Salting kinetics and salt diffusivities in farmed Pantanal caiman muscle[1]

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Abstract – The legal Pantanal caiman (*Caiman crocodilus yacare*) farming, in Brazil, has been stimulated and among meat preservation techniques the salting process is a relatively simple and low-cost method. The objective of this work was to study the sodium chloride diffusion kinetics in farmed caiman muscle during salting. Limited volumes of brine were employed, with salting essays carried at 3, 4 and 5 brine/muscle ratios, at 15%, 20% and 25% w/w brine concentrations, and brine temperatures of 10, 15 and 20^{o}C. The analytical solution of second Fick's law considering one-dimensional diffusion through an infinite slab in contact with a well-stirred solution of limited volume was used to calculate effective salt diffusion coefficients and to predict the sodium chloride content in the fillets. A good agreement was obtained between the considered analytical model and experimental data. Salt diffusivities in fillets were found to be in the range of $0.47x10^{-10}$ to $9.62x10^{-10}$ m^2/s.

Index terms: *Caiman crocodilus yacare*, mass transfer, meat, preservation, processing, brines.

Cinética de salga e difusividades de sal em carne de jacaré do Pantanal criado em cativeiro

Resumo – A criação de jacaré do Pantanal (*Caiman crocodilus yacare*) em cativeiro tem sido estimulada, e entre as técnicas de processamento de sua carne, a salga é um processo de conservação relativamente simples e de baixo custo. O objetivo deste trabalho foi estudar a cinética de difusão de cloreto de sódio em carne de jacaré do Pantanal criado em cativeiro, durante a salga úmida. Foram utilizados volumes limitados de salmoura e os experimentos foram realizados com relações salmoura/músculo de 3, 4 e 5, com concentrações de salmoura de 15%, 20% e 25% em peso e temperaturas de 10, 15 e 20^{o}C. A solução analítica da segunda lei de Fick, considerando difusão unidimensional em uma placa infinita em contato com uma solução bem agitada de volume limitado, foi utilizada para calcular os coeficientes de difusão efetivos de sal e estimar o conteúdo de cloreto de sódio nos filés. Obteve-se boa concordância entre o modelo analítico considerado e os dados experimentais. As difusividades do sal nos filés ocorreram na faixa de $0,47x10^{-10}$ a $9,62x10^{-10}$ m^2/s.

Termos para indexação: *Caiman crocodilus yacare*, transferência de massa, carne, preservação, processamento, salmoura.

Introduction

Pantanal caiman (*Caiman crocodilus yacare*) is abundant in Brazilian states of Mato Grosso and Mato Grosso do Sul and it is illegally hunted to skin commercialization. As a consequence, many authorities claimed that the caiman had been over-exploited in the Pantanal, generating pressure for a monitoring program for caiman populations (Mourão et al., 2000).

As an alternative to reduce the clandestine harvest, the legal caiman farming has been stimulated, in such a way that the study and development of processing techniques for the caiman meat are essential in order to increase its commercial interest as a complementary activity to the leather trade. The salting process, which is a relatively simple, low-cost method of meat preservation and could be employed even in distant, hard to access places, such as the caiman farms, would be a very interesting way of processing the caiman meat and improving its potential for human consumption. In a previous work, supported by sensorial analyses, Romanelli (1995) reported excellent acceptance for caiman salted meat.

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The wet salting is a specific modality of osmotic dehydration, which is conducted by immersion in concentrated salt solutions. Water loss and solid uptake during osmotic dehydration has been modeled by using the second Fick's law. Most works apply analytical solutions for one-dimensional mass transfer based in laboratory studies carried out with a large excess of agitated solution, so as to ensure negligible variation in the solution composition and to simplify involved calculations (Raoult-Wack, 1994). Romanelli & Felício (1995) used the same approach to determine the effective diffusivity of salt in caiman meat. Nevertheless, the management of large volumes of solution is critical to the process at industrial scale, leading to increased production costs. On the other side, employing lower solution/product volumetric relations, in spite of resulting in significant changes in solution composition, could make possible the adoption of a process control strategy based on a mass balance (Medina-Vivanco et al., 2002).

