Modeling of salt diffusion in Atlantic salmon muscle

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Wang, D., Correia, L.R. and Tang. J. 1998. **Modeling of salt diffusion in Atlantic salmon muscle**. Can. Agric. Eng. 40:029-034. A finite difference model was developed to predict salt concentration in *post-rigor* Atlantic salmon (*Salmo salar*) muscle during salting in 20% (w/v) brine at 10°C. The model was validated by experimental salt uptake data and salt diffusivity was estimated by minimizing the mean sum of the squares of the deviations between the observed and predicted salt uptake. The salt diffusivity, D, was salt concentration dependent: $D = (1.08 + 0.59C) \times 10^{-10}$ m^2/s for salt concentration, C, from 0.012 to 0.748 kg/kg salt-free solids.

Un modèle mathématique a été développé afin de prédire la concentration saline de la chair musculaire du saumon de l'Atlantique (*Salmo salar*) lors de la période *post-rigor*. Une saumure contenant 20% (mass/volume) de sel et maintenue à une température constante de 10°C a été utilisée pendant les essais expérimentaux. Ce modèle qui est basé sur la méthode des différences finies, a été validé expérimentalement à la suite de mesures de l'absorption de sel dans la chair du poisson. À l'aide de la méthode d'analyse statistique des valeurs observées et des valeurs prédites, on a trouvé que la diffusivité de la salinité, D, varie selon la concentration saline, C, et peut-être, $D = (1.08 + 0.59C) \times 10^{-10}$ m^2/s pour une valeur de C entre 0.012 à 0.748 kg/kg de sel.

INTRODUCTION

Salt diffusion is an important process in smoked salmon production as salting is usually required before smoking. To determine salt uptake and distribution as a function of processing time, it is necessary to know the salt diffusivity. However, no quantitative data on the salt diffusivity in Atlantic salmon muscle are available in the literature. Most studies on salt diffusion in other fish assumed constant salt diffusivities (Sakai and Suzuki 1985; Rodger et al. 1984; Peters 1971) and analytical solutions were commonly used to simulate the salt diffusion processes. Del Valle and Nickerson (1967) reported that the diffusion coefficient for the penetration of salt into swordfish (*Xiphias gladius*) muscle was dependent on the salt concentration in the muscle. They also used an analytical solution and constant salt diffusion coefficients to describe the salt diffusion process in small increments of salt concentration.

Numerical methods can be used to simulate a diffusion process where diffusion coefficient is concentration dependent (Crank 1975). Although there is no literature on the application of numerical methods to study salt diffusion in fish, those methods are extensively applied for other foodstuff. For example, Drusas et al. (1988) evaluated the salt diffusivity in green olives using an implicit finite difference method. A good summary on techniques, including analytical and numerical methods to predict moisture diffusivity in various food materials, was provided by Zogzas et al. (1994).

The objectives of this study were to develop a finite difference model to predict the salt diffusivity and to evaluate the rate of salt uptake in the Atlantic salmon muscle at 10 °C, which is a common brining temperature in industry.

MATHEMATICAL MODEL

To simplify the analysis, the following assumptions were made in developing the mathematical model: (a) the dorsal muscle of Atlantic salmon was assumed to be homogenous; (b) the initial salt distribution (C_0) was uniform in the flesh; (c) the surface salt concentration immediately reached equilibrium concentration (C_1) when submerged in brine and the concentration of the brine was constant during diffusion; (d) there was no edge effect; and (e) salt diffusivity was linearly dependent on concentration. Salt concentration in the muscle was expressed as kg/kg salt-free solids (SFS).

Governing equation

The governing equation for salt infusion in a one-dimensional slab (slice) with concentration-dependent diffusivity is given by Crank (1975):

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

where:

- C = concentration of salt in fish muscle (kg/kg SFS),
- C_1 = equilibrium salt concentration in fish muscle (kg/kg SFS),
- C_0 = initial salt concentration in fish muscle (kg/kg SFS),
- t = salting time (s),
- x = space coordinate (m), and
- D = salt diffusivity (m^2/s), given by:

$$D = d_0 + d_1\frac{C-C_0}{C_1-C_0} \qquad (2)$$

in which d_0, d_1 = estimated parameters (m^2/s).

Initial and boundary conditions

The initial condition is:

$$C(x,0) = C_0 \qquad \text{at } -l < x < l \tag{3}$$

where l = half thickness of the slice (mm).

