PS4.07 Ions Transport through Beef Meat Tissue during Marination 389.00

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***Abstract* - There is an increasing interest in marination of beef meat. Equilibrium and unidirectional migration experiments were carried on small samples of four types of beef meat tissues. They showed no effect of animal age and muscle type, a negligible incidence of marinade pH on Cl^- and Na^+ transports and a slight incidence of the two ions on protons transport. The apparent diffusivities of protons (3.5 10^{-11} m^2/s) is about 10 times lower than that of Cl^- and Na^+ (3.2 10^{-11} m^2/s) at 10°C.**

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***Index Terms*—chloride, diffusion, sodium, pH, proton.**

I. INTRODUCTION

There is an increasing industrial interest in marination of beef meat because this process can help to develop new beef products from lower value and/or underestimated cuts. The present empirical practice could benefit from a better knowledge of the mass transfers involved since water activity, ions concentrations and pH determine the biochemical and textural changes. The general objective of our work is to simulate by calculations these mass transfers; this require assessing the apparent diffusivities of the chemical components. As regard chloride or sodium ions most of the recent works dealt with poultry [1] and pork [2, 3, 4, 5]. A particular attention was paid to proton migration since no data were found on its apparent diffusivity. In addition animal age and muscle type which affect structure were considered.

II. MATERIALS AND METHODS

A. Samples and marinades

The samples were excised from *Semimembranosus* (SM) and *Semitendinosus* (ST) muscles of less than 3 years heifers (young) or more than 7 years cows (old).

First, very simplified mixture of either water and NaCl or water and acetic acid (AA) were carried out. Then, more realistic marinade compositions were used with various concentrations of the following components: water, acetic acid, sodium chloride, sodium acetate, sodium lactate, sodium ascorbate (Table 1). In all experiments, contrary to practice, the amount of marinade was in a large excess in comparison to the sample weight so that changes in marinade composition versus time can be neglected.

		ST		SM		Figure N°
		3y	7y	3y	7y	
pH	0.01 M ; pH sol = 3.39 ; pH meat = 4.50	4 d		6, 4 & 2 d		4 and 6
	0.005 M ; pH sol = 3.54 ; pH meat = 4.64			4 d		
	0.001 M ; pH sol = 3.90 ; pH meat = 4.84	4 d	4 d	4** d	4 d	
	0.0005 M ; pH sol = 4.06 ; pH meat = 4.91			4 d		
	0.0001 M ; pH sol = 4.49 ; pH meat = 5.27	4 d		4 d		
NaCl	1.5% NaCl ; pH sol = 5.6			4 & 2 d		3 and 7
	3% NaCl ; pH sol = 5.6			4 & 2 d		7
	10% NaCl ; pH sol = 5.7			4 d		7
pH + NaCl	0.01 M and 1.5 % NaCl ; pH sol = 3.31 ; pH meat = 4.06			4 & 2 d		3 and 4
	0.01 M and 3 % NaCl ; pH sol = 3.28 ; pH meat = 4.14	2 d	2 d	7, 4 & 2 d	2 d	2a
Marinade	0.01 M + 1.5 % NaCl + 1% Acétate/Lactate + 0.125% Ascorbate ; pH sol = 5,421			6 & 4* d		2b
	0.01 M + 1.5 % NaCl + 0.5% Lactate + 0.125% Ascorbate ; pH sol = 4,648			4 d		
	0.01 M + 1.5 % NaCl + 0.5% Lactate ; pH sol = 4,551			6, 4 & 2 d		
	0.01 M + 1.5 % NaCl + 0.5% Acétate + 1% Lactate + 0.0125% Ascorbate ; pH sol = 5,419			4 & 2 d		

d = days / 3y = less than 3 years / 7y = more than 7 years
* duplicated / ** tripled

Table 1: Marinade composition and time of contact used in the unidirectional migration experiments

B. Experiments

Two types of experiments were performed: (1) ‘equilibrium’ to assess the pH of the meat tissue after equilibration with the solution and (2) ‘migration’ to record chloride and sodium ions content profiles and pH profiles within meat.

Equilibrium experiments: thin strips (25 x 10 x 2 mm) of meat tissue were soaked into the solutions during 16 hours at 10°C; preliminary tests showed that their pH was stable for longer times.

