4.2. EFFECTIVE WATER DIFFUSIVITY

4.2.1. Method 1: experiments developed in a drying tunnel

The raw meat used in LTU had the following composition: initial moisture content of 72.7 ±1.64 %, fat content of 3.28 ±1.12 % and protein content of 22.73 ±1.15 %.

The experimental drying curves can be observed in Figure 4.2.1. The drying curves are used to fit different diffusion models, which boundary conditions effect, the water contents range effect and the dependence on water contents and shrinkage are considered.

4.2.1.1. Effect of boundary conditions on D_e

In this section, the experimental drying curves were used to fit two different diffusion models. The first model considered boundary conditions (B.C.) type I, and the second model considered B.C. type II. The water content and shrinkage dependence were neglected in both models.

To be able to consider B.C. type II, the external mass transfer coefficient (k_y) was necessary. k_y was previously experimentally determined in our laboratory dryer. The value obtained was 0.0185 kg/m^{2}s. However, its determination is a difficult task and it may involve several sources of error.

Using the model with B.C. type II, k_y and D_e were considered constant along the process, but Bi changed during the process due to the sorption isotherm slope change, which was considered by the Bi calculation (section 3.2.1.3). It was observed that Bi changed very fast at the first stages of the process. At the begining of the drying process, Bi was 5.9, and at 150 minutes Bi reached values above 100. This period of time represents a low proportion in front of the time that takes the whole process (over 3000 minutes).

It was written previously (section 1.6.1.2) that when Bi>100 the drying process is controlled by the internal mass transfer (D_e), and therefore, the external mass transfer (k_y) can be neglected (Welty, 1994). In such case, B.C. type I can be used.

By applying both models (B.C. I and B.C. II), it is observed that the global fitting obtained is similar for both models. The sum of squared residues (SSR) is slightly smaller in B.C. type I. This result is in agreement with the result obtained from the Bi analysis, in which most of the process (95%) is controled by De, and therefore B.C. I can be used.

Figure 4.2.1 shows the fittin of the different models for one of the samples. The evolution of the calculated moisture profiles inside of the meat during the process are shown in the uper right corner of the figure. The profile at every fifth experimental point is plotted.

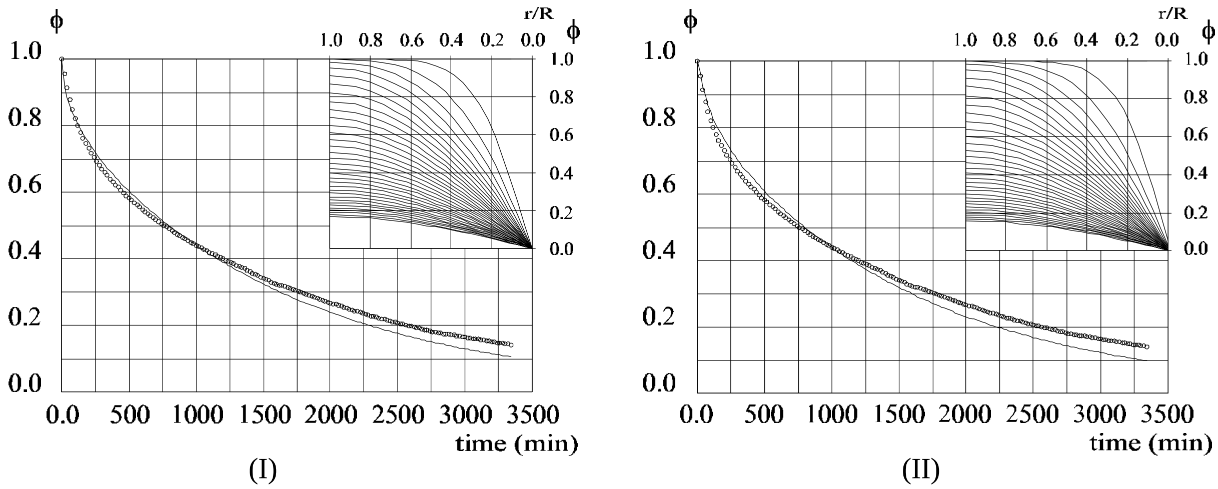
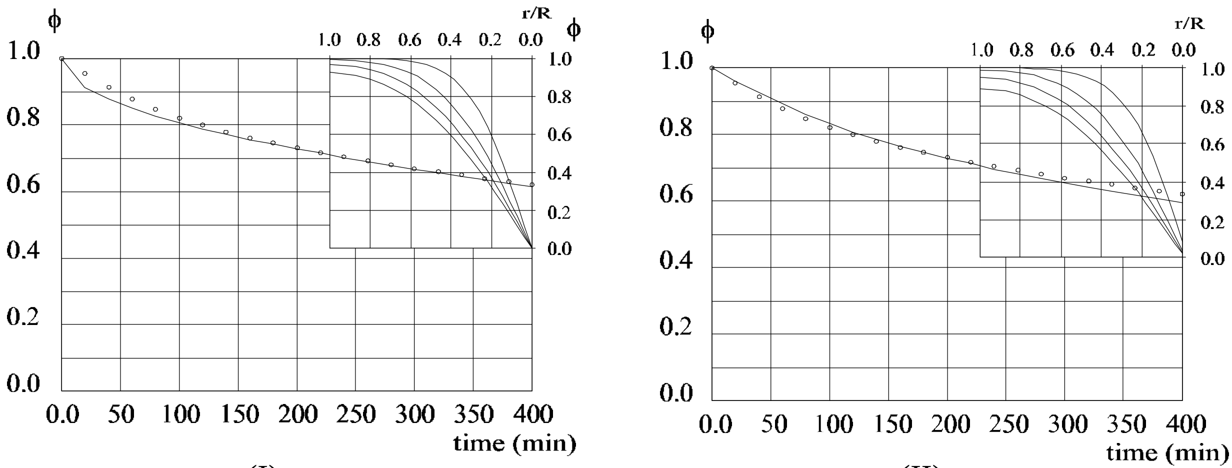


Figure 4.2.1 Drying curve of meat at 26.9ºC and 20.7 % R.H. ϕ: dimensionless moisture content. r/R dimensionless local distance. (◦) Experimental points. (—) Calculated points. (I) Model B.C. type I (SSR=0.0038). (II) Model B.C. type II (SSR=0.0058).

In the final part of the drying process, the loss of water is overestimated in both models. This could be due to the fact that D_e is considered constant in the whole process. As stated before, the meat has big structural changes during its drying process, and they are not considered in the model. Only one effective diffusion coeficient is obtained, which can have difficulties to explain the water transfer in all the process.

Therefore, being aware of this structural changes, the model has been applied to the initial part of the drying curve (meat from 2.87 to 1.80 kg H_2O/kg d.m.), in which the structural changes of the meat are considered to be smaller (Figure 4.2.2).



