


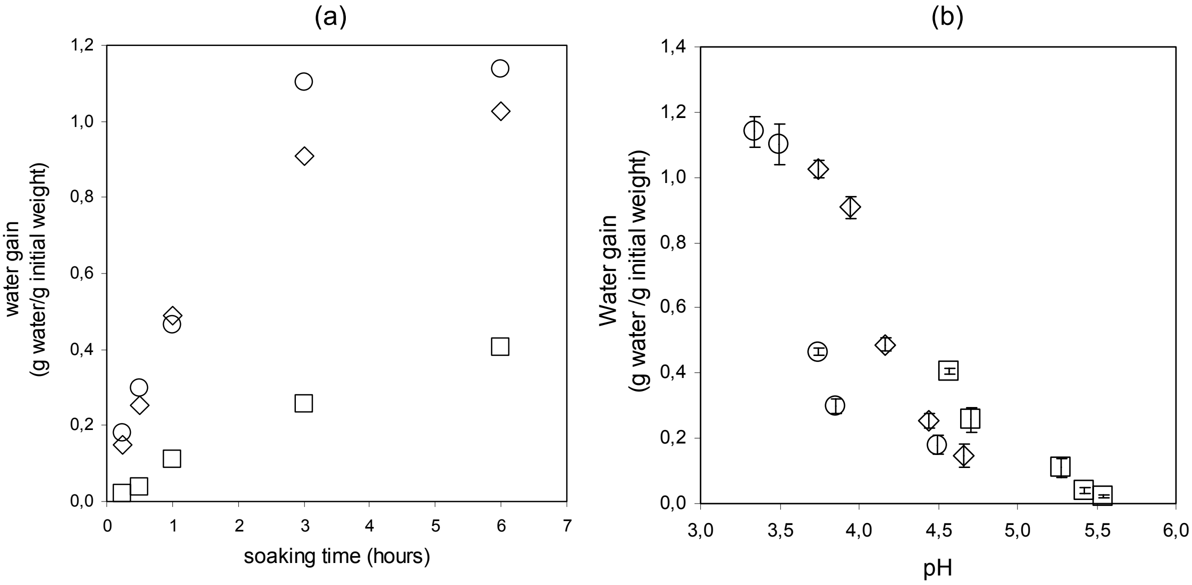
Figure 1. Variation of pH (a) and acid gain (b) in turkey meat with immersion time in acetic acid solutions at: (○) 1.03 mol.kg^{-1}; (◇) 0.24 mol.kg^{-1}; (□) 0.03 mol.kg^{-1}

A fast and intense decrease in the pH is observed as the concentration in acetic acid of the solution increases. A significant buffering capacity of the meat can be noted: the pH reached in the meat are 4.6, 3.7 and 3.3 whereas those of the soaking solutions are respectively 3.1, 2.7 and 2.4, for 0.03, 0.24 and 1.03 mol.kg^{-1} . Calculation shows that the major part of the protons resulting from the dissociation of the acetic acid are fixed on the various components of the meat. The free protons in the meat represent less than 0.5% of the acetic acid present in the meat, all forms considered.

Table 1. pH and titratable acidity, comparison between turkey meat and soaking solution

The system	pH (at equilibrium)		Acidity of the solution	Titratable acidity of the meat (meq.H^+/100g)
	meat	solution	(meq.H^+/100g water)	
Untreated meat	5.75 ± 0.01	---	---	16.14 ± 0.79
Soaking solution				
0.03 mol.kg^{-1}	4.57 ± 0.02	3.10	3.3	7.03 ± 0.72
0.24 mol.kg^{-1}	3.74 ± 0.02	2.70	24	28.79 ± 0.42
1.03 mol.kg^{-1}	3.34 ± 0.11	2.40	103	93.59 ± 1.30

The equilibrium state is reached quickly, after approximately 3 hours of immersion. It is noticed that for a low concentration soaking solution, there is no acid gain because of the leaching of lactic acid present initially in the meat. The initial concentration of this acid is about 15 meq for 100g of meat, whereas the concentration in acetic acid in the soaking solution is 3.3 mmol. for 100g of solution. Despite everything a reduction in the pH is observed, certainly by transfer of protons (H_30^+ ions), whose concentration in the meat passes from 10^{-6} to $10^{-4.5}$ meq./l, because of its relatively high level in the soaking solution ($10^{-3.1}$ meq./l). Moreover, during the immersion in diluted solution, a significant proportion of molecules are probably extracted from the meat, which play a capital role in the buffering capacity, explaining the significant decrease of pH whereas titratable acidity does not evolve.
Figure 2 shows the time-course of water gain for turkey fillets soaked in acetic acid.