Migration experiments (Figure 1): unidirectional mass transfers were promoted at 10°C along the main axis of a meat cylinder placed into a plastic sample holder and maintained in contact from one base with the marinade (cylinder of about 20 g and 6 cm in length; 250 ml of marinade). After 2, 4 and 6 days the cylinder was cut into slices about 2 mm in thickness, orthogonal to the mass transfer direction and chemical analysis were performed on each slice. To build the profiles the actual thickness was calculated from the slice weight in comparison to the cylinder weight.

C. Analysis of meat tissue samples after grinding

Water content were assess from oven drying at 104°C for 24 h. Chloride and sodium ions contents were measured using a chloride analyzer (Sherwood, MHII-926) and a flame photometer (Jenway, clinical PFP7) respectively. A MP230 (Mettler) probe was used for pH measurements.

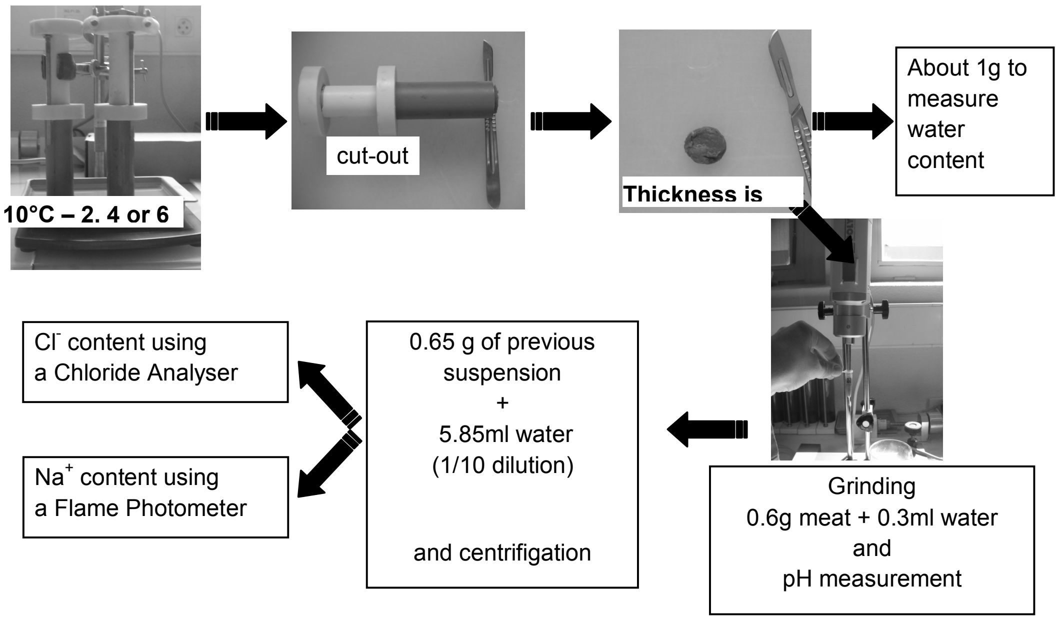


Figure 1: Procedure used in the unidirectional ‘migration experiments’

III. RESULTS AND DISCUSSION

Whatever the marinating conditions used no effect of animal age or muscle type was observed according to measurements accuracies. Thus, all the results presented in the figures correspond with the experiments carried out with SM muscles of less than 3 years heifers (cf. table 1).

