

Salt diffusivities and salt diffusion in farmed Atlantic salmon muscle as influenced by rigor mortis

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Abstract

Salt infusion in farmed Atlantic salmon muscle as affected by rigor mortis during salting was investigated. A finite-difference model was developed to determine the salt diffusivity and to simulate salt infusion in the salmon muscle. Experiments verified that the model gave good fits for pre-rigor, in-rigor and post-rigor states. Salt diffusivities in the Atlantic salmon muscle were determined to be $(8.77 + 0.88C) \times 10^{-11}$, $(0.23 + 4.81C) \times 10^{-10}$ and $(1.08 + 0.59C) \times 10^{-10}$ m²/s (at 10°C) for pre-rigor, in-rigor and post-rigor fish, respectively; where C is the salt concentration (g/g salt-free solids) in the muscle. Simulation results revealed that the pre-rigor salmon had the lowest salt concentration when compared with in-rigor and post-rigor salmon after the same salting time. Salt distribution inside the salmon samples was less uniform than in-rigor and post-rigor fish. The equilibrium salt concentrations had a significant impact on the concentration profile for the in-rigor salmon fillets. © 2000 Elsevier Science Ltd. All rights reserved.

Nomenclature

α	thermal diffusivity
\tilde{D}	dimensionless salt diffusivity
φ	dimensionless salt concentration
τ	dimensionless time
C	concentration of salt (g/g SFS)
C_0	initial C in the muscle (g/g SFS)
C_1	equilibrium C (g/g SFS)
D	salt diffusivity (m ² /s)
d'	d_1/d_0
d_0, d_1	diffusion parameters (m ² /s)
F^*	lack of fit mean square/pure error mean square
FDM	finite difference method
Le	the Lewis number
l	half thickness of the fish slab (m)
M_t	amount of salt uptake at time t [(g/g SFS) mm]
s_{d_0}	standard error of d_0
s_{d_1}	standard error of d_1
SFS	salt free solids
t	salting time (s)
u	dimensionless distance along x -axis
x	diffusion distance (m)

1. Introduction

Fish have been salted during much of human history, yet the approach to these practices has been mostly empirical. Until about 30 years ago, little attention was given to the understanding of the basic mechanisms involved in salting fish. It is now generally accepted that salt migration by diffusion plays an important role in salting. Several researchers applied Fick's second law of diffusion to study fish salting (Peters, 1971; Stefanovskaya, Stefanovskii & Samoilova, 1976; Sakai & Miki, 1982; Rodger, Hastings, Cryne & Bailey, 1984; Sakai & Suzuki, 1985). They assumed constant salt diffusivities and obtained various solutions to Fick's second law for different boundary conditions and geometry of fish samples. An earlier study showed that the salt diffusion coefficient in swordfish muscle depended on salt concentration and sample temperature (Del Valle & Nickerson, 1967). Del Valle and Nickerson used Cranks (1975) analytical solution and assumed that salt diffusivity was constant within each increment of salt concentration of the brine. This assumption may lead to erroneous solution because of the non-uniform salt distribution in the fish muscle at a fixed brine concentration. This problem can now be easily solved by using numerical methods. Finite difference techniques have been used in studying mass transfer of solutes in solid

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foods (Drusas & Vagenas, 1988; Teixeira & Shoemaker, 1989; Moreira, Oliverira, Silva & Oliveira, 1993; Ateba & Mittal, 1994) and can be used to study salt diffusion in Atlantic salmon in which salt diffusivity may depend upon salt concentration.

