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# Influence of cod freshness on the salting, drying and desalting stages

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**Abstract**

Freshness is one of the most important parameters of fish quality in most markets for fresh and lightly preserved fish. However, the role of this attribute in industrial processing of cod to salt-cured, dried salt-cured and finally desalted and rehydrated cod is not known.

The aim of this work was to analyze the influence of cod freshness (ice stored for 0, 7 and 12 days) on the pile salting, drying and desalting operations with respect to mass transfer, sensory quality and microbial status. With respect to weight yield, and transport kinetics, the results obtained indicate that the main influence of cod freshness occurs during the salting operation, as the freshest raw material gives the lowest overall yield, and the lowest salt uptake. With respect to sensory quality and microbial status after desalting, the freshest raw material tended to give a harder fish with less flakiness. The content of spoilage bacteria immediately after desalting was slightly lower for freshest raw material than for the others, but the difference hardly had any influence on the storage stability of the product. However, the desalted fish from the freshest raw material had more different strains than the other raw materials after desalting.


*Keywords:* Cod; Freshness; Salting; Drying; Desalting

## 1. Introduction

Salt-cured cod, wet or dried, plays an important economic and cultural role in Spain. It is a half-finished product imported mainly from Norway or Iceland or produced on Spanish factory ships. The fish contains 15–20% salt, and has to be desalted before it can be prepared to many traditional dishes. Usually the salted cod is soaked in tap water for at least 24 h and the desalting process is done at room temperature or under refrigeration (Barat, Rodríguez-Barona, Castelló, Andrés, & Fito, 2004a). Consumer trends have evolved towards ready-to-use products, which present difficulties for the commercialization of heavy-salted cod due to the desalting process, which nowadays is partially done by retailers (Gallart-Jornet, Rodríguez-Barona, Barat, Andrés, & Fito, 2003; Kurlansky, 1999; Skjerdal, Lorentzen, Joensen, & Akse, 1997; Skjerdal, Pedro, & Serra, 2002).

Quality is an arbitrary term and one causing confusion among consumers, processors and researchers. Fish quality is, therefore, a very complex concept (Bremner, 2000; Nielsen, Hyldig, & Larsen, 2002), which includes nutritional, microbiological, biochemical and physiochemical attributes related to this term.

For fresh fish and fish fillets, freshness is one of the most important parameters of fish quality in most markets (Ólafsdóttir et al., 1997) and, in particular, in the case of wild and farmed cod (Nielsen et al., 2002; Sigurgisladóttir, Torrissen, Lie, Thomassen, & Hafsteinsson, 1997). Traditionally, three quality levels

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in fresh cod can be defined: the first level (up to 6 days of ice-storage, which can be used for fresh or frozen consumption), the second level (between 6 and 10 days of ice-storage, which is suitable for fresh and smoked products) and the third level (between 10 and 14 days of ice-storage, which is used for smoked and salted products) (Burgess, Cutting, Lovern, & Waterman, 1987). The effects of this wide variation in freshness are not clearly defined with respect to the salting and drying operations used to obtain heavy salted cod, and the necessary desalting operation prior to its consumption, even though cod of all freshness categories are used as raw materials for these products.

In the Norwegian fishing industry the storage time of the raw material prior to salting varies substantially. In coastal fisheries and onboard fishing boats the cod may only be stored for a few hours. It is, however, much more common to store the fish, headed and gutted, on ice for a week or more, up to 12 days, which is the maximum permitted storage time according to Norwegian regulations (Anonymous, 1998).

In 1992, Icelandic scientists reported that they obtained a much lower yield from cod salted pre-rigor onboard, compared to fish from the same catch salted in a shore based factory after storage on ice until it was in a post-rigor state (Gudmundson & Arason, 1992). Sørensen, Brataas, Nyvold, and Lauritzen (1997) observed that rigor mortis also seriously influenced the yield of lightly salted cod fillets. Akse and Joensen (1996a) concluded that salting of pre-rigor cod resulted in a lower product yield, compared to salting of post-rigor raw materials. However, Akse and Joensen (1996b) found that pre-rigor raw materials produced a better quality product after desalting, compared with raw materials stored in ice for 8 and 12 days before salting. The greater weight loss during salting of pre-rigor raw materials, compared to post-rigor, was partly regained during desalting.

To investigate the possible advantages and disadvantages of varying raw material freshness for salting, the aim of this work was to analyze the influence of cod freshness (ice stored for 0 days—pre-rigor state, 7 and 12 days at 0 °C) on yield during the pile salting, drying and desalting operations, and in addition the mass transfer kinetics in the desalting operation, as well as on the sensory quality and microbial status of the desalted fish.

## 2. Materials and methods

### 2.1. Fresh raw material

Atlantic cod (*Gadus morhua* L.), mean weight 3.0 ± 0.5 kg, harvested by Danish seine off the coast of Northern Norway in April 2000, was used as the raw material in the experiments. Mean water weight fraction ($x_0^w$) of fresh raw material was 0.8.

Cod were bled, slaughtered and thoroughly washed. Gutted and headed cod were stored on ice and kept in a refrigerator at 4 °C for three different periods; for a few hours (before rigor mortis occurred), 7 days and 12 days. At each of the three sampling points, 10 cods were randomly selected and filleted using standard industrial procedures for the production of fillets with skin on.

### 2.2. Salted raw material

Each cod fillet individually tagged immediately before salting by penetrating plastic number tags through the skin using a Marking pistol (Floy Tag and MFG, INC Seattle, WA, USA), and randomly selected for the three batches prior to the salting process with food grade salt. Each batch of fillets was salted for a total of 16 days at 4 ± 1 °C. Cod salting consisted of pickling (starting with saturated brine) in plastic containers without drainage (during the first 5 days) and pile salting with alternating layers of salt (for the remaining days).