Knowledge of the diffusion rates is important since it allows the accurate determination of the necessary processing time, taking into account both the final salt concentration and distribution inside the product. Several works have been published on mass transfer and salt diffusivities in meat and fish (Guiheneuf et al., 1997; Medina-Vivanco et al., 1998; Sabadini et al., 1998; Teixeira & Tobinaga, 1998; Wang et al., 2000; Chiralt et al., 2001). Salting of alternative meats with a focus on the quality attributes of the resulting products were also studied, as in the works of Paleari et al. (2000), who evaluated the salted and cured buffalo meat, and Zegeye (1999), who studied salted and smoked camel meat products. About caiman meat salting, only the study of Romanelli & Felício (1995) and the work of Lopes Filho et al. (2002), who determined sorption isotherms of salted caiman meat, are available.

The objective of this work was to study the sodium chloride diffusion kinetics in farmed caiman muscle during salting.

Material and Methods

Longissimus dorsi muscle samples were obtained from farmed caimans (*Caiman crocodilus yacare*) weighing between 20 and 22 kg. The meat was cut into fillets, parallel to the muscle fiber orientation, with individual weight between 80 and 120 g. Their thickness and averaged width were obtained by direct measurement with a digital caliper, being in the range of 0.51 to 0.65 cm and 15 to 20 cm, respectively.

Experiments were carried out with brine concentrations of 15%, 20% and 25% (w/w), at temperatures of 10, 15 and 20°C, and volume ratios of brine/muscle (V^L/V^S) of 3, 4 and 5.

Fillet densities, before salting and at different periods after salting were measured by the liquid displacement method, using toluene as the immersion liquid (Mohsenin, 1986). Brine densities were measured by means of a pycnometer at 25°C.

Fillets were weighed and placed inside flasks of 500 mL containing brine at a predetermined volume, temperature and salt concentration. Flasks were then maintained in a refrigerated orbital agitator, removed at different time intervals, when brine was drained and weighed, and fillets were dried with absorbent paper, weighed and ground. Three aliquots of muscle were taken out to determine moisture content and two aliquots for salt content, estimated as the ash contents in muffle furnace at 550°C. Two aliquots of brine were taken to measure salt content.

The muscle moisture content was determined by drying to constant weight in vacuum oven at 68°C to 72°C (AOAC International, 1997). The salt content was obtained according to the Mohr's method (James, 1995).

The governing equation for the unsteady-state one-dimensional diffusion in a plane slab was given by the second Fick's law, also called the diffusion equation, and the analytical solution of the stated problem was given by Crank (1975) as:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(\frac{-D_{eff} q_n^2 t}{L^2}\right) \quad (1)$$

where M_t is the total amount of solute in the solid at time t; M_∞ is the corresponding quantity at equilibrium; L is half of the slab thickness and q_n are the non zero positive roots of the equation

$$\tan q_n = -\alpha q_n, \quad (2)$$

where tan is tangent.

In order to adjusting equation (1) to experimental data and to obtain effective diffusivity values, it was necessary firstly to determine parameters m, α, and q_n.

The partition coefficient, m, was determined based on equilibrium conditions. The equilibrium sodium chloride contents in the muscle at different experimental conditions were obtained by adjusting equation (3), presented by Azuara et al. (1992), to experimental curves of salt content versus time.

$$M_t = \frac{\beta t(M_\infty)}{1+\beta t}. \quad (3)$$

In equation (3), M_t (% w/w, wet basis) represents the average salt content of muscle at time t; β is an adjustable constant related to the rate of incoming of soluble solids to the foodstuff, and M_∞ is the extrapolated salt concentration at equilibrium (% w/w, wet basis).

To convert weight concentrations (M_∞) to volumetric concentrations (C_∞^S), it was necessary to use the muscle densities at the equilibrium (ρ_∞^S). These values were obtained by extrapolating experimental data of muscle density versus moisture content to the equilibrium moisture content, which in turn was determined by extrapolation of an experimental curve of muscle moisture content versus time.

Similarly, the equilibrium salt contents in brine (C_∞^L) were obtained by extrapolating the experimental curves of brine salt contents versus time and brine densities versus salt content.