The values of salt diffusivity in fish depend upon species, temperature, muscle orientation, fat content, the presence or absence of skin, and other factors. In the literature, the values of salt diffusivity in cod, herring, chum salmon, pike, swordfish and tuna range from 1.14×10^{-10} to 1.45×10^{-9} m²/s (Del Valle & Nickerson, 1967; Peters, 1971; Stefanovskaya et al., 1976; Sakai & Miki, 1982; Rodger et al., 1984; Sakai & Suzuki, 1985). No data are, however, available for the salt diffusivity in Atlantic salmon (*Salmo salar*), especially in relation to the influence of rigor mortis. Rigor mortis may affect fish flesh quality (Stroud, 1968; Nakayama, Toyoda & Ooi, 1994). Some widely used methods for assessing rigor include measuring Rigor Index (Bito, Yamada, Mikumo & Amano, 1983; Ando, Toyohara, Shimizu & Sakaguchi, 1991), shear strength (Montero & Borderias, 1990), isometric muscle tensions (Nakayama, Liu & Ooi, 1992), rigorometer methods (Attrey & Sharma, 1980; Korhonen, Lanier & Giesbrecht, 1990), and measurement of ATP and its breakdown products (Karube, Marsuoka, Suzuki, Watanabe & Toyoma, 1984; Watanabe, Endo, Takeuchi, Hayashi & Toyoma, 1986; Iwamoto, Yamanaka, Watabe & Hashimoto, 1987; Huynh, Mackey & Gawley, 1992). Since the Rigor Index measurement is simple, direct and effective for cultivated Atlantic salmon (Wang, Tang, Correia & Gill, 1998b), this method was used in this research to monitor the development of rigor mortis. Berg, Erikson and Nordtvedt, 1997 recently used a low-frequency vibration method combined with a neural network to classify rigor states of Atlantic salmon. Their idea was partially adopted into this research in which three rigor states were defined.

The objectives of this study were: (a) to use a simulation model based on a finite difference method (FDM) to determine the salt diffusivity in cultivated Atlantic salmon muscle at pre-rigor, in-rigor and post-rigor states, and validate the simulation model by experimental data; (b) to predict the salt distribution in the Atlantic salmon muscle during salting.

2. Materials and methods

Fresh cultivated Atlantic salmon of 2.34 ± 0.81 kg ($n = 9$) were starved for two days before capture. Upon harvest each fish was sacrificed by a sharp blow to the head, bled at the gills, and stored in ice. The rigor state of each fish was determined by measuring the Rigor Index according to Bito et al. (1983). In the Rigor Index definition, the whole head and up to half of the fish body

was spread on a horizontal table with the other half of the body (tail part) off the table. Rigor Index (%) = $[(L_0 - L)/L_0] \times 100$, where L_0 and L represent the distance of the base of caudal fin from the horizontal line of the table immediately after the death (time = 0) and during storage, respectively. Rigor Index first increased (pre-rigor) and then decreased (post-rigor) after it reached a maximum. The Rigor Index–time profile was bell-shaped (Wang et al., 1998b). Rigor mortis began to set in about 8 h after death and was fully resolved 60–72 h after death. Maximum muscle contraction was observed 24–30 h after death. Pre-rigor was defined as the state when Rigor Index was less than 10%, in-rigor was the state when Rigor Index was between 80–100%, and post-rigor was the state when Rigor Index fell below 10%.

The salting experiments were carried out in triplicates for each rigor state. The fish were skinned and filleted. The dorsal muscle was cut into 10 pieces of $30 \times 30 \times 5$ mm³, then soaked in 2 litres of a 20% (w/v) NaCl solution at 10°C. The mean half thicknesses (l) were 2.36 ± 0.18 mm ($n = 3$), 2.40 ± 0.13 mm ($n = 4$) and 2.46 ± 0.41 mm ($n = 4$) for pre-rigor, in-rigor and post-rigor fish, respectively. Samples were taken out at pre-determined times (2, 15, 30, 45, 60, 75, 90, and 120 min) after salting and excess solution on the surface was removed by an absorbent tissue. The salt content of each sample was determined by using the AOAC Official Method 937.06 (AOAC, 1995). The initial salt concentration in the muscle was 0.012 g/g salt free solids (SFS). The equilibrium salt uptake of the dorsal muscle in 20% (w/v) brine was determined from two slices of fish after soaking for 48 h in the brine (Wang et al., 1998b). The total solid content in the fresh dorsal muscle was determined by using the AOAC Official Method 952.08 (AOAC, 1995), and the lipid content by using the procedure of Bligh & Dyer (1959). The total fat content in the muscle was $4.24 \pm 0.56\%$ ($n = 27$). Three fishes at each of the three rigor states were used for the experiments. Three muscle samples from each fish were taken for the fat analysis.