A strong swelling of the meat is observed related to the acidification (figure 2a). This swelling is well correlated to the pH, especially for each soaking solution taken separately (figure 2b). For the most diluted solution a significant swelling is noticed, related to the pH, since the acid content of the meat did not vary (cf. figure 2a). Gault [3] and Rodger *et al.*, [3, 5] mentioned this swelling and two principal explanations were advanced, an electrostatic and an osmotic theory. The electrostatic theory is based on the repulsion of the proteic chains when the pH moves away from the isoelectric point, and that consequently the forces of attraction between proteic chains decrease. This explains the absorption of water, the swelling, well correlated with the increase in tenderness. For the myofibrillar proteins, the isoelectric point is located between pH 5 and 5.5. Figure 2b shows well the very strong increase in the water gain with the pH decrease, about 0.5 g/g of meat/pH unit, on the scale of pH 5.5 to 3.5. Swelling being related to the pH and not only to the acid content, we understand how important it is to control the final pH during the marination operation. Hence it is interesting to try to predict the operational pH according to the processing parameters. In a complex matrix like the meat, it is not possible to obtain directly by calculation the relative proportion of the various chemical constituents, because a large part of the protons resulting from the dissociation of the used acid will be neutralized by the meat components. An easily realizable approach to make prediction of the pH in an acidified minced meat, or during the marination at a high ratio meat/solution would consist in carrying out a preliminary titration of the meat by a strong acid. This would allow to establish a relation between the pH and the H^+ ions bound to the meat (called here H^B) [6]. Figure 3 shows this relation for the turkey meat used in our experiments. Being an immersion of meat pieces in solution in non limiting transfer conditions, until equilibrium. Such a relation could be established by assessing the buffering capacity of the meat taking into account the loss of soluble compounds due to immersion. This could be done by titration of the meat after a rinsing in water during 6 hours. Knowing this new relation $[H^B] = f(pH)$, after titration of the meat by a strong acid, we should be able to approach the value of the pH reached in the meat at equilibrium state by using the pK_a of the acid and the acid concentration of the soaking solution.

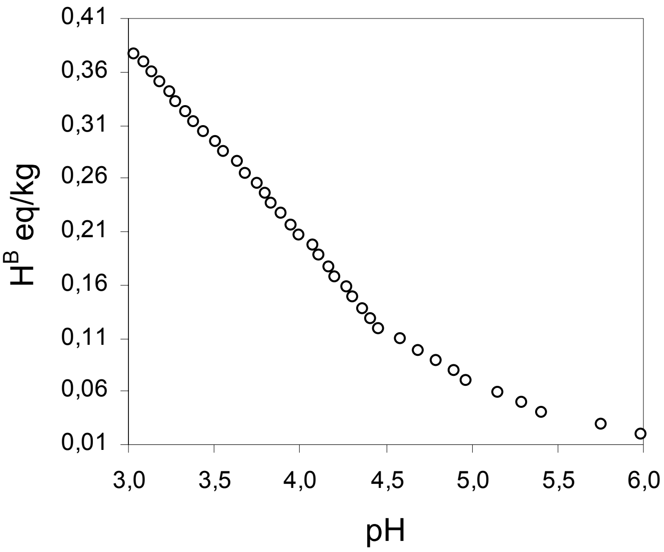


Figure 3 : Evolution of the quantity of bound protons per kg of turkey meat as a function of the pH of the meat.