The boundary condition of the fish slice submerged in brine is expressed by:

$$C\Big|_{x=\pm l} = C_1 \qquad \text{at } t > 0 \tag{4}$$

where C_1 = equilibrium salt concentration of fish muscle in a given brine (kg/kg SFS).

Non-dimensional analysis

To further simplify the numerical calculations and save computer time, the non-dimensional forms of concentration (ϕ), time (τ), space coordinate (u) and diffusivity ($\tilde{D}$) are defined as:

$$\phi = \frac{C - C_0}{C_1 - C_0} \qquad \tau = \frac{d_0}{4l^2}t \qquad u = \frac{x}{2l} + \frac{1}{2} \qquad \tilde{D} = \frac{D}{d_0} \tag{5}$$

Subsequently, the governing equation (Eq. 1) becomes:

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

and Eq. 2 can be written as:

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

where:

$$d' = \frac{d_1}{d_0} \tag{8}$$

The initial and boundary conditions become:

$$\phi(u,0) = 0 \qquad \text{at } 0 < u < 1 \tag{9}$$

$$\phi\Big|_{u=0} = 1 \qquad \text{at } \tau > 0, \text{ and} \tag{10}$$

$$\phi\Big|_{u=1} = 1 \qquad \text{at } \tau > 0 \tag{11}$$

Numerical analysis

Eq. 6 was solved with the initial condition (Eq. 9) and boundary conditions (Eqs. 10 and 11). A one-dimensional slab finite difference framework consisting of 100 layers of equal thickness was used to model the salt concentration in a fish slice during salting. One hundred and one nodes in total, 0th and 100th on the outer surfaces, were assigned. To approximate the solution of Eq. 6, an implicit finite difference method (FDM), using second-order central differentiating in space and a first-order backward difference in time, were employed.

Salt uptake M in the salmon slice was calculated from:

$$M = \int_{-l}^{l} C(x,t)\,dx \tag{12}$$

The values of d_0 and d_1 were determined from the salt uptake profiles by minimizing the mean sum of the squares of the errors (MSE) between the observed values (M) and the predicted values ($\hat{M}$). The minimum of the criterion was:

$$MSE = \frac{\sum_{i=1}^{n}\left(M_i - \hat{M}_i\right)^2}{n-2} \tag{13}$$

where:

M = experimental salt uptake value [(kg/kg SFS) mm],
$\hat{M}$ = predicted salt uptake value [(kg/kg SFS) mm], and
n = number of experimental measurements.

The FDM was implemented using a FORTRAN77 program on a HP-UNIX® mainframe system.

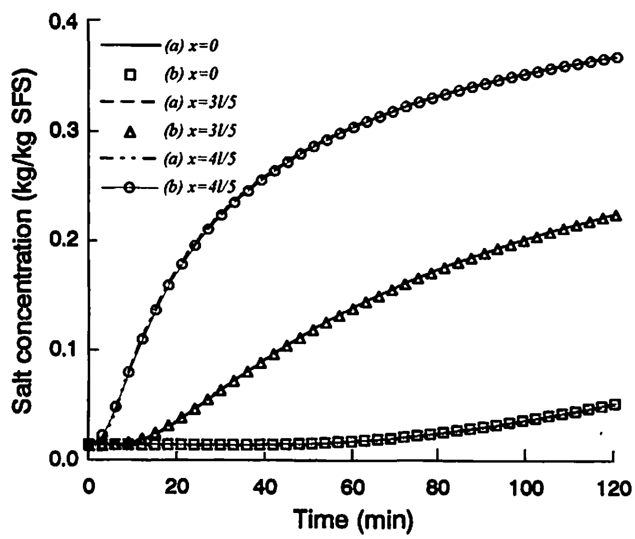

Fig. 1. Concentration predictions by FDM using different time step sizes. (a) Δt = 0.6 s; (b) Δt = 60 s.

Concentration sensitivity analysis of FDM code for time step size

The sensitivity of the FDM model to time step (Δt) was considered. Figure 1 represents the concentration sensitivity analysis for Δt. There was no apparent difference in the concentration profile for Δt less than 60 s. Therefore, this time increment was selected for further analysis.