(I) (II)

Figure 4.2.2 Drying curve of meat at 26.9ºC and 20.7 % R.H. ϕ: dimensionless moisture content. r/R dimensionless local distance. (◦) Experimental points. (—) Calculated points. (I) Model B.C. type I (SSR=0.0014). (II) Model B.C. type II (SSR=0.0012).

In this case, the calulated Bi is 4.6 at the begining of the process, and it takes about 213 minutes to achive a value of 100. This period of time represents an important proportion in front of the time that takes the whole process (400 min.) (Figure 4.2.3). Therefore, in this case it would be better to use the B.C. type II, because it takes into account the external mass transfer.

The variation of the Bi number obtained in these experiments is in agreement with the analysis of Bi got in other studies. For instance, Rovedo *et al.* (1998) also showed the variation of Bi along the drying process of potato slabs.

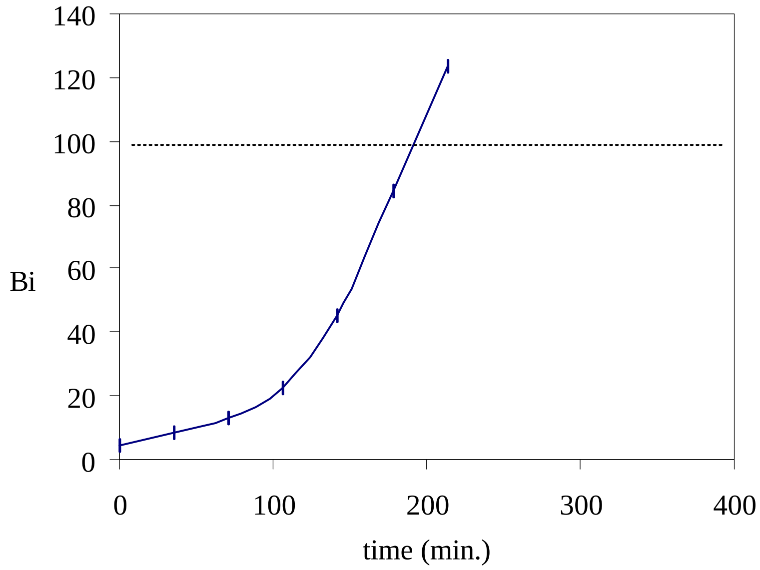


Figure 4.2.3 Evolution of Bi number for the drying process developed in LTU.

The averaged results of D_e obtained from the different models used are shown in Table 4.2.1.

Table 4.2.1 D_e of meat at 26ºC considering different type of B.C. and different range of water content.

Range of water content kg H_2O/kg d.m.	D_e B.C. Type I (10^{-11} m^2/s)	D_e B.C. Type II (10^{-11} m^2/s)
2.87 - 1.80	7.62 ±0.94	10.83 ±1.44
2.87 - 0.37	6.34 ±0.49	7.00 ±0.00

No significative differences are shown in the values of D_e obtained using the first part of drying curve (from 2.87 to 1.80 kg H_2O/kg d.m.) or the whole drying curve (from 2.87 to 0.37 kg H_2O/kg d.m.) when type I B.C. is used. On the contrary, the values of D_e obtained using the first part of drying curve (from 2.87 to 1.80 kg H_2O/kg d.m.) or the whole drying curve (from 2.87 to 0.37 kg H_2O/kg d.m.) are significatively different when the type II B.C. is used.

From these results, it is possible to observe that the modeling using type I or type II B.C. give similar results when the reduction of water content during drying is high. On the contrary, if only small amounts of water content of the meat are reduced, the model with type II B.C. should be used. Using type II B.C. the D_e value obtained is underestimated because it does not consider the effect of k_y. In the range of water content considered in this experiment, k_y should be taken into account because 53% of the drying process is controlled by the external and internal mass transfer.

When B.C. type II are used, the differences of D_e obtained in both ranges of water content, shows that D_e decreases along the drying process. This may be due to the effect of reduction of water content or to structural changes.

Since the values obtained are different using different ranges of water content in the analysis, in the further section, the dependence of water content and shrinkage will be considered.

4.2.1.2. Effect of water content dependence and shrinkage on D_e

The effect of water content dependence and shrinkage is considered by using the model developed in section 3.2.1.4. From the drying curve, the average water content of the meat at each step of the drying process is obtained. As stated previously (section 3.2.1.3), the shrinkage of the meat sample is determined by computer image analysis, from which, the evolution of the sample area during drying is obtained (e.g. Figure 4.2.4). The squared of the area was plotted against moisture content, from which a linear relationship between shrinkage and water content is obtained. The same analysis is made for each one of the meat samples.