3. Finite difference modelling

The following assumptions were made to model salt diffusion in the muscle: (1) the initial salt distribution was uniform (C_0); (2) at the surfaces the salt concentration rose quickly to the constant equilibrium value (C_1); (3) the edge effect was negligible and (4) the medium was homogeneous. Food materials are typically non-homogeneous, but if their non-homogenous parts are small compared to the size of the solid food and uniformly distributed their effect on diffusivity is small (Schwartzberg & Chao, 1982). The Atlantic salmon muscle was assumed to be homogeneous with the fat

distribution considered as non-homogeneous. The lipids in Atlantic salmon muscle are stored in the connective tissue (myosepta) instead of the muscle fibres (Zhou, Ackman & Morrison, 1995) and are small (4.2% by weight) compared with the size of the slice. Therefore, it was assumed that salt diffusivity in Atlantic salmon muscle was uniform at fixed salt concentrations.

The Lewis number Le ($= \alpha/D$, where α is thermal diffusivity and D is salt diffusivity) indicates the significance of heat transfer in mass diffusion problems. For Le greater than 60, the temperature profile develops so rapidly that an isothermal condition can be assumed (Young, 1969). For fish muscle, Le was estimated to be in the order of 1000. Therefore, it was assumed that the temperature gradients in fish muscle during salting were negligible even when the samples were brought into the brine at different temperatures.

The governing equation for one-dimensional salt infusion is given by

$$\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial C}{\partial t}, \tag{1}$$

where it is assumed

$$D = d_0 + d_1 \frac{C - C_0}{C_1 - C_0}, \tag{2}$$

Initial conditions:

$$C = C_0 \quad \text{for } -l < x < l \text{ at } t = 0, \tag{3}$$

Boundary conditions:

$$C = C_1 \quad \text{for } x = -l \text{ and } x = l \text{ at } t > 0. \tag{4}$$

Salt uptake (M_t) is calculated from

$$M_t = \int_{-l}^l C(x,t) dx. \tag{5}$$

3.1. Non-dimensional analysis

To simplify the calculation and reduce computer time, variables were non-dimensionalized as

$$\varphi = \frac{C - C_0}{C_1 - C_0}, \quad \tau = \frac{d_0}{4l^2} t, \quad u = \frac{x}{2l} + \frac{1}{2}, \quad \tilde{D} = \frac{D}{d_0},$$

$$d' = \frac{d_1}{d_0}.$$

Consequently Eqs. (1)–(4) become

$$\frac{\partial}{\partial u} \left(\tilde{D} \frac{\partial \varphi}{\partial u} \right) = \frac{\partial \varphi}{\partial \tau}, \tag{6}$$