A. *Profiles analysis*

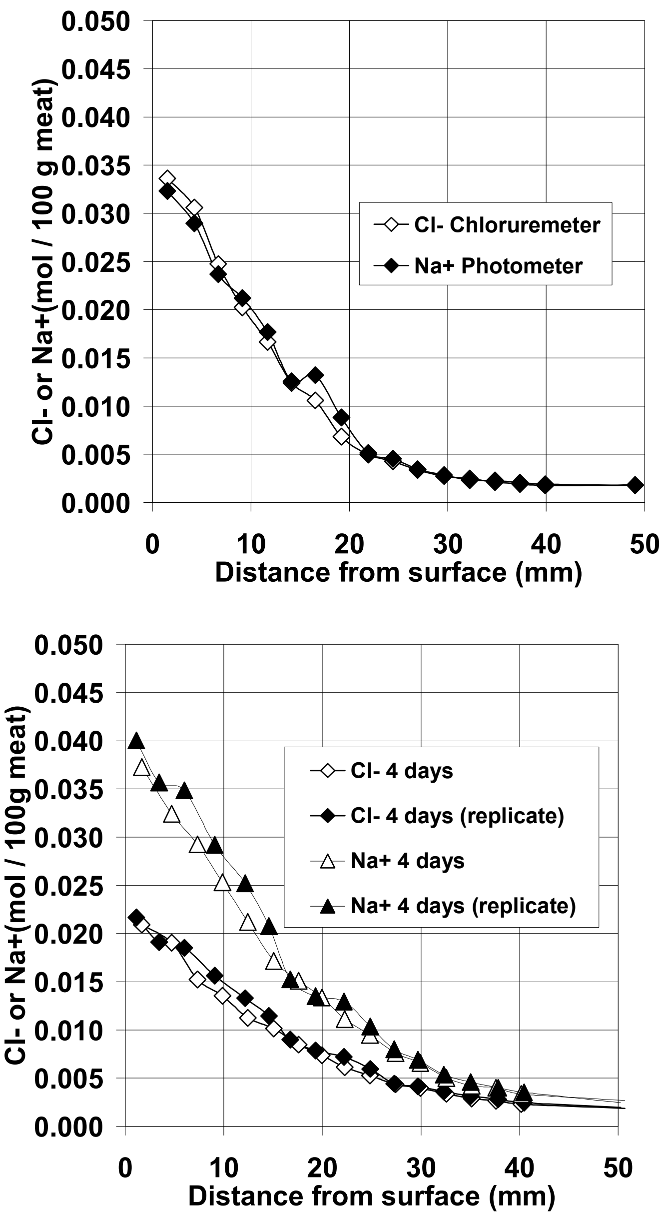


Figure 2: Comparison of Cl^- and Na^+ contents profiles (cf. table 1): (a) simplified marinade made of water, AA and NaCl and (b) complex marinade.

Figure 2 shows the Cl^- and Na^+ profiles, expressed in mole per gram, in two cases. When NaCl was the unique salt into the marinade (Fig.2a) the two profiles superimpose. This means that the apparent diffusivities of these two ions are equal and that NaCl content can be deduced from just one profile. With the complex marinade (Fig. 2b) the results indicate a good repeatability and the Na^+ content profiles are logically above the Cl^- content profiles. At any distance from the contact surface the molar concentration ratio Na^+/Cl^- is approximately constant (mean 1.7, St. Dev. 0.2) but is higher than that into the marinade (1.38); this could be due to interactions between Na^+ with the other anions.

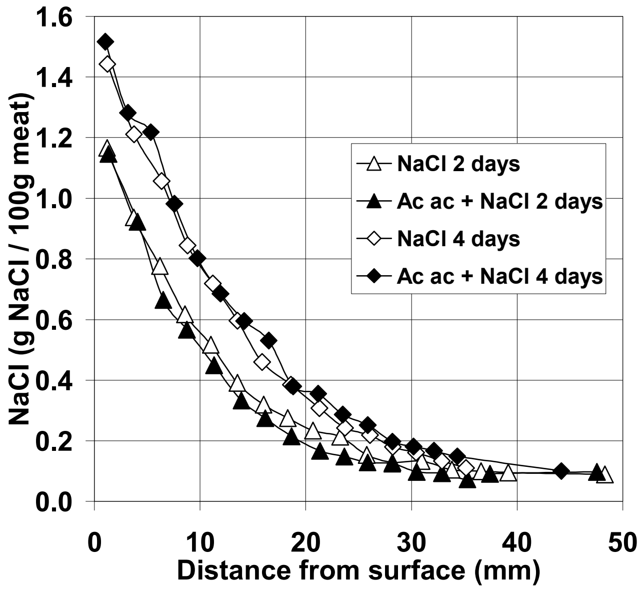


Figure 3: Incidence of the presence of acetic acid (marinade pH = 3.3 instead of 5.6) on salt penetration.