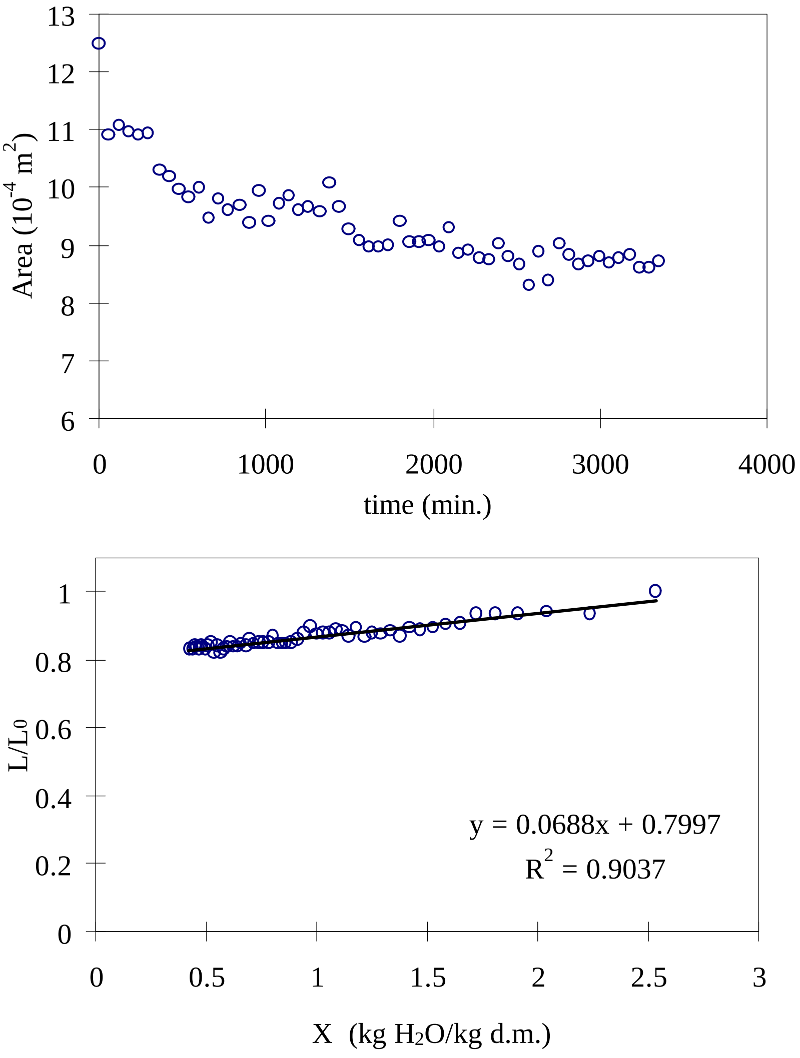


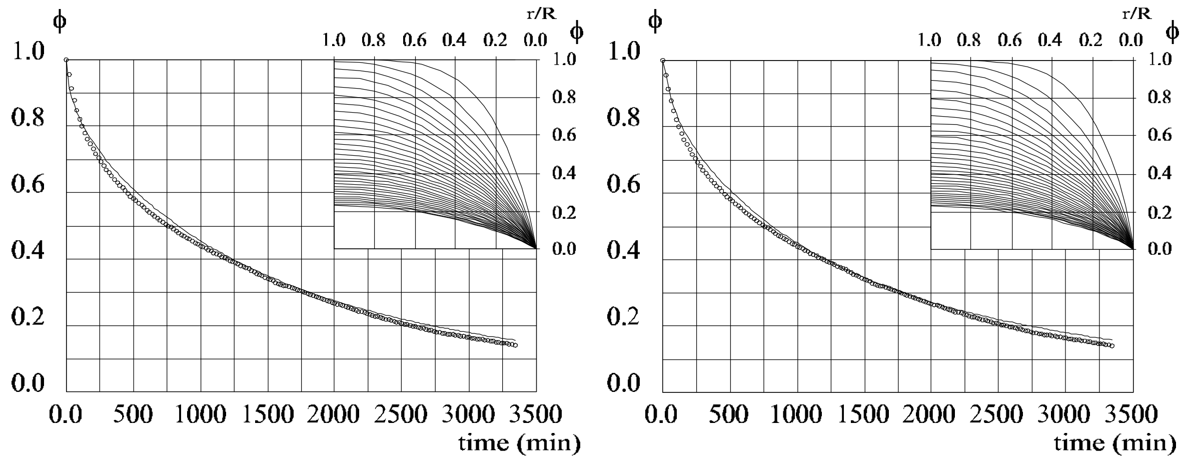
Figure 4.2.4 Shrinkage of a meat sample at 26.9ºC and 20.7% R.H. (◦) Experimental points. (—) Calculated curve.

From this curves the empirical shrinking coefficient (s_1) is calculated (equation 3.2.28). The averaged value obtained from the meat samples is s_1=0.157, which is used in the model considering shrinkage.

The equation (4.2.1) is used to obtain the D_e dependending on water content. The parameters d_1 and d_2, obtained after numerical calculations (section 3.2.1) of unsalted meat samples at 26ºC, are shown in Table 4.2.2. The effect of B.C. and shrinkage are also considered where the range of drying is from 2.87 to 0.37 kg H_2O/kg d.m.

$$D_e(X)=d_1X^{d_2} \qquad 4.2.1$$

The obtained parametes (d_1 and d_2) of equation (4.2.1) come from minimasing SSR of all the fitting curves at the same time. The model considering the water content dependence fits in very well in all the drying curves (e.g. Figure 4.2.5) independently of the B.C. used.



(I) (II)

Figure 4.2.5 Drying curve of meat at 26.9ºC and 20.7 % R.H. considering the water content dependence and neglecting shrinkage effects. ϕ: dimensionless moisture content. r/R dimensionless local distance. (∘) Experimental points. (—) Calculated points. (I) Model B.C. type I. (II) Model B.C. type II.

When the model considering shrinkage is used, the accuracy of the fitting is lower. As the problem comes up when including the shrinkage in the model, the first to think would be that the obtained shrinking coefficients are not the proper ones, even when the individual s_1 are used instead of the average.

The fitting of these models to the experimental curve is shown in Figure 4.2.6 for all the samples. Even though the accuracy of the fit is not the best one, the parameters d_1 and d_2 of equation (4.2.1) are considered to be comparable between the models (Table 4.2.2).