$$\tilde{D} = 1 + d' \varphi \tag{7}$$

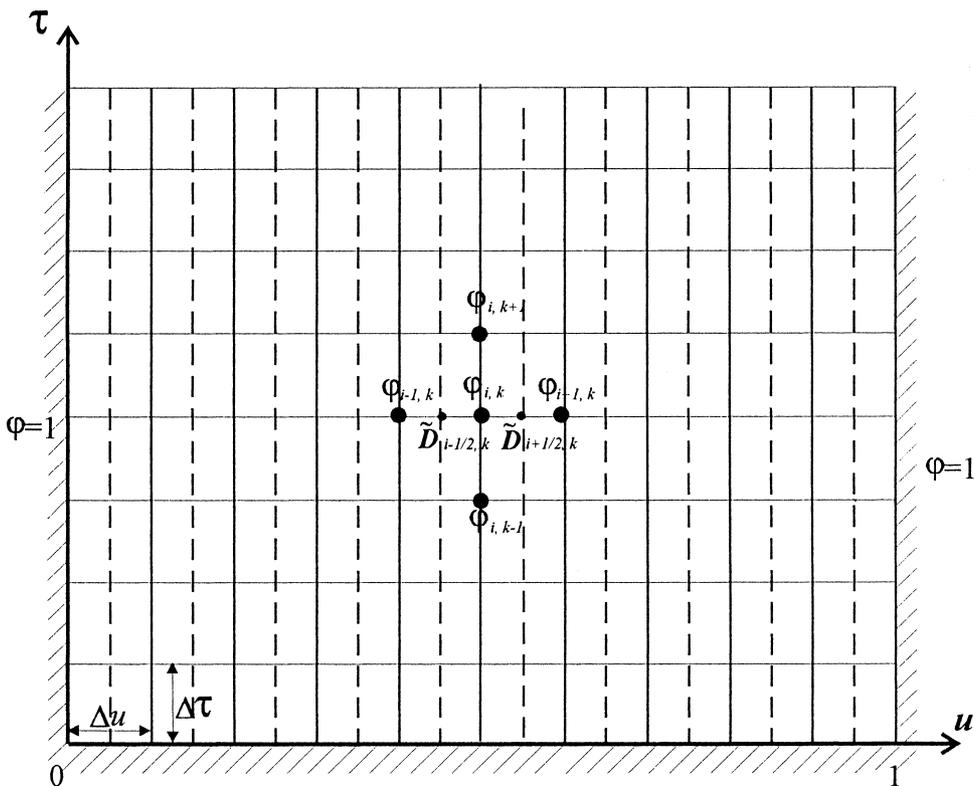


Fig. 1. Schematic of Atlantic salmon slice discretization.

$$\varphi = 0 \quad \text{for } 0 < u < 1 \text{ at } \tau = 0, \tag{8}$$

$$\varphi = 1 \quad \text{for } u = 0 \text{ and } u = 1 \text{ at } \tau > 0. \tag{9}$$

3.2. Finite difference method (FDM)

To approximate the solution of Eq. (6), an implicit one-dimensional finite difference scheme, using second-order central differentiating in space and a first-order backward difference in time was used (Fig. 1). The values of d_0 and d_1 were determined from the salt uptake data by minimizing the mean squares of deviations between observed and predicted salt uptake values. The simulation model was written in FORTRAN 77 and run on a HP-UNIX® (HP 700 Series) mainframe computer. The lack of fit test was applied to check if the FDM model was adequate (Wang, Correia & Tang, 1998a).

4. Results and discussion

4.1. FDM Model verification and determination of salt diffusivity

The equilibrium salt concentration in the pre-rigor, in-rigor and post-rigor Atlantic salmon muscle salted in 20% (w/v) brine at 10°C were 0.53 ± 0.07 ($n=6$), 0.66 ± 0.07 ($n=6$) and 0.75 ± 0.02 ($n=6$) g/g SFS, respectively. The value for pre-rigor fish was lower than that of in-rigor which was in turn slightly lower than that of post-rigor fish.

The FDM model verification involved comparison with experimental data. In the simulation, the time step was 60 s. Fig. 2 shows a comparison of observed and predicted mean salt uptake as a function of salting time for pre-rigor, in-rigor, and post-rigor Atlantic salmon. The simulation results followed the trend of the experimental data for all three rigor states. The mean differences between the FDM model predictions and

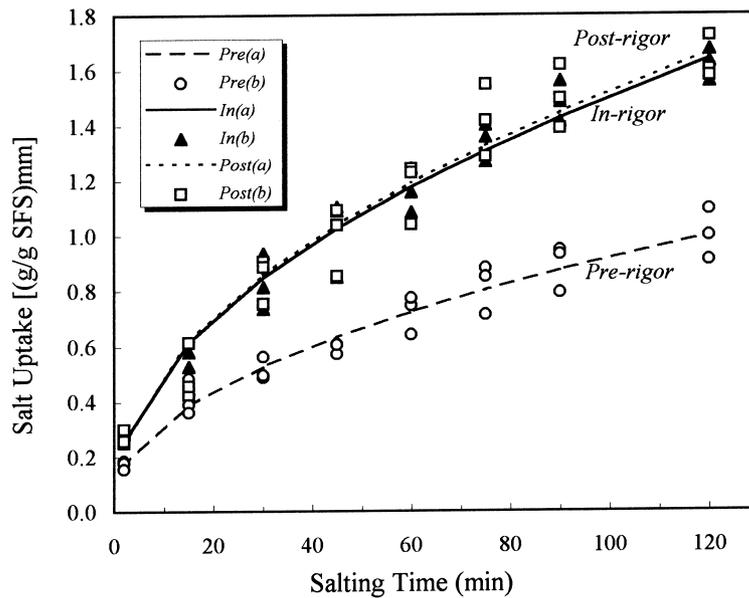


Fig. 2. Comparison of experimental data with FDM predicted salt uptake: (a) – predicted value and (b) – experimental value.