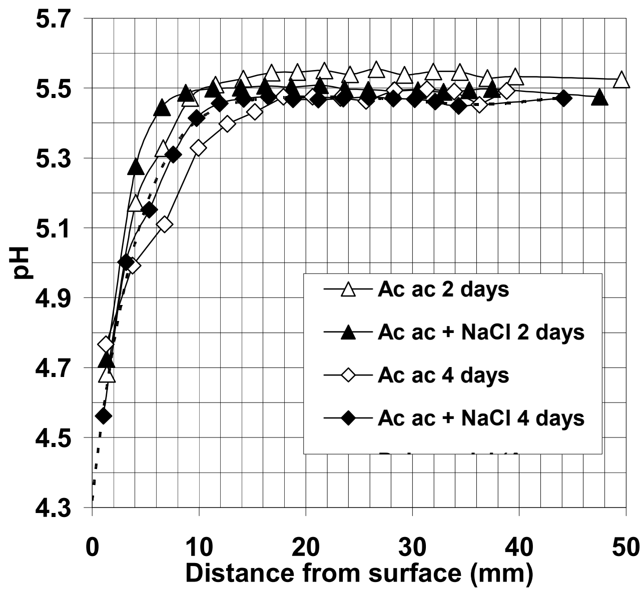
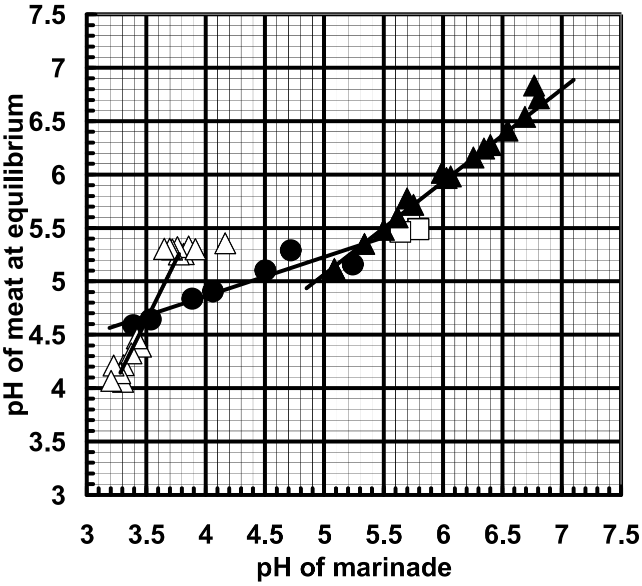


Figure 4: Incidence of the presence of NaCl (1.5 %) on the pH profiles.

Figure 3 shows examples of NaCl content profiles, calculated from chloride measurements, and figure 4 of pH profiles measured after 2 and 4 days. After 2 days the thickness of the outer layer where meat pH changed significantly is less than 1.5 cm. NaCl migration affects a layer which thickness is at least the double. Extrapolations of the measured profiles at the meat surface suggested that the surface reached rapidly an 'equilibrium' value for all ions. For Cl^- and Na^+ ions this value was approximately equal to their content into the marinade. For protons, probably due to complex interactions between all the ions and the proteinous matrix, the situation is more complex. The equilibrium pH of the meat tissue depends on the marinade composition (Figure 5) and three linear correlations were derived: (i) pure acetic acid solution, (ii) mixtures of acetic acid and NaCl in the range 1% to 10% g/L and (iii) complex marinades.



Figures 5: Meat pH versus marinade pH at equilibrium. Black triangle - complex marinades, black triangle – pure AA solutions, white triangle – AA + NaCl, white square – pure NaCl solutions.

B. Assessment of apparent diffusivities

Experiments with mixture pure acetic acid solutions were used to estimate protons apparent diffusivity from pH profiles and experiments with NaCl solutions were used to estimate NaCl diffusivity.

The analytical solution of the second Fick's law for diffusion in a slab was used to fit the measured profiles. In the equation below x is the distance from the meat surface, t is the time, $C_{(x,t)}$ are the measured content values of the molecule or ion considered, C_0 is its value at time 0 within the sample, l is the meat cylinder length and D is the unknown diffusivity which is assumed to be constant :

$$\left(\frac{C_{(x,t)}-C_0}{C_{surf}-C_0}\right)=\frac{4}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{(2n-1)}Cos\left(\frac{(2n-1)\pi(1-x/l)}{2}\right)\exp\left[-(2n-1)^2\frac{\pi^2 D\,t}{4l^2}\right]$$

The boundary condition C_{surf} was set at the marinade value for NaCl diffusion and derived from figure 5 for protons diffusion.

Regarding proton migration, in first approximation, the pH was deduced from the proton content by assuming that the proton activity coefficient was equal to 1.

As illustrated in figures 6 and 8 reasonable accuracy in the profiles predictions has been achieved using constant diffusivities. The best fits were obtained for a proton mean apparent diffusivity equal to 3.5 10^{-11} m^2/s and a NaCl mean apparent diffusivity equal to 32 10^{-11} m^2/s which is about 10 times higher. This latter value is in accordance with the results of Djelveh and Gros [6].