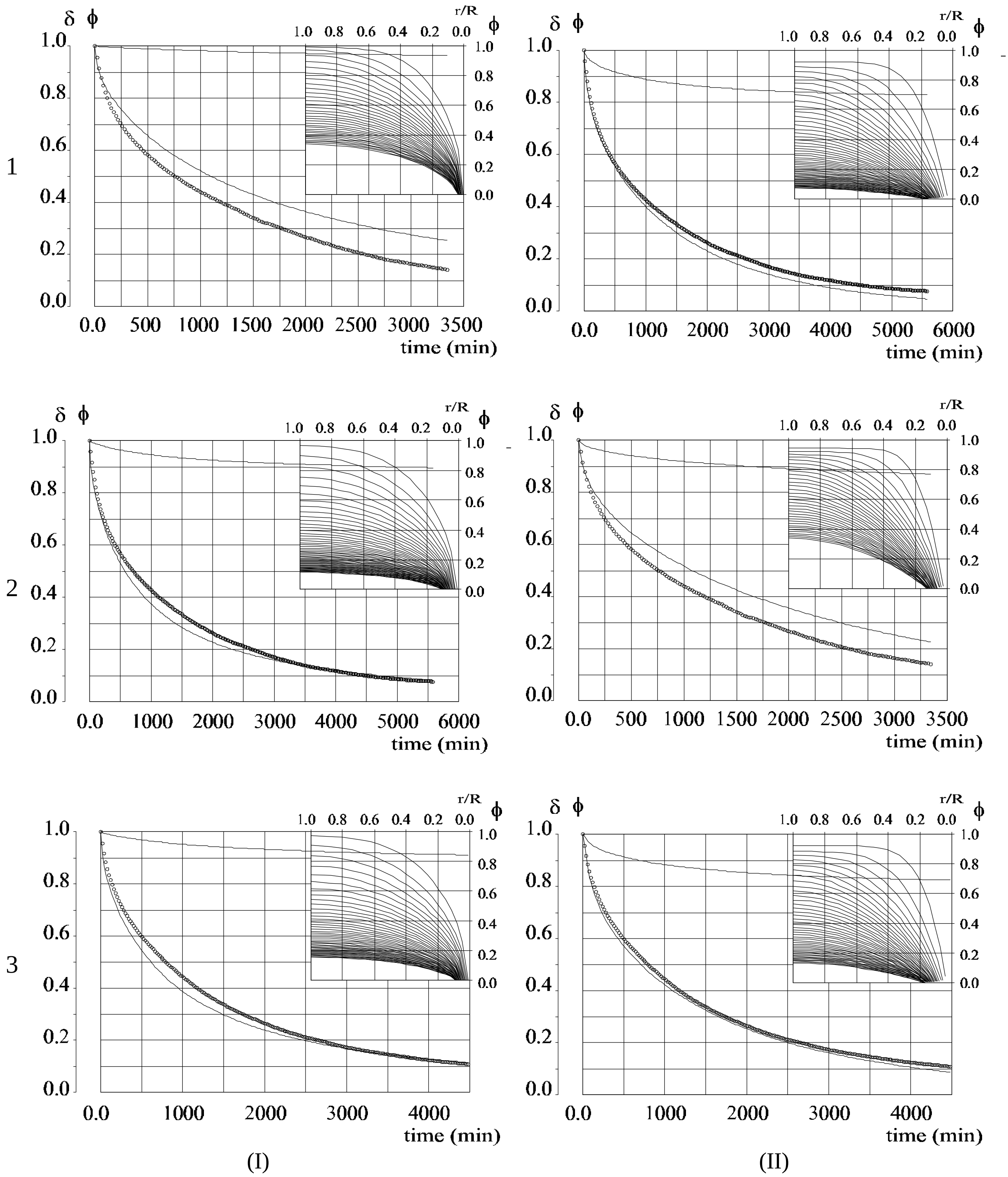


Figure 4.2.6 Drying curve of meat at 26.9ºC and 20.7 % R.H. considering the water content dependence and shrinkage (using the average of s_1). ϕ: Dimensionless water content. δ: dimensionless thickness. r/R dimensionless local distance. (◦) Experimental points. (—) Calculated points. (I) Model B.C. type I. (II) Model B.C. type II. Meat sample number: 1,2,3.

Table 4.2.2 Parameters of equation $D_e(X) = d_1 \cdot X^{d2}$ for meat at 26ºC obtained by using different models, in which the water content dependence is considered, and also the shrinkage and different type of B.C. may be considered.

Parameters	D_e B.C. Type I $\cdot 10^{-11}$ m^2/s	D_e B.C. Type II $\cdot 10^{-11}$ m^2/s	D_e B.C. Type I $\cdot 10^{-11}$ m^2/s	D_e B.C. Type II $\cdot 10^{-11}$ m^2/s
	No Shrinkage		With Shrinkage	
d_1	6.912	7.326	4.837	3.028
d_2	0.416	0.522	0.964	0.257
SSR	0.0028	0.0029	0.0189	0.0132

The variety of results obtained using the different mathematical models are easier observed in Figure 4.2.7.

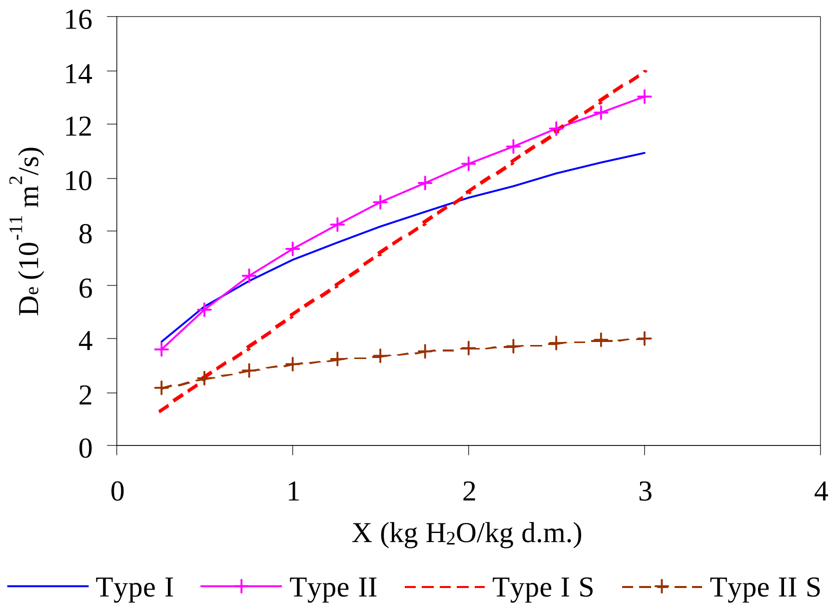


Figure 4.2.7 Results of D_e using different methods of calculation. By considering different water content dependence, type of B.C. (Type I, Type II) and the effect of shrinkage (S).

Non-shrinking models have a better fit that the shrinking ones. The models considering shrinkage give D_e values generaly lower than those which do not consider shrinkage.

When no shrinkage is considered, the model applying type I B.C. gives D_e lower at high water contents than if type II B.C. are considered. When the water content decreases, the D_e

value obtained in both models is similar. These results are in agreement wiht the results observed in section (4.2.1.1.).

When shrinkage is considered, the model applying type I B.C. gives D_e values similar to the previous ones. Using type II B.C., the D_e seems not to depend too much on water content. This results do not agree with the previous ones. This effect could be due to some error on the parameters estimation used in B.C. type II (ρ, s_1).

4.2.2. Method 2: experiments developed in a drying-box

As described previously (section 3.2.2), the methodology used in this laboratory was different than the methods developed in LTU. The process of drying was much longer. In this case, the effect of air relative humidity on the methodology is evaluated. The mathematical model used is a series of development, from which, the use of different number of terms has been studied. The effect of sample length has also been considered. Finaly, the D_e at different salt contents in meat, drying temperature, fiber direction and the ham muscle is determined.

It is assumed no external mass transfer resistance. If this assumption is be false, D_e will be under estimated. The water content dependence and shrinkage have not been considered in the mathematical model. The meat samples are generally dryed until a reduction of 40% of its initial weight. The water content at equilibrium is obtained from the meat sorption isotherms.

4.2.3. Air relative humidity used in the drying-box method

The drying process with this methodology is a very slow process. This means that during the drying period, other secondary aspect may become of interest. For instance, as it was mentioned before (section 1.6.3.8), the formation of a crust on the surface or the growing of micro-organisms may become important. These aspects may be controled by the relative humidity (R.H.) of the air. High R.H. allows the growth of microorganisms at the surface, which can affect the equilibrium water content on the meat and may also accelerate structural changes of the meat due to the proteolysis. Low R.H. may lead to crust formation.

From the experiments, it is possible to withdraw that the best experience is developed at R.H. of 80%., while at 90% R.H. the growth of microorganisms is more intens. At R.H. of 60 % the crust formation developes very soon. This proves that drying curves are not very reliable. R.H. of 70% can be difficult to model since the sorption isotherms of salted meat has a break point at a_w of 0.75, and some times this break point can be found in experimental points at a_w of 0.70 (section 4.1).

4.2.4. Study of the D_e stimation using different number of terms on the analytical solution

The analytical solution of 2nd Fick's law takes the form of a series development (equation 3.2.22). In long periods of time only the leading term in the series expansion is needed. At shorter time periods more terms need to be considered. The error made by neglecting terms can be calculated by the equation (1.6.16). Figure 4.2.8 also shows the evolution of D_e considering differents terms of the equation (3.2.22).

From this figure it can be observed that, when increasing the number of terms over 5, there is no important change on the D_e values obtained. However, using only one term, the obtained D_e is two times bigger.