Table 1
FDM predicted salt diffusivities in Atlantic salmon muscle

Rigor state	d_0 (m ² /s)	s_{d_0} (m ² /s)	d_1	s_{d_1}	Salt diffusivity $\times 10^{11}$ (m ² /s)	F^*	F(0.95; 6, 16)
Pre-	8.78×10^{-11}	3.91×10^{-12}	4.60×10^{-12}	7.53×10^{-13}	$8.77 + 0.88C$	0.32	2.75
In-	2.86×10^{-11}	4.11×10^{-19}	3.11×10^{-10}	1.20×10^{-11}	$2.27 + 48.1C$	1.18	2.75
Post-	1.09×10^{-10}	5.01×10^{-12}	4.34×10^{-11}	4.11×10^{-12}	$10.8 + 5.90C$	1.52	2.75

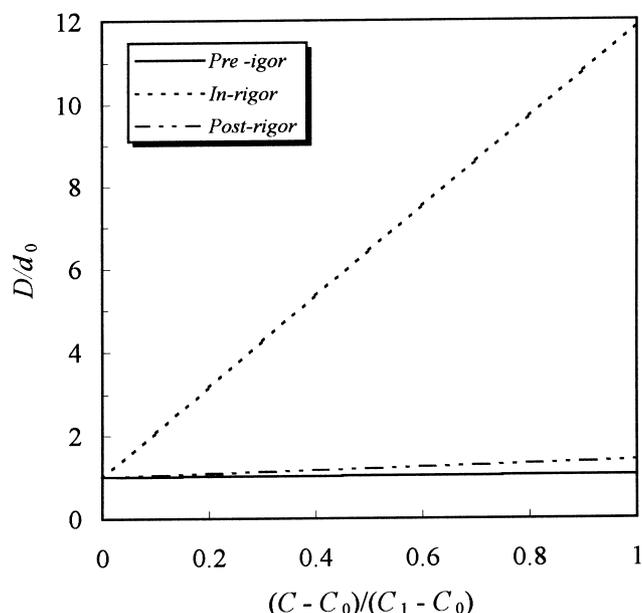


Fig. 3. Relationship between dimensionless salt diffusivity and dimensionless salt concentration in salmon muscle.

measurements were 0.013, 0.034 and 0.049 [(g/g SFS) mm] (or a relative difference of 2.4%, 5.2% and 6.2%). A lack of fit test indicated that the FDM model ade-

quately fitted the experimental data ($P < 0.05$) for all three rigor states (Table 1).

The predicted parameters d_0 and d_1 in Eq. (2) for diffusivity in cultivated Atlantic salmon are listed in Table 1. The predicted salt diffusivity (D) was calculated by substituting d_0 and d_1 into Eq. (2). The values of D ranged from 0.878 to 0.924×10^{-10} m²/s at $C = 0.012$ – 0.533 g/g SFS for pre-rigor fish; 0.286 to 3.40×10^{-10} m²/s at $C = 0.012$ – 0.659 g/g SFS for in-rigor fish; and 1.09 to 1.52×10^{-10} m²/s at $C = 0.012$ – 0.748 g/g SFS for post-rigor. The standard errors of the predicted parameters d_0 and d_1 were estimated by the bootstrap method (Efron & Tibshirani, 1993; Wang et al., 1998a) replicated one hundred times (sample size = 24). The standard errors of d_0 and d_1 (s_{d_0} and s_{d_1} , respectively) for each rigor state (Table 1) are less than 4% of the estimated d_0 and d_1 values for pre-rigor and in-rigor, and 4.6% and 9.5% of the d_0 and d_1 values of post-rigor fish, respectively.

A plot of dimensionless diffusivity $\tilde{D} (= D/d_0)$ vs. dimensionless concentration $\varphi [= (C - C_0)/(C_1 - C_0)]$ is shown in Fig. 3. The slope of in-rigor fish, d_1/d_0 , is the largest among the three rigor states. This means that the value of d_1 was distinguishable from the value of d_0 , and there was a linear relationship between salt diffusivity and concentration for in-rigor fish. It is