Lack of fit test

A 'lack of fit' test was conducted to determine whether the numerical model adequately fitted the experimental salt uptake data (Neter et al. 1985). The appropriate statistic test is:

$$F^{*} = \frac{\dfrac{\sum_{j=1}^{8}\sum_{i=1}^{3}(M_{ij} - \hat{M}_j)^2 - \sum_{j=1}^{8}\sum_{i=1}^{3}(M_{ij} - \overline{M}_j)^2}{k-2}}{\dfrac{\sum_{j=1}^{8}\sum_{i=1}^{3}(M_{ij} - \overline{M}_j)^2}{n-k}} \quad (14)$$

where:

$\overline{M}_j = \frac{1}{3}\sum_{i=1}^{3} M_{ij}$ = mean salt uptake of three replications,

k = 8 since there are eight distinct times with replicates, and

n = 24 which is the total number of data points.

If $F \le F(1-\alpha; k-2, n-k)$, the numerical model is adequate;

If $F > F(1-\alpha; k-2, n-k)$, the numerical model is inadequate.

For this research, when $\alpha = 0.05$, $F(1-\alpha; k-2, n-k) = F(0.95; 6, 16) = 2.75$.

Bootstrap estimate of standard deviations

Since d_0 and d_1 are two independent parameters estimated from the FDM model rather than simple linear equations, a bootstrap method was applied to obtain their standard deviations. The bootstrap estimate of standard deviation requires no theoretical calculations and is available no matter how mathematically complicated the estimator $\hat{M} = f(t)$ may be. The method is described in detail by Efron and Tibshirani (1993). Twenty four salt uptake data were chosen randomly with replacement from 24 observations as a bootstrap sample. A random number generator was used as a subroutine to make 100 bootstrap samples (Dyck et al. 1984). Values of d_0 and d_1 that minimized MSE were obtained for each bootstrap sample. This procedure was repeated 100 times to obtain 100 values each for d_0 and d_1 from which the standard deviations were calculated.

MATERIALS and METHODS

Atlantic salmon (*Salmo salar*) were cultivated in aerated sea water at the Aquatron Laboratory (Department of Oceanography, Dalhousie University). Live fish, with masses of 2.11 ± 0.51 kg, were used in this research. The fish were starved for 2 days before capture. Upon harvest, each fish was killed by a sharp blow to the head, bled at the gills, and stored in a cooler with ice, then transported to the chill room (about 3 ± 1 °C) in a half hour. The fish were kept intact on ice for 60 to 72 h to ensure that they were in the post-rigor state (Wang et al. 1998). They were then filleted and the skin was carefully removed. The dorsal muscle was cut into 10 pieces with approximate dimensions 30 × 30 × (4 - 5) mm. The mass and thickness of each piece were recorded. Each of the ten pieces of dorsal muscle was soaked in separate beakers containing 200 mL of a 20% (w/v) sodium chloride solution in an incubator. Brining temperature was chosen as 10 °C because it is within the temperature range of 2-15 °C which was applied in the smoked salmon industry (Truelstrup Hansen et al. 1995; Sakai and Suzuki 1985). After the predetermined soaking time, one beaker was removed from the incubator and the sample was taken out. Excess solution on the sample surface was immediately removed with an absorbent tissue and the sample was stored at -35 °C. The salt content of each piece was determined later. Salt infusion tests were carried out in triplicates. The equilibrium salt uptake of the dorsal muscle was determined from two samples kept for 48 hours in the brine. The sodium chloride content and the total solids content in the dorsal muscle were determined by AOAC (1995) Official Methods 937.06 and 952.08, respectively. The initial and equilibrium salt concentrations in the dorsal muscle were 0.012 and 0.748 kg/kg SFS, respectively. The lipid content of the dorsal muscle of Atlantic salmon was determined by the procedure of Bligh and Dyer (1959). The average total solid and lipid contents in the dorsal muscle were 28.0 and 3.90%, respectively.

RESULTS and DISCUSSION

Validation of FDM model

To validate the finite difference method (FDM) computer program, the predicted concentration values were compared to the corresponding Crank's (1975) analytical solution for constant diffusivity:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left\{-D(2n+1)^2\pi^2 t / 4l^2\right\} \quad (16)$$

where M_∞ = equilibrium total salt uptake in the salmon slice [(kg/kg SFS) mm]. Since the series in Eq. 16 converged quickly, three terms were used while C_o = 0.012 kg/kg SFS, C_1 = 0.533 kg/kg SFS, l = 2.40 mm, and $D = 8.78 \times 10^{-11}$ m^2/s. For the FDM analysis, an infinitely large slab of finite thickness was discretized into 100 equally thick slices. The time step, Δt, was selected as 60 s. The salt concentration at the center node and a sub-surface node should have two extremes of salt uptake rates. Therefore, the comparison of the analytical solution with FDM predictions was based on the salt concentrations at these two nodes. As can be seen from Fig. 2, results from the FDM agree with the analytical solution. After 6 h, the difference between the analytical solution and the FDM prediction was less than 0.7 and 0.4% of the equilibrium concentration for the two nodes.