Once the partition coefficient had been calculated for each experimental condition, parameter α was obtained by means of equation (4) (Crank, 1975):

$$\alpha = m\frac{V^L}{V^S}, \quad (4)$$

where V^L and V^S are the solution and solid volumes, respectively, and the parameter m is the partition or distribution coefficient. This coefficient accounts for the differences between the interfacial solute concentrations within the solid and in the solution, and is defined as (Wang & Sastry, 1993):

$$C_\infty^L = mC_\infty^S. \quad (5)$$

In the above equation C_∞^L and C_∞^S are the volumetric solute concentrations (in g NaCl/cm^3) in the solution and solid, respectively, at the equilibrium. Measuring values of C_∞^L and C_∞^S for specific experimental conditions permits evaluation of the equilibrium partition coefficient.

Finally, the effective diffusivities were obtained by a non-linear adjustment of the first six terms of the series corresponding to equation (1), which was performed by using the software Statistica (StatSoft Inc., 1995).

Results and Discussion

Muscle density increased with decreasing moisture content, which is supposed to be due to the salt gain that accompanied water loss (Figure 1). Volume of NaCl molecules would had limited the extent of muscle shrinkage, in an effect already pointed out by Eichler et al. (1997) who studied shrinkage of hydrophilic gels during dehydration. A linear regression of experimental data is represented by equation (6), which resulted in a good determination coefficient (R^2 = 0.993);

$$\rho^S = 1.728 - 0.846X^S. \quad (6)$$

In equation (6) muscle density (ρ^S) is given in g/cm^3, while X^S is the muscle moisture content in % w/w (wet basis).

A fast increase in the muscle salt content was observed in the first ten hours of the process, followed by a slower increasing until equilibrium has been attained (Figure 2). Faster salt gain at the first hours of salting process is due to a larger concentration gradient between brine and muscle. This gradient is probably reduced with time elapsing as a consequence of a high salt content layer that is formed on the muscle surface and acts as a barrier against further salt uptake (Mujaffar & Sankat, 1998).

As expected, the rate of solute gain increased with increasing temperature, mainly when temperature changed from 10°C to 15°C (Figure 2). At 10°C the salt equilibrium content in the muscle was not reached even after 60 hours of immersion in brine. Nevertheless, at 15°C and 20°C only about 30 hours were necessary for caiman muscle reaching equilibrium with brine, attaining a salt content of about 11% (w/w, wet basis). According to Chiralt et al. (2001), higher temperatures affect not only the rate of diffusional phenomena but also the viscoelastic properties of solid matrix, with a softening of the structure accom-

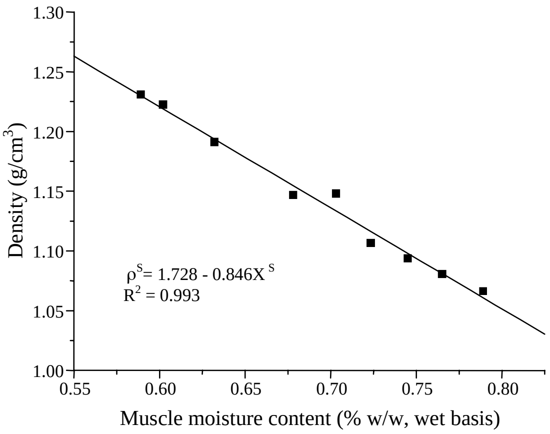

Figure 1. Density of Pantanal caiman muscle as a function of moisture content.

panying the temperature increase. An additional positive effect in salt gain rates could arise from the reducing brine viscosity at higher temperatures.

A marked influence of the brine initial salt concentration was observed in the salt uptake of caiman muscle (Figure 3). Chiralt et al. (2001) pointed out that brine concentrations determines the salting driving force associated with diffusional mechanisms and thus process times. Also the use of limited brine volumes affected the total amount of salt available for penetrating the solid, which in turn affected the final salt concentration of caiman muscle.

