

3.1. MEAT SORPTION ISOTHERMS

The moisture desorption isotherms of meat and salted meat at three different levels of NaCl content were obtained in duplicate at three temperatures (5°, 13° and 26 °C). The desorption isotherms were determined gravimetrically by exposing the meat samples to several atmospheres of known relative humidities controlled by different salts according to the COST 90 method (Wolf *et al.*, 1985).

3.1.1. Sorption Equipment

The sorption equipment consisted of a chamber containing eleven sorption containers (1 litre PVC jars), covering the water activity range from 0.11 to 0.98. Each PVC jar had the capacity for four meat samples, which were located on a perforated plastic tray hang from the lid of the jar (Figure 3.1.1).

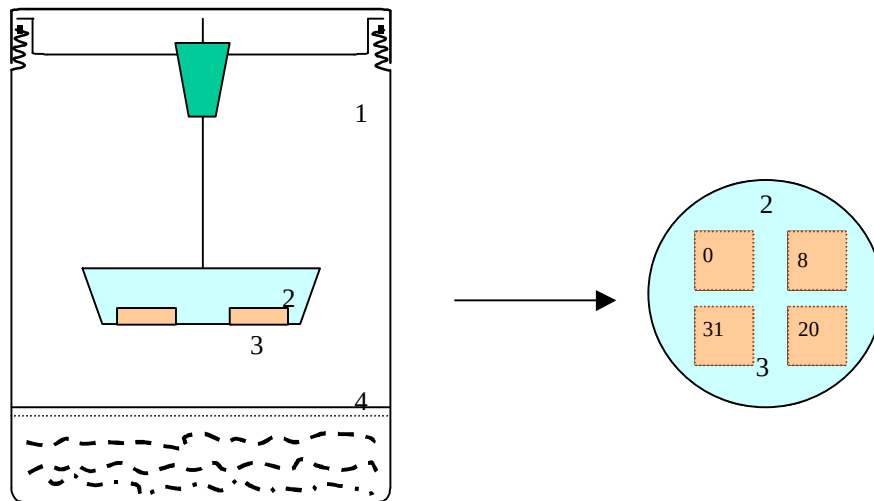


Figure 3.1.1 Sorption Container. 1. PVC jar; 2. Perforated plastic tray; 3. Meat samples at different NaCl content (0, 8, 20, 31 % d.m.); 4. Saturated salt solution.

Salts and distilled water, in the proportions given by Wolf *et al.*, (1985) were mixed in the sorption containers (Table 3.1.1). The solutions were stirred once a day for seven days to assure the right formation of the saturated solution. Afterwards, the sorption containers were kept at the experimental temperature ($\pm 0.2^\circ\text{C}$).

Table 3.1.1 Quantities of salt and distilled water used in the preparation of saturated salt solutions (Wolf *et al.*, 1985).

	Salt (kg)	H ₂ O (kg)	a _w
LiCl	0.075	0.042	0.112
CH ₃ COOK	0.200	0.075	0.226
K ₂ CO ₃	0.200	0.090	0.438
Mg(NO ₃) ₂ ·6H ₂ O	0.150	0.023	0.529
NaBr	0.200	0.080	0.577
SrCl ₂ ·6H ₂ O	0.200	0.050	0.708
NaCl	0.200	0.060	0.753
(NH ₄) ₂ SO ₄	0.200	0.060	0.800
KCl	0.200	0.080	0.843
BaCl ₂ ·2H ₂ O	0.250	0.070	0.903
KNO ₃	0.200	0.080	0.946

3.1.2. Sample preparation

Samples were taken from the *Gluteus medius* muscle from 5 different pork hams, which were selected from the slaughterhouse by temperature ($t < 4^\circ\text{C}$) and pH ($\text{pH}_{24\text{h}} = 5.8\text{-}6.2$). The pH was measured by a lab pH-meter (Crison 507, Crison Instruments S.A., Barcelona, Spain).

Four-millimetre thick slices were obtained from the muscle which was previously cooled at 0°C to obtain enough meat consistency for cutting.

The slices were salted by immersion for 24 hours at 4 °C in three different NaCl solutions, 2%, 5% and 8% of NaCl.