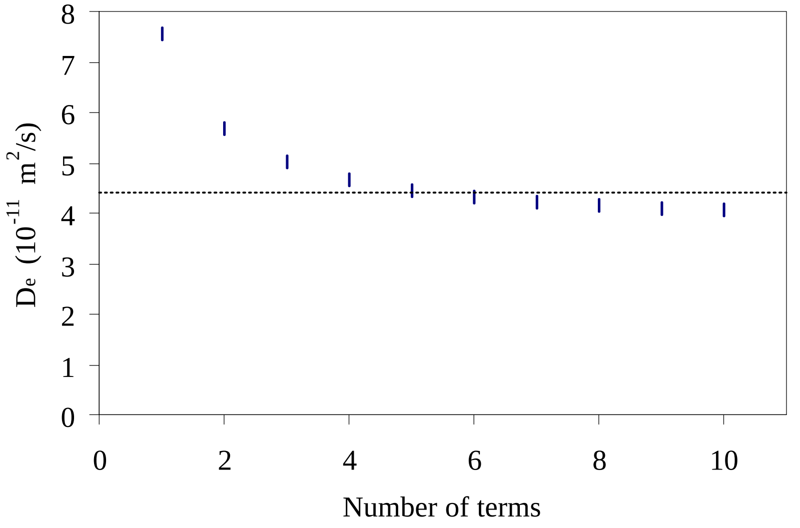


Figure 4.2.8 Evolution of D_e considering different number of terms of the Fick's law solution in an infinite meat slab at 13ºC, 0.09 kg NaCl/kg d.m.

The fitted curves to the experimental points by using one term of the series and then using 5 are shown in Figure 4.2.9. It is observed that the quality of fit in the drying curve using 5 terms (SSR = 0.0006) is better than using 1 term (SSR = 0.029) in the solution of series development (Figure 4.2.9). In our study 5 terms were considered to be necessary to determine the D_e in meat using this analytical solution.

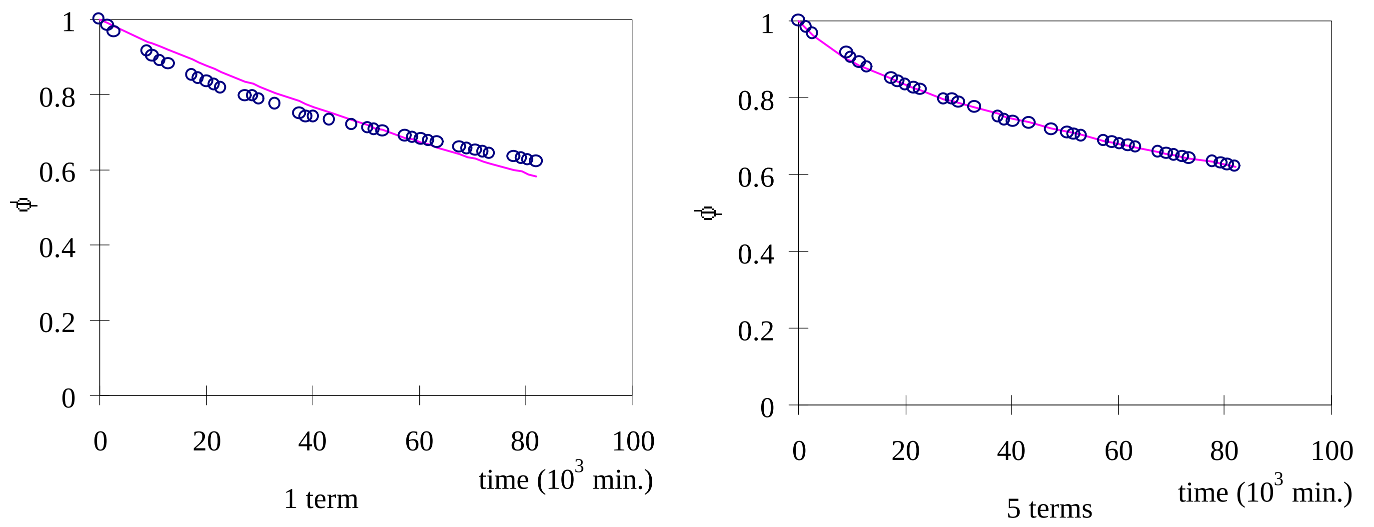


Figure 4.2.9 Drying of salted meat (0.09% kg NaCl/kg d.m.) at 13ºC and 80% R.H. The number of terms used for the fitting model are 1 and 5 terms.

4.2.5. Effect of sample length on the estimated D_e value

Experience 1 (Table 3.2.3) was developed to observe whether sample length could have any effect on D_e estimation or not. The sample length was measured by triplicate, and the standard deviation obtained from the experimental measurements were 0.003 m in samples with high length, and 0.002 m in samples with low length.

Figure 4.2.10 shows that the model applied is sensible to the sample length. At a higher sample length the D_e values obtained are higher. Increasing the sample length in one centimeter, the D_e value increases in $0.3 \cdot 10^{-11}$ m^2/s in meat at 0.09 kg NaCl/ kg d.m. and $0.4 \cdot 10^{-11}$ m^2/s at higher NaCl contents.

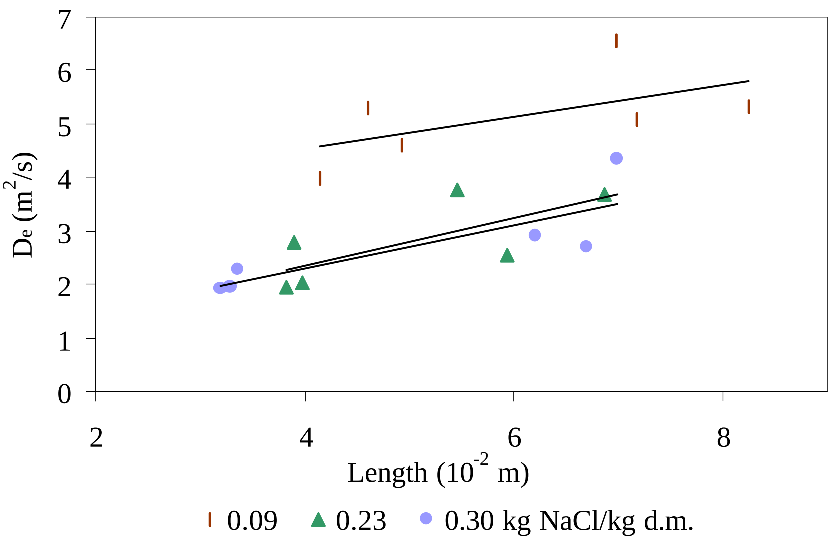


Figure 4.2.10 D_e values obtained for salted meat at 13ºC with different sample length.

Rotstein *et al*. (1974) studied the effects of sample shape and size on the diffusivity constant. They concluded that the cross-sectional area should be incorporated into an analytical model to describe diffusivity. Their study showed that, in particular, the effect of shape had to be taken into account after 100 minutes of drying.