Table 2
Salt diffusivities of fish and lipid content of fish muscle

Fish	Concentration of brine (M)	Temperature (°C)	Lipid (%) ^a	$D \times 10^{10}$ (m ² /s)	Reference
Swordfish (fresh)	0.1	25	2–3	11.8	Del Valle and Nickerson (1967)
	0.7			10.5	
	1.4			9.5	
	2.3			13.7	
	3.1			14.5	
Cod ^b	4.5	23	0.1–0.9	14.1	Peters (1971); Murray and Burt (1972)
		33		9.3	
Tuna ^b	1.0	30	4.1	10.4	Sakai and Miki (1982)
Baltic herring ^b	2.4	2	5–16	1.14	Rodger et al. (1984)
		10		2.44	
		20		2.31	
River chum salmon ^b	2	15	1.9 ^c	7.90	Sakai and Suzuki (1985)
Ocean chum salmon ^b				6.17	
Atlantic salmon (fresh)					
Pre-rigor	3.4	10	4.2 ^c	0.878–0.924	This research
In-rigor				0.286–3.40	
Post-rigor				1.09–1.52	

^a g Lipid/g whole fish, unless indicated otherwise.

^b Frozen then thawed.

^c g Lipid/g fish muscle.

possible that the proteins gradually denatured during salting as the salt concentration in the muscle of in-rigor fish increased, and the cell structure was progressively degraded, resulting in less resistance of diffusion. The slope of the pre-rigor line was so small that \bar{D} hardly changed with φ . Therefore, the salt diffusivity in pre-rigor fish was considered to be constant, i.e. $D = d_0$.

Del Valle and Nickerson (1967) reported that the diffusion coefficient of salt in fresh swordfish muscle was smallest at a particular salt concentration and the rate of salt diffusion increased with further increases in salt concentration. They suggested that there was a ‘barrier’ after a certain concentration had been reached. This phenomenon did not appear in this research.

A comparison of salt diffusivities of different species of fish reported in the literature is shown in Table 2. It appears that salt diffusivities of Atlantic salmon predicted by the FDM model were in the lower range of the salt diffusivities reported in the literature, close to those of Baltic herring. All the reported values on salt diffusivity in fish muscle were from thawed samples except the swordfish. Ice formation and melting during the freezing and thawing cycle might have altered the cell structures resulting in higher salt diffusivities. In our study, on the other hand, we used fish that had not been frozen in all experiments, which may present more closely the industrial practices. The intact muscle structure in our samples used in the experiments might have resulted in lower salt diffusivity than reported in the literature for frozen fish. In particular, in the case of pre-rigor fish significant amounts of ATP were present in the muscle. The ATP-driven ionic pumps were able to maintain concentration gradients across membranes, which might lead to higher resistance to salt distribution.

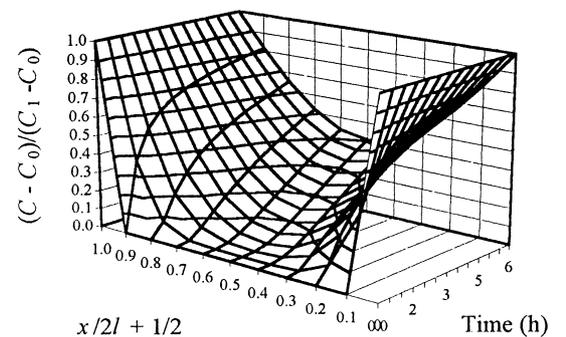
Salt diffusion occurs primarily with occluded solution and the ‘marc’ (the framework of insoluble solids in a leachable solid). The presence of fat structures forces salt to take a tortuous path which significantly reduces salt diffusivity. The higher the fat content in the muscle the more resistance the muscle will have for the transfer of an aqueous solute like sodium chloride (Schwartzberg & Chao, 1982). For example, the diffusivity of Cl^- in pork muscle ($1.9\text{--}2.2 \times 10^{-10} \text{ m}^2/\text{s}$ at $4\text{--}5^\circ\text{C}$) was about eight times as great as that in the pork back fat ($0.28 \times 10^{-10} \text{ m}^2/\text{s}$) (Fox, 1980). Storey (1982) reported that salt uptake depended on the fat content when fatty fish samples of equal size were brined at the same temperature and brine concentration. High fat content result in slower salt uptake.