One half of each slice was used for the analysis of the NaCl content by the Charpentier-Volhard method (A.O.A.C., 1980). The other half of each slice was divided into pieces of 8x8x4 mm which were placed on the perforated plastic tray of each sorption container (Figure 3.1.1).

3.1.3. Measurement procedure

The plastic trays were cleaned carefully, rinsed with distilled water and dried. Thereafter the trays were filled with four meat samples, each one having a different NaCl content. Finally the trays with meat samples were placed in each sorption container containing the saturated salt solution. The sorption containers were closed hermetically, irradiated at 3 kGrey (gamma irradiation ^{60}Co) (Incze *et al.*, 1973; Ehlermann, 1990) and placed in the incubator chambers at 5°, 13° and 26 °C.

The samples from the different muscles were randomly distributed to the different sorption containers.

The end of the equilibrium process was determined with the samples placed at 5°C and at 75% relative humidity, which were weighed periodically until a constant weight was achieved. A period of 54 days was necessary to reach equilibrium.

The water content of the samples was determined by drying at 103 ± 2 °C until reaching constant weight (A.O.A.C., 1980).

3.1.4. Preparation of the NaCl brine

The amount of NaCl used for the salt brine preparation was calculated using equation 3.1.1, which allowed to obtain approximately the desired salt content into the meat.

$$\left(\frac{\text{NaCl}}{\text{H}_2\text{O}} \right)_{\text{brine}} = \left(\frac{\text{NaCl}}{\text{H}_2\text{O}} \right)_{\text{meat}}$$

3.1.1

therefore the required brines were made at the concentrations of 0.02, 0.05 and 0.08 kg NaCl/kg H₂O.

Distilled water at 40°C and NaCl salt was stirred until the total dissolution of NaCl.

The volume of the meat into the brine was considered to prepare the brine solution.

Thereafter, the brine container was kept at 4°C. The brine was stirred periodically to assure the dissolution of the NaCl into water.

3.1.5. Procedure diagram

The determination of meat sorption isotherm experiments have been developed following Figure 3.1.2.