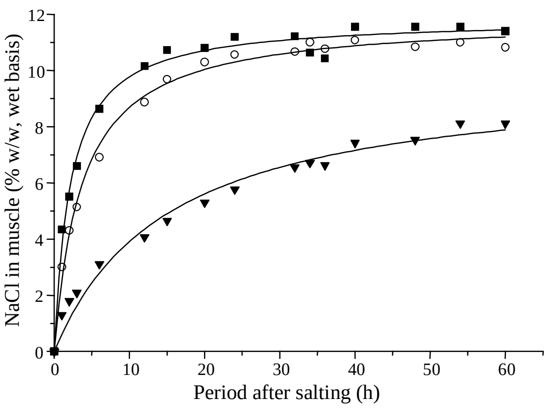

Figure 2. Effect of temperature (20°C: ■; 15°C: O; 10°C: ▼) in the salt uptake by Pantanal caiman muscle at brine initial salt concentration of 15% w/w and at brine/muscle volume ratio equal to 3.

The volume ratio of brine/muscle showed a small effect on the final salt concentration of muscle (Figure 4) and almost no effect on the initial rate of salt gain, as it is verified from the coincidence of the three curves at the first hours of process. Medina-Vivanco et al. (1998) observed a similar behavior in fish muscle of tilapia.

The influence of the tested variables on salt uptake by caiman muscle is clearly seen in Figure 5, where the salt content of muscle after 60 hours in brine immersion was plotted against brine initial concentration and temperature (Figure 5a), and brine initial concentration and brine/muscle ratio (Figure 5b). Statistical analysis indicated that the linear effects of the three tested variables were significant at a 95% confidence level. As it was already detected, increasing brine initial concentration caused a great increase in salt gain, while higher temperatures and brine/muscle ratios had only a slight positive effect in the salting process (Figure 3).

Results of salt effective diffusivity coefficients calculated for caiman muscle were found to be between $0.47x10^{-10}$ and $9.62x10^{-10}$ m^2/s (Table 1). This order of magnitude is comparable to results reported in literature for salt diffusion in meats and fish. Gros et al. (1984) presented a compilation of effective diffusivities of Cl^- ions in pork and beef, which fell in

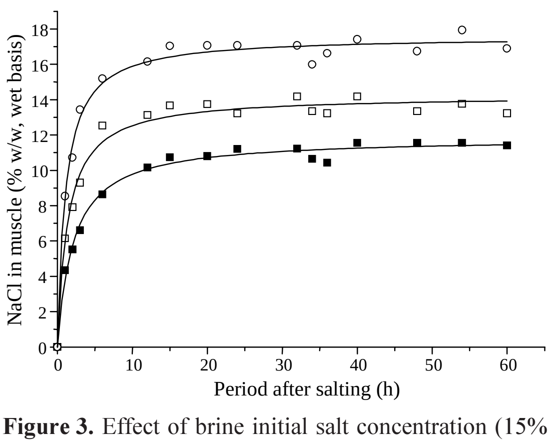

Figure 3. Effect of brine initial salt concentration (15% w/w: ■; 20% w/w: □; 25% w/w: O) in the salt uptake by Pantanal caiman muscle at 20°C and brine/muscle volume ratio equal to 3.

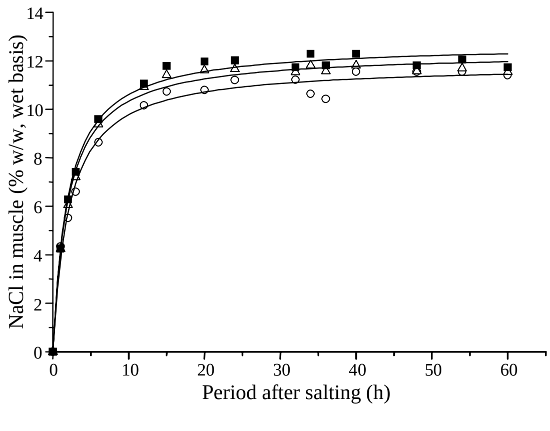

Figure 4. Effect of brine/muscle volume ratio (3: O; 4: Δ; 5: ■) in the salt uptake (20°C, brine initial salt concentration of 15% w/w) by Pantanal caiman muscle.

the range of 1.5x10^{-10} and 4.7x10^{-10} m^2/s at various salt conditions. Chiralt et al. (2001) studied the effect of vacuum in salting of beef and salmon and found effective diffusivities between 0.139x10^{-10} and 4.15x10^{-10} m^2/s with and without vacuum application. Wang et al. (2000) also presented diffusivity values for salt in different fish muscles, which varied from 0.286x10^{-10} and 14.5x10^{-10} m^2/s.