Experimental verification of FDM model

The FDM model verification involved comparison with experimental data during salting. In the FORTRAN77 program, the time step, Δt, was 60 s. The experimental salt uptake profiles of Atlantic salmon muscle were obtained by salting the 30 × 30 × (4 - 5) mm salmon slices in 20% (w/v) (= 3.4M) brine at 10°C for 2 h. The mean half thickness, l, was 2.40 mm. Close agreement was obtained between the experimental and the predicted salt uptake as shown in Fig. 3. The maximum difference between the FDM model predictions and measurements was 0.1240 kg/kg SFS. A lack of fit test was applied to test if the FDM model was adequate. The F* value (= 1.52) is less than F(0.95;6,16). Thus the FDM model adequately fitted the experimental data ($P \le 0.05$).

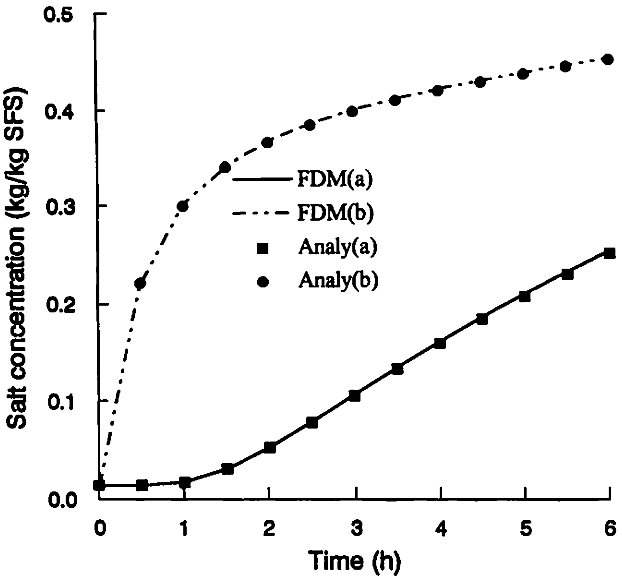

Fig. 2. Predicted concentrations from FDM and analytical solution using a constant diffusivity at two

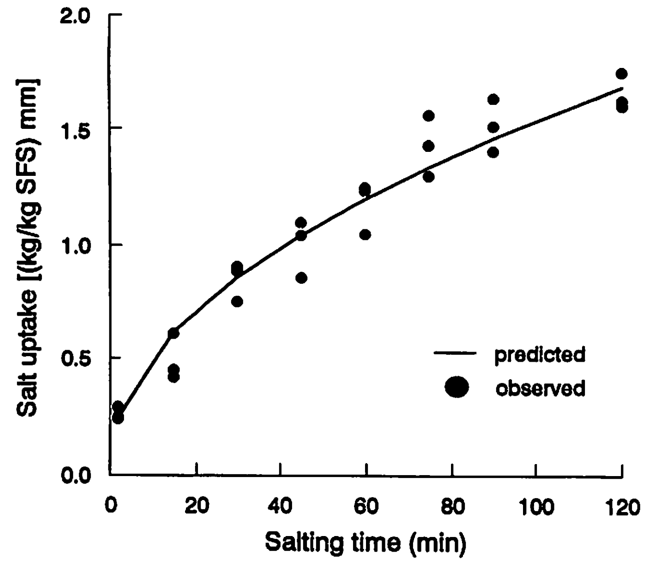

Fig. 3. Comparison of observed and FDM predicted salt uptake.

Salt diffusivity

The predicted parameters d_0 and d_l are displayed in Table I. The predicted salt diffusivity, D, was then calculated by substituting d_0 and d_l into Eq. 2. The value of D increases from 1.09 to 1.52 × 10^{-10} m^2/s when salt concentration increases from 0.012 to 0.748 kg/kg SFS. The standard deviations of d_0 and d_l calculated by the bootstrap method are also listed in Table I. The errors of the predicted d_0 and d_l were 4.6% and 9.5%, respectively. Del Valle and Nickerson (1967) found the salt diffusion coefficient in fresh swordfish muscle appeared to have a minimum value at a particular salt concentration and increased with increasing salt concentration beyond this particular salt level. They believed that there was a "barrier" after a certain concentration had been reached. This phenomenon did not appear in this research. One possible reason is that the denaturation of protein during salting took place gradually as salt concentration in the muscle increased and the cell structure was gradually degraded, resulting in less resistance to diffusion for higher salt concentration.