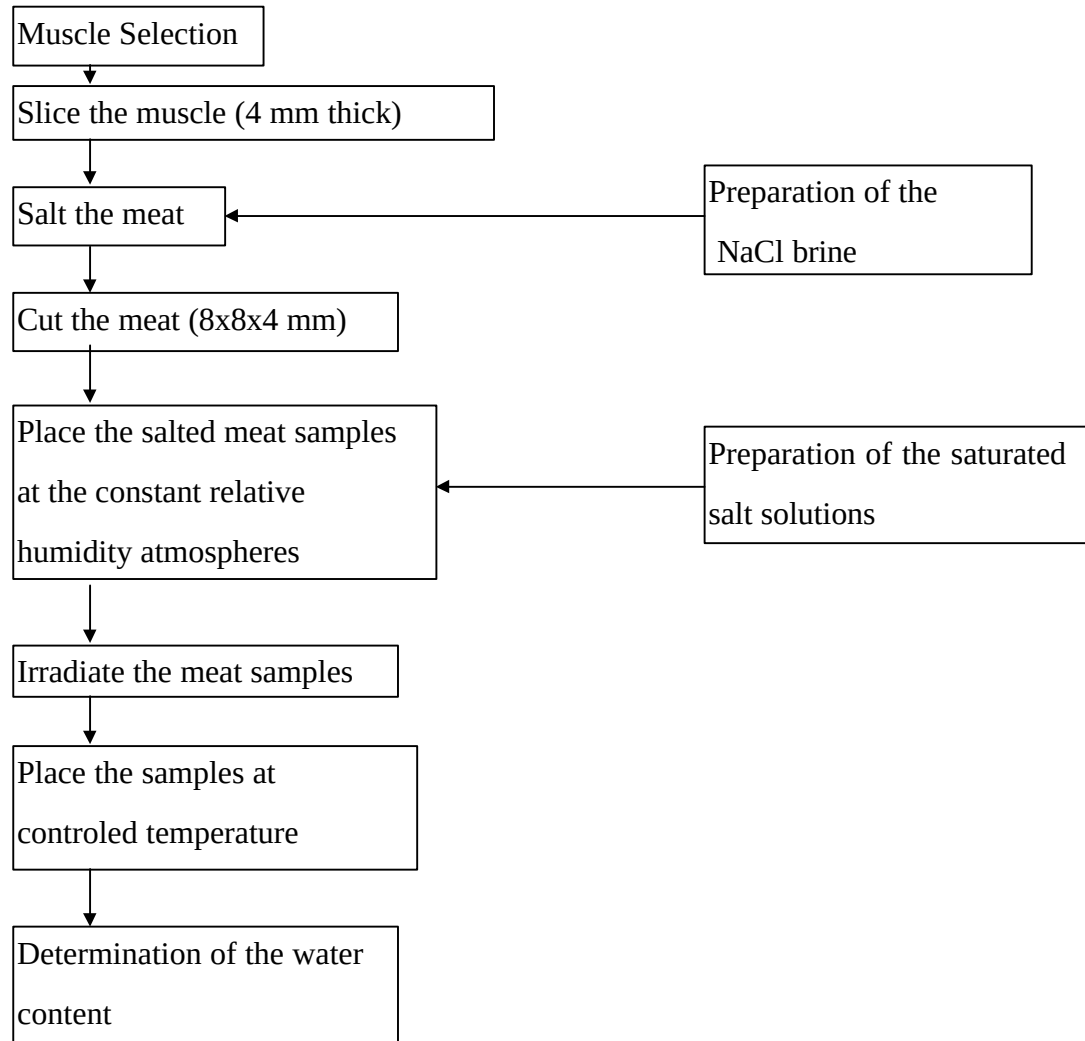


Figure 3.1.2 Procedure diagram of sorption isotherm experiments.

3.1.6. Sorption isotherm mathematical models

The experimental data is fitted to theoretical and empirical models (GAB, BET, Oswing, Mujica and Halsey models). The temperature effect has been considered by using two different ways. The first one is using the Clausius Clayperon equation (section 1.5.5.1). The second one is using equations reported by other authors in their studies. The NaCl effect has also been considered by using two different ways. The first one is adding some empirical parameters to the mentioned equations. The second one is using the predictive methods for solid mixtures (section 1.5.4).

3.1.6.1. Theoretical and empirical sorption isotherm models applied to meat

3.1.6.1.1. Model type I. Isotherm equations considering the effect of temperature and salt content by means of coefficients

The experimental isotherm data has been fitted with several models presented in Table 3.1.2, among them the theoretical models BET, GAB, the empirical models of Oswin and Mujica (Mujica et al., 1989) and the modified Halsey equation (Chirife and Iglesias, 1978).

The way in which the temperature effect was considered in the models has been taken from literature, while the NaCl effect has been considered as a linear and exponential relationship in the coefficients of the above equations, as it is shown in Table 3.1.2.

In order to fit the equations representing the isotherms of the model type I, the spreadsheet Microsoft Excel 5.0TM (Microsoft Corporation, 1992) is used. From the spreadsheet containing the experimental data of moisture content versus water activity, the equation constants are determined using the SOLVER tool included in Excel that uses an optimisation method (Newton or Conjugate Gradient) to identify the unknown variables by minimising the total sum of squared deviations between the experimental and calculated average moisture contents.

Table 3.1.2 Models used to describe the meat isotherms at temperatures from 5 to 26 °C and NaCl content into the meat from 0 to 0.31 kg NaCl/ kg d.m.