The relationship between length and D_e is significative. The D_e increases $0.36 \cdot 10^{-11}$ m^2/s in each length cm. The major length differences are between the samples of muscle *Gluteus medius* and those of muscle *Biceps femoris*. Nevertheless, the difference between the mean length of the samples of these muscles is lower than 2.9 cm. This means that the differences of D_e due to the variation of sample length will be lower than $1.04 \cdot 10^{-11}$ m^2/s. Although it is important to use samples of similar length to the determine the D_e by the method used in this study.

From the theoretical point of view, the estimated D_e value should not be affected by sample length. The results obtained, where D_e is slightly dependent of the sample length, can be explained by the fact that the model is very simple and do not consider many factors that may effect D_e. For instance, water content, shrinkage, k_y among others are not taken in consideration.

4.2.6. Remarks on the drying-box methodology

About slow drying methods (like the one used in drying dry-cured ham, the following factors should be considered:

- To determine the D_e by using this method, the best air relative humidity range used is around 80%, because at other air relative humidities, microbiological spoilage or crust formation may affect the D_e determination.

- The samples used to determine the D_e should have similar length because D_e is affected by sample length, which can be due to the fact that this method do not takes into account the effect of water content, shrinkage and others factors.

- To determine the D_e from the drying curve, several terms of the 2^{nd} Fick's law analytical solution must be considered, because, the D_e value obtained is overestimated about 50% using only one term.

4.2.7. Effect of NaCl content and temperature on D_e

This experiment (experience 2 of Table 3.2.3) allowed to determine the effect of NaCl content and temperature on D_e of meat. The NaCl content of samples immersed in 2, 5 and 8% NaCl solutions was 8.7 ±1.2, 22.8 ±2.1, and 30.1 ±2.3 kg NaCl/ kg d.m. respectively.

The average water content of samples after salting was 4.71 ±0.64 kg H_2O/kg d.m., and at the end of drying was 2.87 ±0.48 kg H_2O/kg d.m.

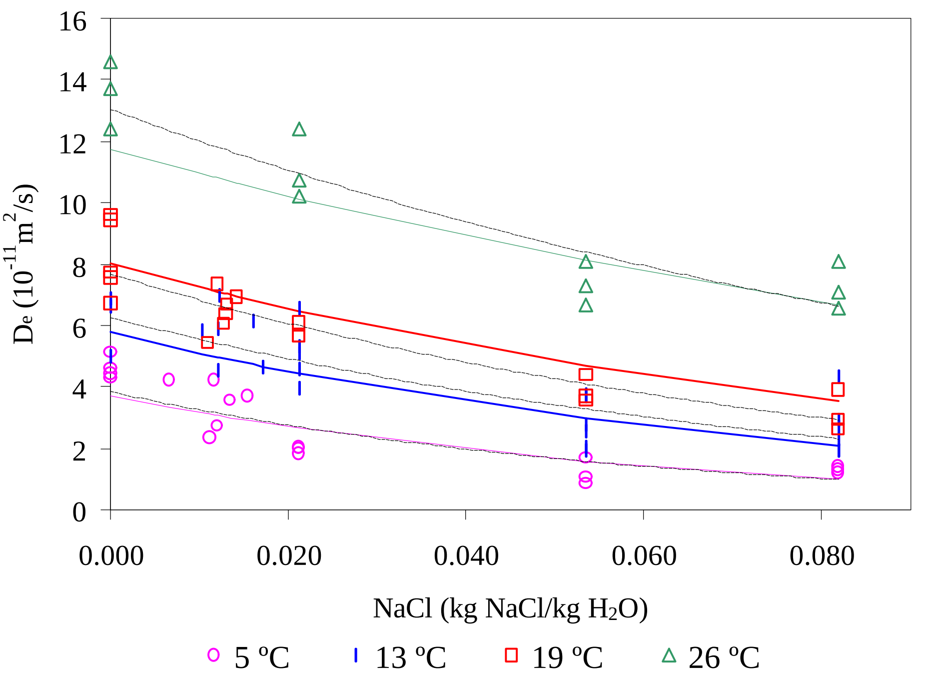


Figure 4.2.11 D_e in meat at different NaCl content (w.b.) and temperature. (●, ◆, ■ or ▲): Experimental points. (——) Calculated curve from equation 4.2.2. (---) Calculated curve from equation 4.2.3.

Figure 4.2.11 shows the results of D_e obtained for different temperature and NaCl content. The NaCl is expressed in water basis (w.b.). There was an effect of temperature and NaCl content on D_e . As temperature increases, the D_e also increases, although the D_e at 13ºC and D_e at 19ºC is not significantly different ($P<0.05$). At 5ºC, the D_e in different NaCl contents is not significantly different either. At higher temperatures, as NaCl content increases the D_e decreases. The interaction between NaCl content and temperature could be due to a different degree of fat melting as shown by DSC (Roos, 1992).

Palmia *et al.* (1993) reported values of $1.8x10^{-11}$ m^2/s at 20ºC and 8 %NaCl(dm) which are smaller than the D_e values obtained in our study. It could be due to the lower water content of the samples used by these authors (0.4-1.0 kg H_2O/kg dm). This agrees with other studies which show the negative correlation between the D_e and the water content (Okos *et al.*, 1992).

The higher D_e values obtained by Gou *et al*. (1996): $9.28x10^{-11}$ m^2/s at 13ºC and 0.30 kg NaCl/ kg d.m. could be due to the fact that these authors used only one term of the series development of Fick's solution equation. Figure 4.2.8 shows the different results obtained using one or several terms in the same drying curve.

The data was fitted to an exponential type equation at each temperature (equation 4.2.2).

$$D_e = a \cdot \exp(b \cdot [NaCl]_{wb}) \qquad 4.2.2$$

The coefficients of this exponential equations have been plotted against the temperature (Figure 4.2.12) from which a relationship of D_e depending on NaCl content and temperature is obtained (equation4.2.3).

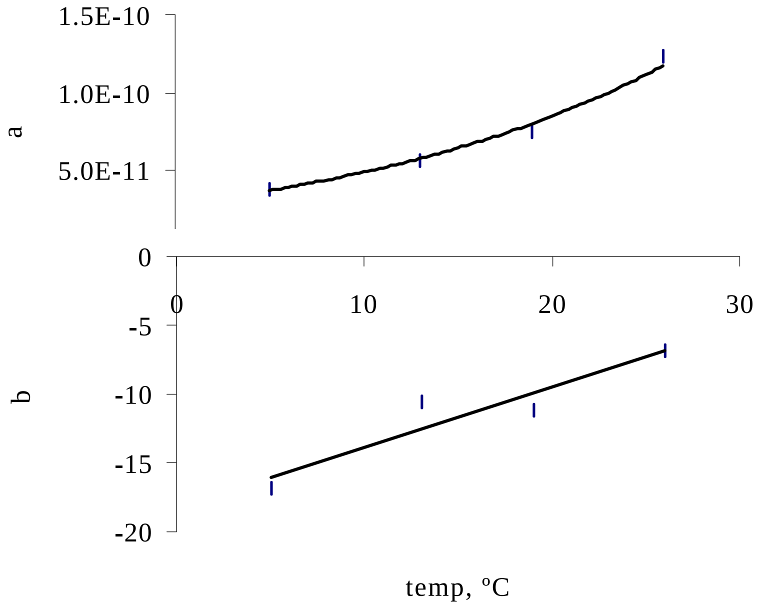


Figure 4.2.12 Relationship between coefficient of NaCl exponential equation and temperature

$$D_e = 2.83 \cdot 10^{-11} \cdot \exp(5.47 \cdot 10^{-2} \cdot t) \cdot \exp([NaCl]_{wb} \cdot (0.435 \cdot t - 18.2)) \quad 4.2.3$$

The accuracy of the fit of this equation is R^2 = 0.968. This is a phenomenological equation without any physical meaning.