Del Valle and Nickerson (1967) reported the diffusion coefficient of sodium chloride in fresh swordfish muscle ranged from 0.95 to 1.45 ×10^{-10} m^2/s at 25°C, which is close to the results from this research. Although in the lower range, the predicted value of salt diffusivity in Atlantic salmon muscle agrees with the literature values of other fish species (Sakai and Suzuki 1985; Rodger et al. 1984; Sakai and Miki 1982; Peters 1971). The salt diffusivity in cod was reported as 14.1 × 10^{-10} m^2/s when salted in 4.5 M brine at 23°C (Peters 1971). Rodger et al. (1984) obtained a value for salt diffusivity of 2.44 × 10^{-10} m^2/s for herring (*Clupea harengus membranus*) muscle in 2.4 M brine at 10°C. All fish samples reported in the literature, except the swordfish (mentioned above), were frozen prior to salt diffusivity determination while only fresh samples were used in this study. Ice formation and melting during the freezing and thawing cycle might have caused damages in the cell structures, resulting in less resistance to salt diffusion into the cell, and therefore higher salt diffusivities reported in the literature (Sakai and Suzuki 1985; Rodger et al. 1984; Sakai and Miki 1982; Peters 1971).

Table I: FDM predicted salt diffusivity in Atlantic salmon muscle

d_0 (10^{-10} m^2/s)	SD_{d0} (10^{-12})	d_l (10^{-11} m^2/s)	SD_{dl} (10^{-12})	Salt diffusivity (10^{-10} m^2/s)
1.09	5.01	4.34	4.11	1.08 + 0.59C*

* C was between 0.012 and 0.748 kg/kg SFS.

Sakai and Suzuki (1985) obtained a salt diffusivity value of 6.17 × 10^{-10} m^2/s for pre-spawning ocean chum salmon muscle in 2.0 M brine at 15°C, which is about five times the values obtained in this study. Although Sakai and Suzuki (1985) did not mention the fat content of their samples, it can be as low as 1.9% in the dorsal muscle of pre-spawning chum salmon (Ando et al. 1996). Diffusion occurs primarily within the occluded solution and the marc (framework of insoluble solids) which restricts the diffusion path and strongly affects the rate. Therefore, the higher fat content in the muscle, the bigger resistance it will generate for an aqueous solute like sodium chloride to transfer (Schwartzberg and Chao 1982). The diffusivity of Cl^- in pork muscle (*semimembrasus*) at 4-5°C was about eight times that in pork back fat (0.28 × 10^{-10} m^2/s) (Fox 1980). Atlantic salmon is a kind of fatty fish. The fat content in the dorsal muscle of the Atlantic salmon used was twice that of pre-spawning ocean chum salmon used by Sakai and Suzuki (1985). The higher fat content may be

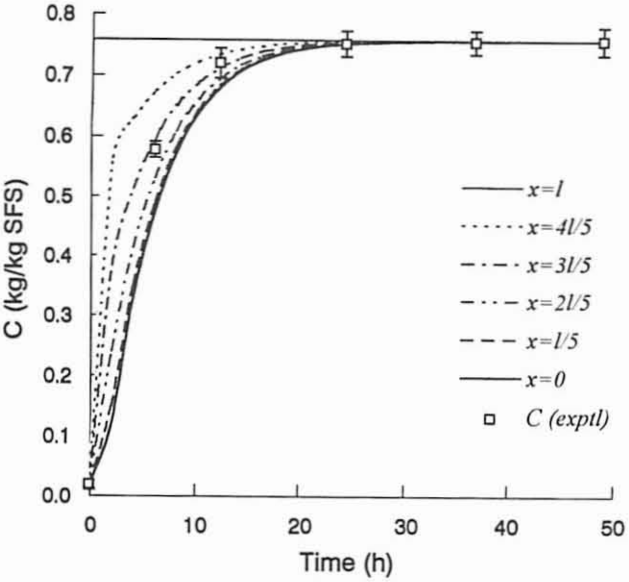

Fig. 4. Predicted local salt concentration and experimental average salt concentration in a salmon slice as a function of the salting time (l = 2.40 mm).