The acid (in the case of a weak monoacid) dissociates in the soaking solution as following :

$$AH_s + H_2O \leftrightarrow A^-{}_s + H_3O^{F+}{}_s \qquad (1)$$

Where AH_S, $A^-{}_s$, $H_3O^{F+}{}_s$ are respectively the protonated form of the acid, the anion form of the acid and the « free protons » in the solution. it's possible to establish experimentally the relation

$$[H^B{}_m] = f(pH) = f([H_3O^{F+}{}_m]) \qquad (2)$$

Where $[H^B{}_m]$ and $[H_3O^{F+}{}_m]$ are respectively the cconcentrations of the protons bound to the meat constituents and of « free protons » in the meat. Knowing that C_0, the concentration in the meat (noted C_0) at the equilibrium state (see table 1) is equivalent to that of the soaking solution.

$$C_o = AH_S + A^-{}_s = AH_m + A^-{}_m \qquad (3)$$

Thus we should be able to draw from the acid constant, K_a, the concentration of free protons in the meat, $[H_3O^{F+}{}_m]$, which determines its pH value.

$$K_a = \frac{\left[A^-{}_m\right]\left[H^-{}_m\right]}{\left[AH_m\right]} \tag{4}$$

We conclude from (2), (3) and (4) a relationship which makes it possible to calculate the pH of the meat at the equilibrium state according to the pK_a of the acid and C_o, the acid concentration of the soaking solution:

$$K_a = \frac{\left(\left[H^B{}_m\right]+\left[H^{F+}{}_m\right]\right)\left[H^{F+}{}_m\right]}{C_0-\left(\left[H^B{}_m\right]+\left[H^{F+}{}_m\right]\right)} \tag{5}$$

Figure 4 allows recapitulating the principal chemical constituents present, which are involved in the determination of the pH of both the solution and the meat during the operation of marination.

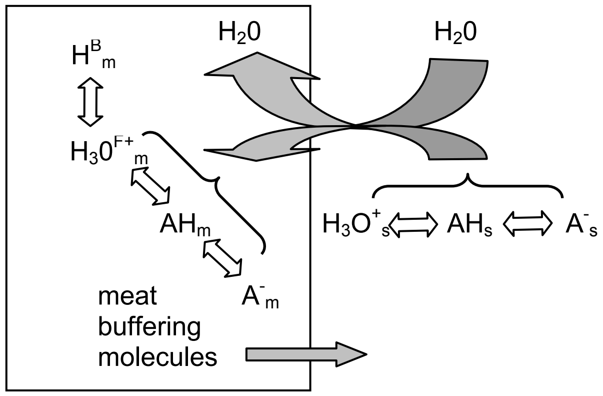


Figure 4 : principal chemical constituents present during the marination of turkey meat in organic acid solution

Where:
$H^B{}_m$: protons bound to the meat constituents
$H_30^+{}_{Fm}$: free protons in the meat solution
AH_m : undissociated form of the acid in the meat solution
$A^-{}_m$: anion form of the acid in the meat solution
$H_3O^+{}_s$: free protons in the soaking solution
AH_s : undissociated form of the acid in the soaking solution
$A^-{}_s$: anion form of the acid in the soaking solution

4. Conclusion

This work made it possible to study the kinetics of acidification and swelling of the turkey meat *Pectoralis major* subjected to an immersion in water-acetic acid solution at concentrations between 0.03 and 1.03 $mol.kg^{-1}$. These experiments confirmed the significant buffering capacity of the meat, as well as the effect of the pH on the swelling, which can exceed 1g/g when the pH decreases below 4. They also showed that after 3 hours of immersion, under agitation in non limiting transfer conditions the acid concentration of the meat reaches an equilibrium state with that of the soaking solution. The pH being very influential on all the quality modifications of the meat (tenderness, conservation), it would be interesting to propose prediction tools of the pH at equilibrium state. The titration of the meat after maceration in water, to evaluate the protons fixing capacity according to the pH, should allow an approach. In parallel, a study taking into account the modifications of quality in the presence of NaCl often employed in pickling, must be carried out, because of the capacity of this molecule to modify considerably the transfers of water in the meat. Moreover, part of the acid which migrates in the meat accompanies probably a flow of water " pumped " in the meat at the time of the significant water gain which is also likely to be modified by the presence of NaCl.

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