The temperature dependence of the water diffusion coefficient can also be described by the Arrhenius equation (equation 1.6.28).

$$D_e = D_o \exp\left(-\frac{E_a}{RT}\right)$$

When plotting experimental results, according to equation (1.6.28), a straight line was adjusted (Figure 3.2.13). The energies of activation (E_a) are calculated from the slopes (Table 3.2.3).

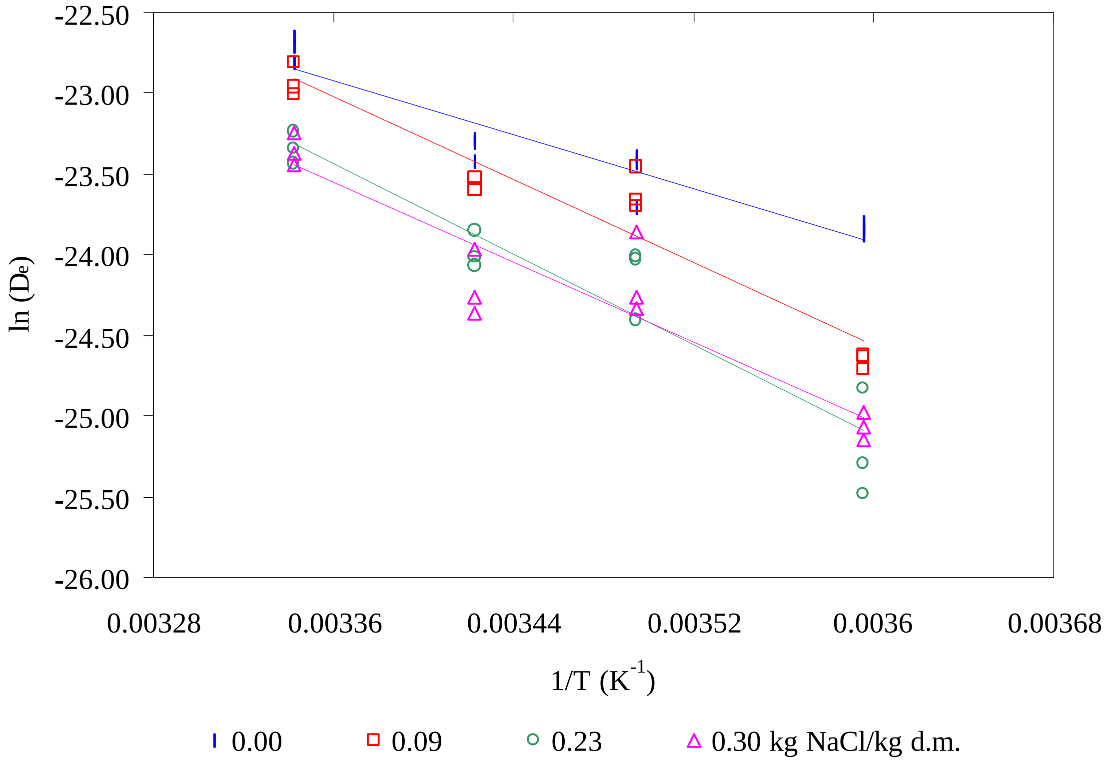


Figure 4.2.13. Ln (D_e) versus 1/T.

Okos *et al*. (1992) stated that E_a may depend on the amount of solutes in water because when this amount increases the proportion of free water molecules available for water diffusion decreases. The E_a of raw meat is significantly different that the one obtained in salted meat, however, in salted meat, the E_a obtained at different NaCl content are not significantly affected within the range of NaCl contents studied in salted meat. The E_a values obtained in this study are slightly higher than those obtained by Palmia *et al*. (1993) in non-salted pork meat (22-28 kJ/mol).

Table 4.2.3. Energy of activation (E_a)

	0.00 kg NaCl/kg d.m.	0.09 kg NaCl/kg d.m.	0.23 kg NaCl/kg d.m.	0.30 kg NaCl/kg d.m.
E_a (J/mol)	35105	53467	58654	51782
D_o (m^2/s)	0.0002	0.2432	1.3091	0.0727
R^2	0.892	0.910	0.892	0.860

4.2.8. Effect of meat fiber direction on D_e

Fiber direction on D_e has been studied at 5ºC. The meat used for the experiment had 0.75 ±.0.07 kg protein/kg d.m. and 0.07 ±.0.01 kg fat/kg d.m.

After salting, the average water content of samples was 2.79 ±.0.20 kg H_2O/kg d.m. and the NaCl content was 0.086 ±0.015 kg NaCl/ kg d.m. At the end the average water content was 1.26 ±0.16 kg H_2O/kg d.m.

The results obtained (Figure 4.2.14) show the results of D_e depending on the fiber direction of meat. When the average of D_e values obtained considering the diffusion of water along the meat fibers (L) are compared with the D_e values obtained considering the diffusion of water across the meat fibers (T), it is possible to observe that D_e in L fiber direction is slightly higher ($D_{e\,L}$= $3.71 \cdot 10^{-11}$ m^2/s, and $D_{e\,T}$= $2.65 \cdot 10^{-11}$ m^2/s). These differences can be due to the fact that the samples used to determine the D_e in L fiber direction are 6.7 cm length, while the samples used to determine the D_e in T fiber direction are 3.5 cm length. But afterwards, it was found that, as it was shown in section 3.2.5, the differences in length could explain the different results of D_e obtained, which would correspond to a difference of $1.15 \cdot 10^{-11}$ m^2/s between them. Therefore, the differences can be atributed only to fiber directions. When TC is considered, the D_e values obtained show a higher variability. It can be due to the non-uniformity of the connective tissue, and also because it can have a layer of fat of different thickness included, which also can affect the diffusion of water. The D_e

average obtained is not significatively different to the ones obtained for L and T fiber direction.

From the results obtained in this section it is possible to conclude that the meat behaves as an isotropic product. This results are in agreement with the ones obtained by Ruiz-Cabrera (1999) in non-salted meat. On the contrary, Godsalve (1977) and Thorvaldsson and Skjöldbrand (1996) reported that the transport of water in beef meat perpendicular to meat fibers was slower than the water diffusion parallel to meat fibers. In the studey of Thorvaldsson and Skjöldbrand (1996), the mass transport of water is about 20-25% slower in the direction perpendicular to the meat fibers. We must be aware that our study was developed at 13ºC in salted meat, while the ones reported by those authors were done during heating process from 10 to 100 ºC in non-salted meat.