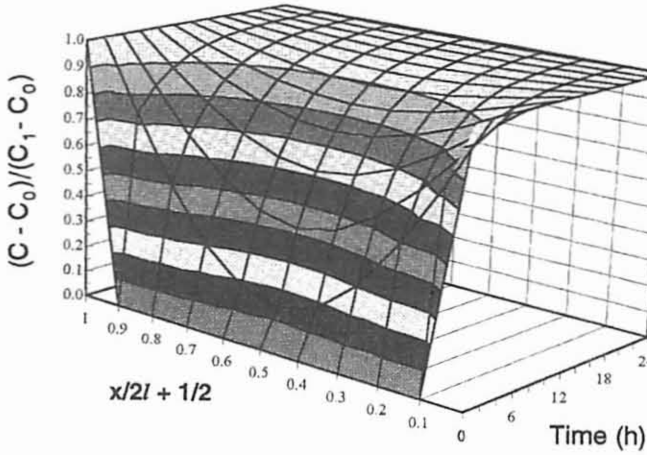

Fig. 5. FDM simulated 3-D concentration profile in a *post-rigor* Atlantic salmon slice.

another reason for the slightly smaller diffusivity in the Atlantic salmon compared with other fish species.

Salt distribution

FDM model simulation of salt diffusion in the Atlantic salmon muscle for 48 h at 10°C is shown in Fig. 4, where C_o = 0.012 kg/kg SFS, C_1 = 0.754 kg/kg SFS, l = 2.40 mm, and Δt = 60 s. The dots with standard deviations expressed as error bars are the measured mean salt concentration in the slices at the same conditions during salting in 20% (w/v) brine at 10°C. They are the means of three replicates. As can be seen, the FDM predictions agree well with the measurements. It takes 24 h for the center of the slice to reach at least 99% of its equilibrium concentration. A three dimensional graph (Fig. 5) was plotted to show the relationships among the immersion time, dimensionless space, u (= $x/2l + 1/2$), and the dimensionless concentration in fish slice, ϕ [= $(C - C_o)/(C_1 - C_o)$]. These relationships apply to a diffusion process in fish slabs where edge effect is negligible. For a salting process of post-rigor Atlantic salmon, they can be used to determine salt distribution and salt uptake as functions of salting time, given the initial and equilibrium salt concentrations. Those values can be obtained by simple experimental tests.

CONCLUSIONS

Salt diffusion in Atlantic salmon (*Salmo salar*) muscle was investigated. A mathematical model was developed to predict the salt concentration in the salmon flesh during salting in 20% (w/v) brine at 10°C by using the finite difference method. The model was first validated with analytical solutions and then verified by the experimental data. It gave good agreements with the experimental values. The lack of fit test also confirmed its adequacy. The predicted salt diffusivity (D) was found to be salt concentration dependent as in the equation: $D = (1.08 + 0.59C) \times 10^{-10}$ m²/s for salt concentration (C) from 0.012 to 0.748 kg/kg SFS. The values of salt diffusivity were between 1.09 and 1.52×10^{-10} m²/s. The standard deviations of the two parameters d_o and d_1 calculated by the bootstrap method were less than 5% and 10% of the predicted parameters d_o and d_1, respectively. The dimensionless diffusivity is linearly related to dimensionless concentration.

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NOMENCLATURE

ϕ	= dimensionless salt concentration
τ	= dimensionless time
Δt	= time step size (s)
C	= concentration of salt (kg/kg SFS)
C_l	= equilibrium C (kg/kg SFS)
$\tilde{D}$	= dimensionless salt diffusivity
D	= salt diffusivity (m^2/s)
d'	= d_o/d_l
d_o, d_l	= diffusion parameters (m^2/s)
F*	= F value for a specific model in F test
FDM	= finite difference method
k, n	= integers
l	= half thickness of the fish slice (mm)
$\hat{M}$	= predicted salt uptake [(kg/kg SFS) mm]
$\overline{M}$	= mean salt uptake [(kg/kg SFS) mm]
M	= experimental salt uptake [(kg/kg SFS) mm]
MSE	= mean sum of squares of errors
SD_{d0}	= standard deviation of d_0
SD_{dl}	= standard deviation of d_l
SFS	= salt free solids (kg)
t	= salting time (s)
u	= dimensionless space coordinate
x	= space coordinate (m)

Subscript

∞	= corresponding to infinite time
0	= initial
i, j	= integers
t	= corresponding to time t