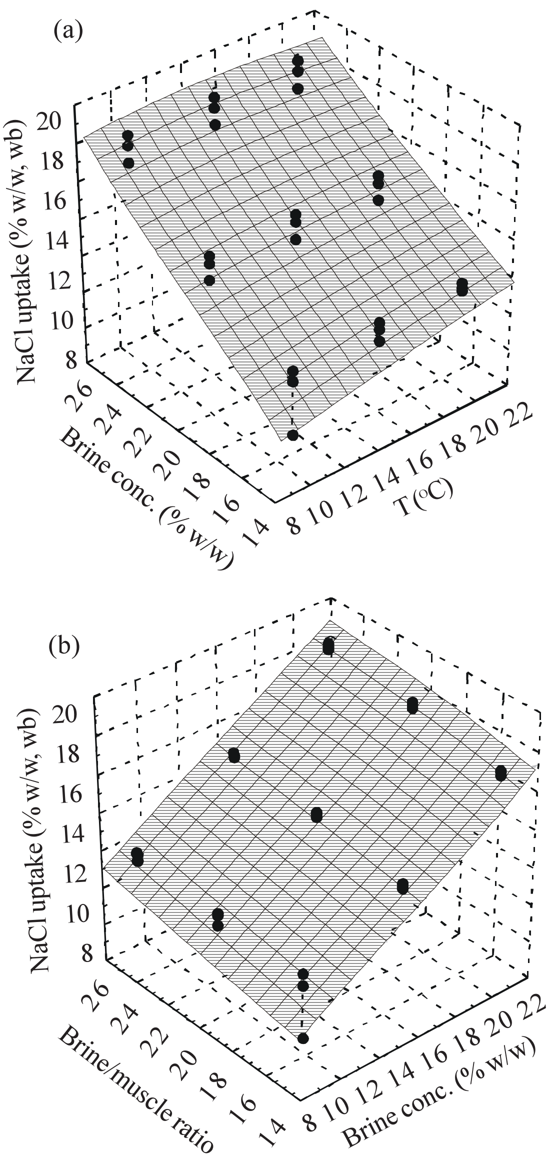

Figure 5. NaCl content in Pantanal caiman muscle after 60 hours in brine as function of: initial brine concentration and temperature (a) and initial brine concentration and brine/muscle volume ratio (b).

Effective diffusivities decreased with decreasing temperatures (Table 1) as expected in view of curves presented in Figure 2. Initial brine concentration also played an important role in mass transfer rates, causing diffusion coefficients to be lower at lower initial salt contents in brine. The less important effect came from brine/muscle ratio, since diffusivities were similar for the same values of temperature, initial brine concentrations, but different brine/muscle ratios.

Table 1. Effective diffusivity and activation energy at different brine/muscle ratio, initial brine concentration and temperature during salting of Pantanal caiman meat[1].

Initial brine concentration (% w/w)	Temperature (°C)	Effective diffusivity ×10^{-10} (m^2/s)	Activation energy (kJ/mol)
	Brine/muscle ratio 3		
	20	9.62	
25	15	6.10	79.40
	10	3.04	(0.994)
	20	7.29	
20	15	4.42	99.32
	10	1.73	(0.987)
	20	5.34	
15	15	2.86	168.13
	10	0.47	(0.966)
	Brine/muscle ratio 4		
	20	8.90	
25	15	6.12	64.68
	10	3.50	(0.994)
	20	7.21	
20	15	4.69	78.61
	10	2.32	(0.990)
	20	5.68	
15	15	3.38	108.94
	10	1.18	(0.981)
	Brine/muscle ratio 5		
	20	8.42	
25	15	6.26	56.99
	10	3.70	(0.987)
	20	7.33	
20	15	4.78	71.41
	10	2.62	(0.995)
	20	5.92	
15	15	3.78	89.18
	10	1.63	(0.985)

(1)Numbers in brackets correspond to determination coefficient (R^2) of activation energy data with significance level (P) of 5%.