The lipid content (4.2%) determined in this study was for dorsal muscle of Atlantic salmon, and could not be directly compared with lipid content of whole fish listed in Table 2. The lipid content of the whole Atlantic salmon from the same batch of fish was, however, determined to be about 10.5% by Ackman, Zhou and

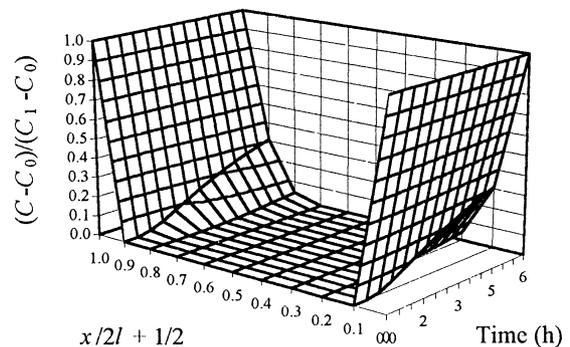
Heras, (1993). This lipid content is significantly higher than those in swordfish, cod and tuna. Thus, the predicted diffusivity values of Atlantic salmon are expected to be smaller than those of less fatty fish species. The lipid content of Baltic herring ranged from 5% to 16% (Rodger et al., 1984), overlapping the common lipid content in Atlantic salmon. Among the fish species listed in Table 2, chum salmon would be comparable to Atlantic salmon. Sakai & Suzuki (1985) reported a value of $6.17 \times 10^{-10} \text{ m}^2/\text{s}$ for pre-spawning ocean chum salmon in 2M brine at 15°C . This is about five times more than the values obtained in this study. Although they did not mention the fat content of their samples, it can be as low as 1.9% in the dorsal muscle of pre-spawning ocean chum salmon (Ando, Shimoyama & Ota, 1996). The average fat content in the dorsal muscle of Atlantic salmon is more than twice as much as pre-spawning ocean salmon, which could be the reason for the much smaller salt diffusivity.

4.2. Simulation of salt infusion

Simulations of salt diffusion in the salmon slices with thickness $2l = 5.0 \text{ mm}$ and $2l = 20 \text{ mm}$ soaking in 20%



(a) $l = 2.5 \text{ mm}$



(b) $l = 10 \text{ mm}$

Fig. 4. Simulated dimensionless concentration profiles of pre-rigor salmon muscle with different thickness ($C_0 = 0.012 \text{ g/g SFS}$, $C_1 = 0.533 \text{ g/g SFS}$).

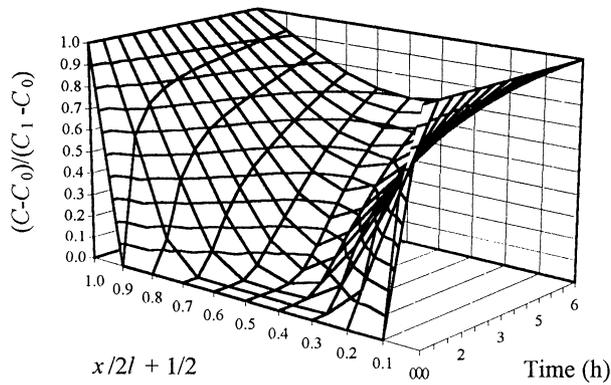
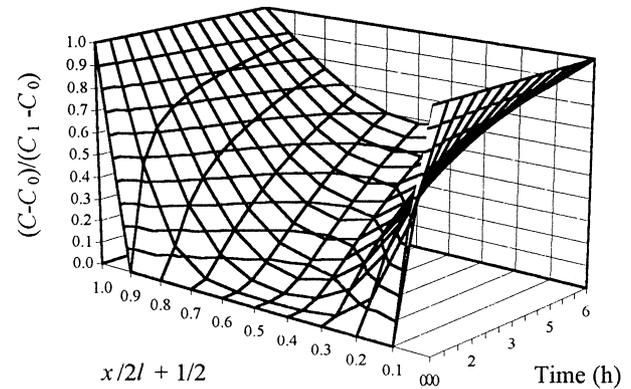
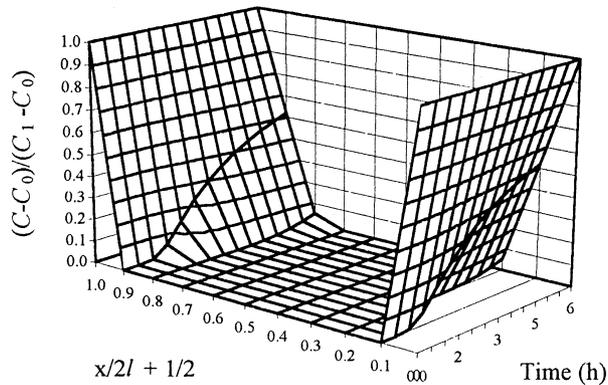
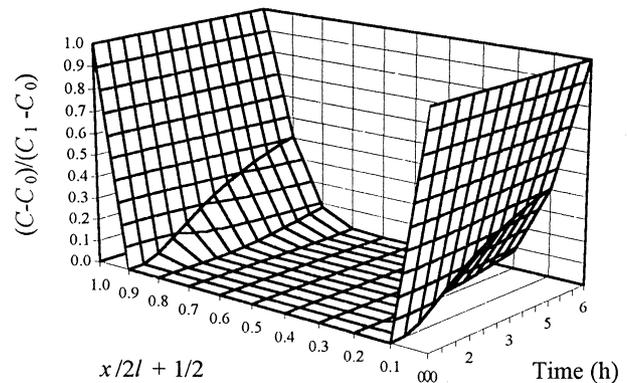
(a) $l = 2.5$ mm(a) $l = 2.5$ mm(b) $l = 10$ mm(b) $l = 10$ mm