Model	Equation	Temperature dependence	NaCl content dependence		References
			$a_w < 0.75$	$a_w \geq 0.75$	
BET	$X = X_{m,sT} \frac{C_{B,sT} a_w}{(1 - a_w) [1 + (C_{B,sT} - 1) a_w]}$	$X_m = A \exp \frac{B}{R T}$ $C_B = C \exp \frac{D}{R T}$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$	Motarjemi, 1988
GAB 1	$X = X_{m,sT} \frac{C_{G,sT} K_{sT} a_w}{(1 - K_{sT} a_w) [1 + (C_{G,sT} - 1) K_{sT} a_w]}$	$X_m = A \exp \frac{B}{R T}$ $C_G = C \exp \frac{D}{R T}$ $K = E \exp \frac{F}{R T}$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$ $E = e_1 \cdot w_s + e_2$ $F = f_1 \cdot w_s + f_2$	$A = a_1 \exp(w_s \cdot a_2)$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$ $E = e_1 \cdot w_s + e_2$ $F = f_1 \cdot w_s + f_2$	Basal and Vasseur, 1992 Van den Berg, 1986 Tsami et al., 1990
GAB 2	$X = X_{m,sT} \frac{C_{G,sT} K_{sT} a_w}{(1 - K_{sT} a_w) [1 + (C_{G,sT} - 1) K_{sT} a_w]}$	$X_m = AT + B$ $C_G = \exp \left(\frac{C}{T} + D \right)$ $K = \exp(ET + F)$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$ $E = e_1 \cdot w_s + e_2$ $F = f_1 \cdot w_s + f_2$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$ $E = e_1 \cdot w_s + e_2$ $F = f_1 \cdot w_s + f_2$	Motarjemi, 1988
Oswin	$X = m \left(\frac{a_w}{1 - a_w} \right)^n$	$m = AT + B$ $n = CT + D$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$	$A = a_1 \exp(w_s \cdot a_2)$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$	Basal and Vasseur, 1992 Motarjemi, 1988
Mujica	$X = \left(\frac{1}{m_{sT} - n_{sT} a_w} \right)^n$	$m = AT + B$ $n = CT + D$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$ $D = d_1 \cdot w_s + d_2$	$A = a_1 \exp(w_s \cdot a_2)$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \exp(w_s \cdot c_2)$ $D = d_1 \cdot w_s + d_2$	Mujica et al., 1989
Halsey modified	$X^{-C} = m \ln a_w$	$m = \frac{1}{-\exp(AT + B)}$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$	$A = a_1 \cdot w_s + a_2$ $B = b_1 \cdot w_s + b_2$ $C = c_1 \cdot w_s + c_2$	Iglesias and Chirife, 1976 Mootarjemi, 1988 Weisser, 1985

3.1.6.1.2. Model type II. GAB and Mujica models considering the effect of NaCl content by means of coefficients and considering the effect of temperature using Clausius-Clapeyron equation

Another way to consider the effect of temperature is by using the Clausius-Clapeyron equation (equation 3.1.2), which can be used to obtain the water activity at different temperatures provided that the heat of sorption (Q_s) is known.

$$\left[\frac{\partial \ln a_w}{\partial (1/T)} \right]_{X=\text{const}} = -\frac{Q_s}{R} \quad 3.1.2$$

By integrating the equation (3.1.2) at a constant moisture content level, the following equation is obtained,

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{Q_s}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 3.1.3$$

In order to fit the equations representing the isotherms of the model type II, the spreadsheet Microsoft Excel 5.0TM (Microsoft Corporation, 1992) is used. From the spreadsheet containing the experimental data, the equation constants are determined using the SOLVER tool included in Excel that uses an optimisation method (Newton or Conjugate Gradient) to identify the unknown variables by minimising the total sum of squared deviations between the experimental and calculated average moisture contents.

3.1.6.2. Predictive methods for solid mixtures

3.1.6.2.1. Mixing rules

The mixing rules used are the following:

- Ross's equation:

$$a_{w\text{ mix}} = (a_{w1}^0) \cdot (a_{w2}^0) \cdot (a_{w3}^0) \dots (a_{wn}^0)$$

3.1.4

It states that the water activity of a complex solution becomes the product of the water activity values of the aqueous solutions of each component, when measured at the same molality as in the complex solution. In other words, the a_w of the mixture is a product of each component water activity at moisture content calculated as if all water contained in the mixture was available to each component independently.

Superscript 0 means that water activity of a given component is calculated as if this component contained all the water available in the system.

Ross's method is useful for solutions and mixtures containing soluble and insoluble solids.