The temperature dependence of water effective diffusivity at the tested salting conditions could be well represented by an Arrhenius type model given by

$$D_{eff} = D_0 \exp\left(\frac{-E_a}{RT}\right), \quad (7)$$

where D_0 is an adjustable constant, E_a is the activation energy for the salting process, R is the ideal gas constant (8.134 J/mol K), and T is the absolute temperature. A linear regression procedure applied to $\ln(D_{eff})$ against (1/T) permitted to calculate the parameters D_0 and E_a for the different salting conditions. Table 1 presents the values of the activation energy as well as the corresponding determination coefficients and Figure 6 shows that salt diffusion coefficients are function of temperature and brine initial salt concentration (brine/muscle volume ratio = 3), illustrates the adjustment of equation (7) to experimental data.

Considering that equation (7) is an empirical model, the magnitude of the activation energy is an indication of the temperature influence on the process. In this way the temperature influence increased as the brine/muscle ratio and initial brine concentration decreased. This is an indication that when there is an excess of salt available for penetrating the muscle, the temperature assumes a secondary role in the process. Nevertheless, as the amount of salt decreases, temperature starts to be an important factor for accelerating the process.

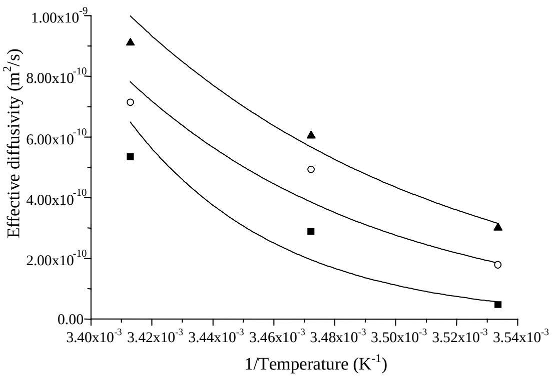

Figure 6. Effective diffusion coefficients of NaCl as a function of temperature and brine initial salt concentration of 15% w/w (■), 20% w/w (O) and 25% w/w (▲), at brine/muscle volume ratio equal to 3, in Pantanal caiman meat. Solid lines indicate data adjustment to Arrhenius type equation.

Conclusions

1. The analytical solution of second Fick's law considering one-dimensional diffusion in a thin slab from a well-stirred solution of limited volume presents a good agreement with the experimental data.
2. The salting process of caiman muscle is greatly influenced by the initial brine concentration and, in a lesser extent, by temperature and brine/muscle volume ratio.
3. Salt effective diffusion coefficients are in the range of 0.47×10^{-10} and 9.62×10^{-10} m^2/s and are well correlated by an Arrhenius type equation.

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References

AOAC INTERNATIONAL (Gaithersburg, United States). **Official methods of analysis of AOAC International**. 16th ed. Gaithersburg, 1997. 988 p.

AZUARA, E.; BERISTAIN, C.; GARCIA, H. Development of a mathematical model to predict kinetics of osmotic dehydration. **International Journal of Food Science and Technology**, Oxford, v. 29, n. 4, p. 239-242, 1992.

CHIRALT, A.; FITO, P.; BARAT, J. M.; ANDRÉS, A.; GONZÁLEZ-MARTÍNEZ, C.; ESCRICHE, I.; CAMACHO, M. M. Use of vacuum impregnation in food salting process. **Journal of Food Engineering**, Oxford, v. 49, p. 141-151, 2001.

CRANK, J. **The mathematics of diffusion**. 2nd ed. Oxford: Clarendon, 1975. 414 p.

EICHLER, S.; RAMON, O.; LADYZHINSKI, I.; COHEN, Y.; MIZRAHI, S. Collapse processes in shrinkage of hydrophilic gels during dehydration. **Food Research International**, Oxford, v. 30, n. 9, p. 719-726, 1997.

GROS, J. B.; DUSSAP, C. G.; GONZALES-MENDEZ, N. Solute diffusivities in meat: a review. In: McKENNA, B. M. (Ed.). **Engineering and food**: engineering sciences in the food industry. Oxford: Elsevier, 1984. v. 1, p. 287-297.

GUIHENEUF, T. M.; GIBBS, S. J.; HALL, L. D. Measurement of the inter-diffusion of sodium ions during pork brining by one-dimensional Na-23 magnetic resonance imaging (MRI). **Journal of Food Engineering**, Oxford, v. 31, n. 4, p. 457-471, 1997.

JAMES, C. S. **Analytical chemistry of foods**. Glasgow: Blackie Academic & Professional, 1995. 177 p.