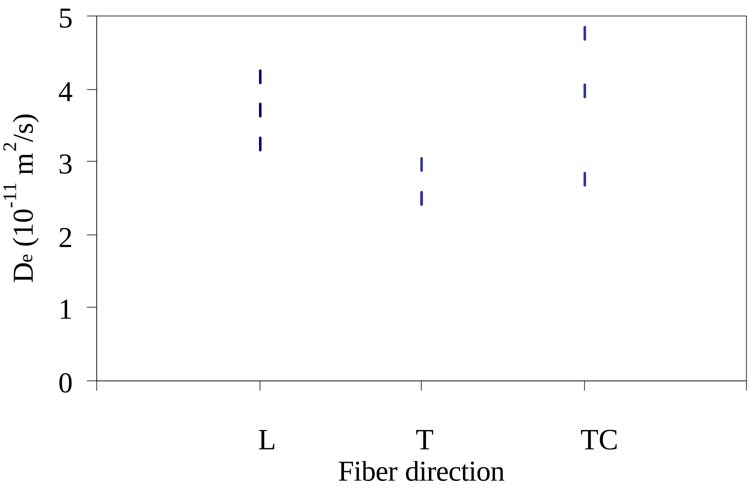


Figure 4.2.14 D_e obtained at different fiber direction. L: D_e along the fibers. T: D_e across the fibers. TC: D_e across the fibers and with connective tissue on the surface.

4.2.9. Effect of muscle on D_e

The D_e in the different muscles of the ham has been evaluated at 5ºC considering the diffusion of water along the meat fibers (Figure 4.2.15). The muscles selected were the most important within the ham: *Biceps femoris* (BF), *Semimembranosus* (SM), *Semitendinosus* (ST). The meat used for the experiment had 0.80 ±0.07 kg Protein/kg d.m. and 0.08 ±0.04 kg fat/kg d.m. After salting the NaCl content of meat was 0.078 ±0.023 kg NaCl/ kg d.m.

The average water content of samples after salting was 2.99 ±0.31 kg H_2O/kg d.m., and at the end of drying was 1.35 ±0.25 kg H_2O/kg d.m.

The results obtained for this muscles are compared to the ones obtained for *Gluteus medius* (GM) in the previous experiences. The statistical analysis show that there is no significative differences when the effect of muscle is considered. The D_e obtained is into a quite narrow range of values (from 2 to $4 \cdot 10^{-11}$ m^2/s).

From this results it is possible to conclude that the ham can be modeled without distinction of muscles. This result will make easier the modeling of dry-cured ham.

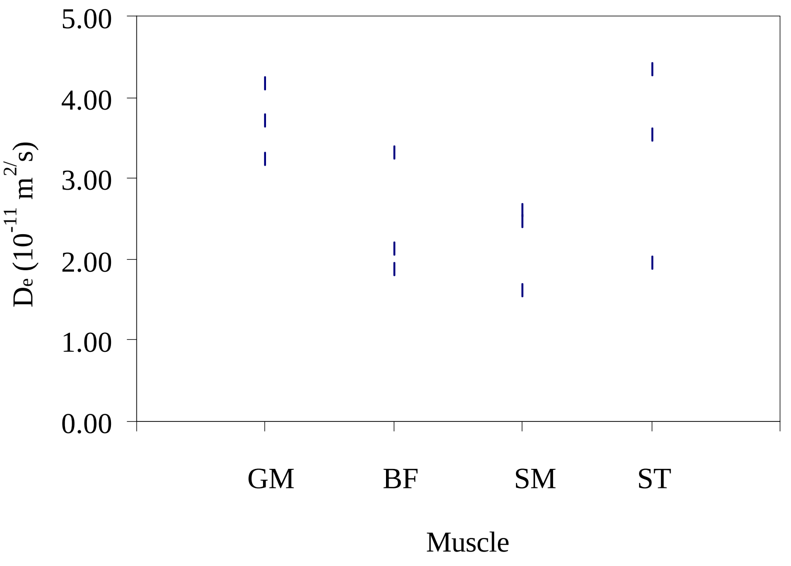


Figure 4.2.15 D_e obtained at different muscles of the ham. GM: *Gluteus medius*. BF: *Biceps femoris*. SM: *Semimembranosus*. ST: *Semitendinosus*.

4.2.10. Effect of DFD muscle on D_e

One of the experiments was designed to obtain the effect of meats with high pH (DFD meat) on D_e. The drying experiment was held at 13ºC. The NaCl content of samples immersed in 2% NaCl solutions were 0.09 ±0.06 NaCl/ kg d.m.

The average water content of samples after salting was 4.49 ±0.55 kg H_2O/kg d.m., and at the end of drying was 2.38 ±0.46 kg H_2O/kg d.m.

The results of D_e are shown in Figure 4.2.16. The average obtained for DFD meat is significatively lower ($2.58\cdot10^{-11}$ m^2/s) than the one obtained in normal meat ($5.14\cdot10^{-11}$ m^2/s).

From this result it can be concluded that pH in meat has some effect on D_e, which should be considered in the modeling of meat. These results shows the same tendency as the one obtained by the water holding capacity (section 1.3.3.2.2)

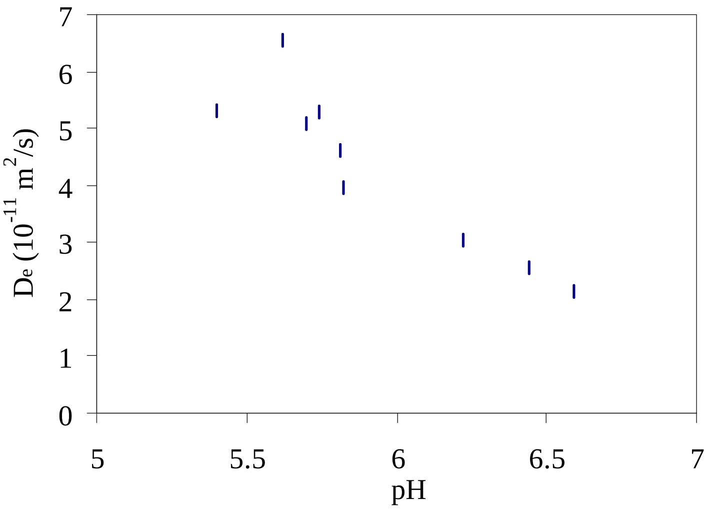


Figure 4.2.16 D_e of salted meat at different pH. Drying experiments held at 13ºC

This result is in agreement with the ones obtained by Arnau *et al*. (1998) in which they found that the water content in DFD dry-cured hams was higher than in the normal pH dry-cured hams (2% difference). A similar phenomenon was found by Stiebing and Rödel (1990) when they studied the pH influence on the drying pattern in dry sausage.