Regarding protons migration (Figure 6) two things must be noticed:

1. The fitted mean apparent diffusivity is much lower than that of protons into pure water (about 2 10^{-9} m^2/s). This can be explained by the buffer property of the proteinous matrix.
2. Better fits at 2 and 6 days needed to use a lower (2 10^{-11} m^2/s) and a higher value (6 10^{-11} m^2/s) respectively. This suggests that the lower the pH the higher the apparent diffusivity but this has no practical implication since marinades pH are generally higher than that used in our experiments.

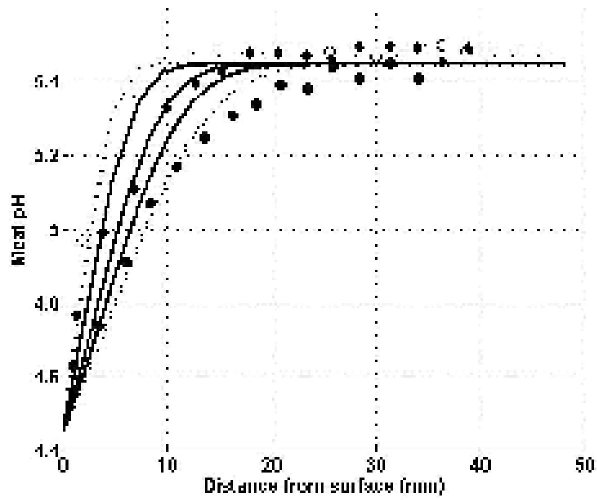


Figure 6: Comparison of the fitted pH profiles to the measurements on meat samples at 2, 4 and 6 days (cf. table1). Continuous lines – overall fit. Dotted lines – particular fits at day 2 or 6.

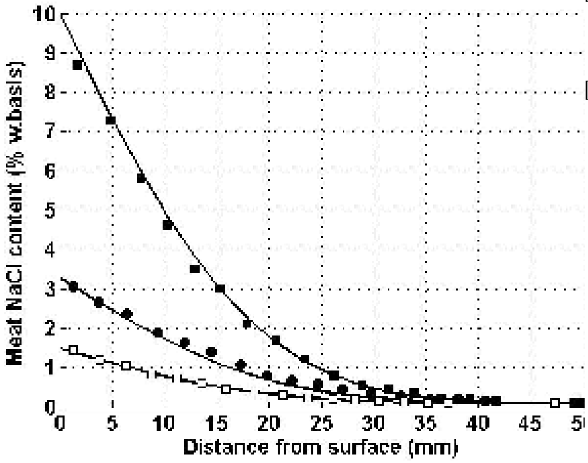


Figure 7: Comparison of the fitted NaCl profiles to the measurements on the meat samples at day 4 for three NaCl contents into the marinades (cf. table 1).

IV. CONCLUSION

Mass transfers in beef meat marination are rather complex due to components interactions which affect both 'equilibrium' at the meat/marinade interface and apparent diffusivities of the components. However, even if further investigations are needed to clarify interactions between Na^+ ions and anions, the present results provide data on which rough calculations can be based to assess NaCl and pH evolutions within beef meat cuts according to their size and marinade composition.

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REFERENCES

[1] Deumier, F., Bohuon, P., Trystram, G., Saber, N., & Collignan, A. (2003). Pulsed vacuum brining of poultry meat: experimental study on the impact of vacuum cycles on mass transfer. Journal of Food Engineering, 58, 75–83.

[2] Graiver, N., Pinotti, A., Califano, A., & Zaritzky, N. (2006). Diffusion of sodium chloride in pork tissue. Journal of Food Engineering, 77, 910–918

[3] Hansen, C.L., Van den Berg, F., Ringgaard, S., Stodkilde-Jorgensen, H., & Karlsson, A. (2008). Diffusion of NaCl in meat studied by ^{1}H and ^{23}Na magnetic resonance imaging. Meat Science, 80 (3), 851-856.

[4] Siró, I., Vén, Cs., Balla, Cs., Jónás, G., Zeke, I., & Friedrich L. (2009). Application of an ultrasonic assisted curing technique for improving the diffusion of sodium chloride in porcine meat. Journal of Food Engineering, 91 (2), 353-362

[5] Vestergaard, C., Andersen, B.L., & Adler-Nissen, J. (2007), Sodium diffusion in cured pork determined by 22Na radiology, Meat Science, 76, 258–265.

[6] G. Djelveh, G., & J.B. Gros, J.B. (1988). Measurement of effective diffusivities of ionic and non-ionic solutes through beef and pork muscles using a diffusion cell. Meat Science, 24 (1), 11–20.