Algorithm for calculating a_{wm} for given (X, t) and composition w_i

1. Calculate effective moisture contents $X_i = w_i/X$
2. Calculate effective water activities $a_{wi}^0 = f(X_i, t)$
3. Calculate water activity of the mixture as product of a_{wi}^0

- Linear mixing rule. Expressing the equilibrium moisture content on a dry basis, the composite equilibrium moisture content for the mixture is calculated in the following manner:

$$X_{\text{mix}} = \frac{\sum w_i X_i}{\sum w_i} \quad 3.1.5$$

where i : meat and NaCl, X_{mix} is equilibrium moisture content of the mixture, dry basis, X_i is equilibrium moisture content of the component i and w_i is the weight fraction of the component i .

- Lang and Steinberg method. The result is the following mass balance:

$$X_{\text{mix}} = \sum X_i \cdot [a_i + b_i \log_{10}(1 - a_w)] \quad 3.1.6$$

Where X_i is moisture content of each component. a_i and b_i are the coefficients of Smith sorption isotherm for the components.

3.1.6.2.2. Application of the predictive methods

To be able to use the predictive methods, it was necessary to have the sorption isotherms for the soluble solid and for the diluted solution.

The sorption isotherms for soluble solids is shown schematically in Figure 3.1.3. The segment O-A describes the increase of water content into the dry solid, following a standard sorption isotherm. In A, the water content is large enough to start dissolving the solid (NaCl). From A to B the water activity remains constant with an increase of water content until all the solid is dissolved. The concentration of water at this moment is equal to the concentration of a saturated solution at a given temperature. With a further increase of water

content the solutions becomes diluted and the water activity increases until it reaches 1 at infinitely high water content (B-C). Varying temperature, the loci of points A form the solid dissolution curve, which is defined by the solid isotherm at moisture activity of the saturated solution. Little temperature influence is observed on the dilution curve (B-C).

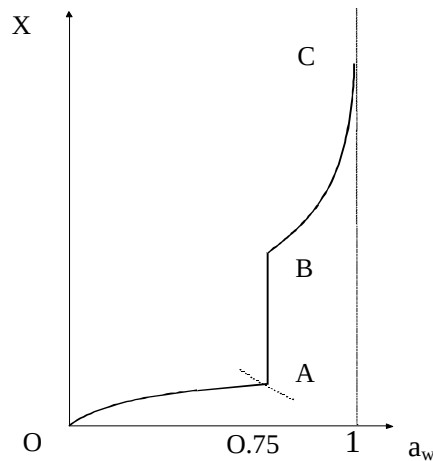


Figure 3.1.3 Sorption isotherms for a soluble solid (broken line - dissolution curve)

To be able to reproduce such isotherm the following information was necessary:

1. *Sorption isotherm equation for the solid (for O-A segment)*

Any of the typical sorption isotherm equations was taken.

2. *Equation relating water activity of saturated solution with temperature*

The experimental data can be fitted with a 3rd order polynomial equation which accommodates possible extrema of the curve as shown in Figure 3.1.4 for NaCl (Greenspan, 1977). The form of polynomial used is equation (3.1.7).

$$a_w = \sum_{i=0}^3 U_i t^i$$

3.1.7

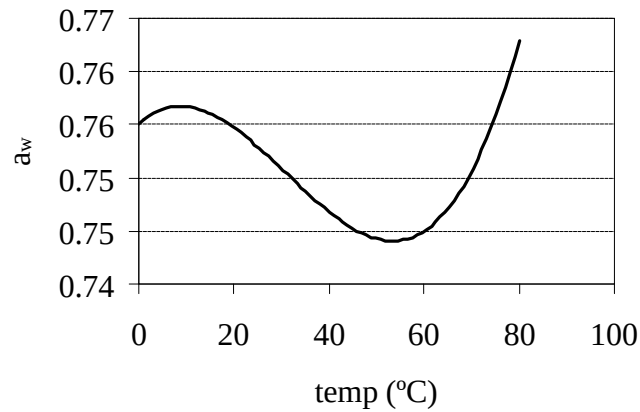


Figure 3.1.4 Water activity of saturated NaCl solution for temperatures in the range 0 to 80 °C (Greenspan, 1977).

3. *Equation relating the water activity to concentration for diluted solution*

The equation used was Norrish equation. Other tests were performed for NaCl, and equations based on Smith's sorption isotherm offered much lower accuracy (differences at second decimal place occur) than Norrish (difference of 1 or 2 at third decimal place) among others.