Fig. 5. Simulated dimensionless concentration profiles of in-rigor salmon muscle with different thicknesses ($C_0 = 0.012$ g/g SFS, $C_1 = 0.659$ g/g SFS).

Fig. 6. Simulated dimensionless concentration profiles of post-rigor salmon muscle with different thickness ($C_0 = 0.012$ g/g SFS, $C_1 = 0.748$ g/g SFS).

(w/v) brine at 10°C were carried out with initial concentration $C_0 = 0.012$ g/g SFS and equilibrium concentration $C_1 = 0.533$ (pre-rigor), 0.659 (in-rigor) and 0.748 (post-rigor) g/g SFS. A slice of 20 mm thickness represented the thickest section in a commercial Atlantic salmon fillet, and 5 mm was close to the thickness of the edge of salmon fillets. The dimensionless concentration profiles of these two thicknesses are compared in Figs. 4–6.

With the 20 mm salmon slice, salt infused about 3/10 of its thickness (6 mm) into the pre-rigor and post-rigor after 6 h soaking in brine at 10°C (Figs. 4b and 5b). For 20 mm in-rigor salmon slice, however, salt infused less than 1/5 of its thickness (4 mm) after salting for 6 h (Fig. 6b). The influence of slice thickness on the dimensionless concentration was significant for all three rigor states of salmon. The predicted salt concentrations in the center of the 20 mm thick slice was negligible while the 5 mm slices attained about 40%, 70% and 58% of their equilibrium concentrations in 6 h for pre-rigor, in-rigor and post-rigor salmon, respectively. In reality, salt distribution inside fillets will be uneven because the

fillet is thick at one end and it tapers down to the tail end. Therefore, it is reasonable to assume that salt diffusion in the salmon fillet would continue during hanging and smoking.

For 5 mm salmon slices salt distribution was least uniform in pre-rigor fish as seen in Figs. 4a, 5a and 6a. This is due to the much smaller salt diffusivity in pre-rigor fish. Hence, in smoking processes, it is likely that curing farmed Atlantic salmon at their in-rigor or post-rigor state will take less time and result in more uniform salting.

5. Conclusions

A FDM model was developed to predict salt concentration distributions in pre-rigor, in-rigor and post-rigor Atlantic salmon muscle during salting assuming the salt diffusivity was linearly dependent on the salt concentration. The model was also verified by experimental data for salting in 20% (w/v) brine at 10°C for

pre-rigor, in-rigor and post-rigor Atlantic salmon slices. Predicted salt diffusivities in the Atlantic salmon muscle were $(8.77 + 0.88C) \times 10^{-11}$, $(0.23 + 4.81C) \times 10^{-10}$ and $(1.08 + 0.59C) \times 10^{-10}$ m²/s for pre-rigor, in-rigor and post-rigor fish, respectively. Salt diffusivity for in-rigor fish had the greatest increase among the three rigor states of salmon with an increase of salt concentration.

Simulation results showed that salt infused about 3/10 of the thickness into pre-rigor and post-rigor salmon fillets with 20 mm thickness in 6 h when soaked in 20% (w/v) brine at 10°C. For in-rigor salmon with 20 mm thickness, salt only infused 1/5 of the thickness after salting for 6 h.

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