LOPES FILHO, J. F.; ROMANELLI, P. F.; BARBOZA, S. H. R.; GABAS, A. L.; TELIS-ROMERO, J. Sorption isotherms of alligator's meat (*Caiman crocodilus yacare*). **Journal of Food Engineering**, Oxford, v. 52, p. 201-206, 2002.

MEDINA-VIVANCO, M.; SOBRAL, P. J. A.; HUBINGER, M. D. Mass transfer during dewatering and salting of tilapia for different volume brine to fillets ratios. In: INTERNATIONAL DRYING SYMPOSIUM, 11., 1998, Halkidiki. **Proceedings**... Thessaloniki: Ziti Publishing, 1998. v. A, p. 852-859.

MEDINA-VIVANCO, M.; SOBRAL, P. J. A.; HUBINGER, M. D. Osmotic dehydration of tilapia fillets in limited volume of ternary solutions. **Chemical Engineering Journal**, Oxford, v. 86, p. 199-205, 2002.

MOHSENIN, N. N. **Thermal properties of foods and agricultural materials**. New York: Gordon and Breach, 1986. 891 p.

MOURÃO, G.; COUTINHO, M.; MAURO, R.; CAMPOS, Z.; TOMÁS, W.; MAGNUSSON, W. Aerial surveys of caiman, marsh deer and pampas deer in the Pantanal Wetland of Brazil. **Biological Conservation**, Oxford, v. 92, p. 175-183, 2000.

MUJAFFAR, S.; SANKAT, C. K. The osmotic dehydration of shark fillets. In: INTERNATIONAL DRYING SYMPOSIUM, 11., 1998, Halkidiki. **Proceedings**... Thessaloniki: Ziti Publishing, 1998. v. A, p. 911-921.

PALEARI, M. A.; BERETTA, G.; COLOMBO, F.; FOSCHINI, S.; BERTOLO, G.; CAMISASCA, S. Buffalo meat as a salted and cured product. **Meat Science**, Oxford, v. 54, p. 365-367, 2000.

RAOULT-WACK, A. L. Recent advances in the osmotic dehydration of foods. **Trends in Food Science and Technology**, Oxford, v. 5, p. 255-260, 1994.

ROMANELLI, P. F. **Propriedades tecnológicas da carne de jacaré do Pantanal (*Caiman crocodilus yacare*)**. 1995. 140 f. Tese (Doutorado em Tecnologia de Alimentos) - Universidade Estadual de Campinas, Campinas, 1995.

ROMANELLI, P. F.; FELÍCIO, P. E. Estudo da salga da carne de jacaré do Pantanal *Caiman crocodilus yacare* (Daudin, 1802)* (Reptilia–Crocodilia). **Ciência e Tecnologia de Alimentos**, Campinas, v. 15, n. 3, p. 251-254, 1995.

SABADINI, E.; CARVALHO, J. R. B. C.; SOBRAL, P. J. do A.; HUBINGER, M. D. Mass transfer and diffusion coefficient determination in the wet and dry salting of meat. **Drying Technology**, New York, v. 16, n. 9/10, p. 2095-2115, 1998.

STATSOFT INC. (Tulsa, United States). **STATISTICA for Windows**: computer program manual. Tulsa, 1995. 19 disks.

TEIXEIRA, M. B. F.; TOBINAGA, S. A diffusion model for describing water transport in round squid mantle during drying with a moisture-dependent effective diffusivity. **Journal of Food Engineering**, Oxford, v. 36, n. 2, p. 169-181, 1998.

WANG, D.; TANG, J.; CORREIA, L. R. Salt diffusivities and salt diffusion in farmed Atlantic salmon muscle as influenced by rigor mortis. **Journal of Food Engineering**, Oxford, v. 43, p. 115-123, 2000.

WANG, W. C.; SASTRY, S. K. Salt diffusion into vegetable tissue as a pretreatment for ohmic heating: determination of parameters and mathematical model verification. **Journal of Food Engineering**, Oxford, v. 20, p. 311-323, 1993.

ZEGEYE, A. A note on the influence of heat treatment, salting and smoking on the acceptability of camel meat products. **Meat Science**, Oxford, v. 53, p. 217-219, 1999.