The average initial weights (±standard deviation) of cod fillets used in salting for the 0, 7 and 12 storage days were 985 ± 167, 748 ± 169 and 814 ± 174 g, respectively.

### 2.3. Drying raw material

Salted cod fillets were dried for 96 h in an industrial oven dryer (Southwind Manufacturing Ltd., Waverly, Nova Scotia, Canada). The programmed conditions for the drying stage, similar to the industrially used, are shown in Table 1. Total weight changes at the end of the drying stage were measured using 10 cod fillets, and three of them were used to determine the composition of the dried cod.

### 2.4. Cod desalting experiments

Dried pieces of salted cod used in the desalting experiments consisted of parallelepiped obtained from the loins with a commercial size of 9.5 × 3.5 × 2 cm (length × width × thickness). The average weight of each

Table 1
Programmed conditions in the industrial oven during the cod drying process

| Time (h) | *T* (°C) | RH[a] (%) | Air velocity (m/s) |
|---|---|---|---|
| 0 | 20 | 50 | 1.9 |
| 24 | 20 | 50 | 2.13 |
| 48 | 22 | 45 | 2.13 |
| 72 | 24 | 40 | 2.4 |
| 96 | 26 | 35 | 2.4 |

[a] RH: air relative humidity.

batch (at 0, 7 and 12 days storage) used for the desalting experiments was 50.1 ± 8.1, 41.7 ± 4.3 and 45.5 ± 4.8 g, respectively. Each piece was identified by means of a plastic label with a number inside and weighed before the desalting operation. All 40 pieces from each batch were desalted together at 4 °C in an open plastic container by submerging the fish, at a 1:9 fish to water ratio, for 30 h in stagnant tap water without stirring.

Ten pieces of cod were periodically weighed and used to determine weight change. NaCl and water content were determined at 1, 6, 12, 24 and 30 h of the desalting process. Three cod samples were randomly analyzed at each of those sampling times.

*2.4.1. Analytical determinations*

During the desalting operation, samples were weighed following drainage for 3–4 min on a plastic grid, turned once in the meantime (it was observed that after 1 min of drainage samples weight remained constant). Water content was determined by oven drying for 24 h at 105 ± 1 °C (Boeri, Davidovich, & Lupin, 1978) until a constant weight was achieved. NaCl for both the muscle and brine was determined using sample homogenization according to the Volhard method (AOAC 937.09, 1995). The samples were homogenized for 1 min in a Dito Sama (K55) Food Processor (Abusson, France) for approximately 1 min before the analysis.

The water activity of each sample was determined by using an Aqualab® dew point hygrometer (Decagon Devices, Inc., WA, USA).

Salt concentration in the fish liquid phase ($z^{\mathrm{NaCl}}$) was estimated from water and NaCl content according to Eq. (1) (Barat, Rodrıguez-Barona, Andrés, & Fito, 2002), being $x^{\mathrm{NaCl}}$ and $x^{\mathrm{w}}$ the NaCl and water weight fraction in the fish flesh, respectively.

$$z^{\mathrm{NaCl}} = \left(\frac{x^{\mathrm{NaCl}}}{x^{\mathrm{w}} + x^{\mathrm{NaCl}}}\right) \quad (1)$$

The significance of weight changes and composition was analyzed using ANOVA test, using the Statgraphics® Plus version 4.0 (Manugistics, Inc., Rockville, MD, USA).

*2.4.2. Sensory analysis*

Sensory analysis was done on desalted samples by seven trained panelists experienced in working with desalted cod. A descriptive profiling with two replicates was carried out on cooked samples. Samples were packed individually in aluminum sheets, and heated over boiling water for 10 min. The following 13 attributes were analyzed: total smell intensity, sharp smell, rancid smell, yellow color, whiteness, hardness, flakiness, cohesiveness, mature taste, salt taste, rancid taste, fibrousness and juiciness using a line scale. The samples were assessed using a 1–10 point hedonic scale, where 10 indicated the strongest intensity. The assessments were performed in a room specifically designed and equipped for sensory analysis (ISO 8589). All the data were electronically registered using Tecators's Senstec System™ (Tecator AB, Höganäs, Sweden).

The significance of sensory differences between samples was analyzed using ANOVA and Tukey's test, using the software Statistical Analysis System SAS™ Windows version 6.12 (SAS Institute, Cary, NC, USA), and principal component analysis (PCA) (Næs & Risvik, 1996), using "The Unscrambler™", version 7.5 (CAMO A/S, Oslo, Norway).

*2.4.3. Microbial studies*

The total viable count (TVC) in the fish was measured prior to salting, after salt-curing, drying, desalting and subsequent chilled storage for 6 days at 4 °C. Pieces of fillets with skin on (3–5 g) were added to 9 parts of 0.1% peptone water with 0.9% or 3% NaCl for fresh and desalted cod, respectively, and homogenized in a Lab-Blender 400 Stomacher™ (Seward Medical UAC House, London, UK). The TVC was determined using a standard plate count agar (Oxoid, Basingstoke, UK) supplemented with 0.9% and 3% NaCl for fresh and desalted fish, respectively, and incubation at 12 °C for 5 days. Three pieces, from three different fishes were measured in duplicate at each sampling point.

The number of different salt-tolerant bacteria on the fish prior to salting was analyzed by exposing the bacteria in the unsalted fish to ten different NaCl concentrations in the range 0–25%. This was done by adding 1 ml of the fish-peptone water homogenized to 9 ml of liquid medium containing in g/l, peptone 5, yeast extract 2.5, glucose 1, and NaCl 0–25%. The inoculated tubes were incubated at 12 °C, and the number of surviving strains was determined after 3 days by plating 100 µl of culture from each of the salt concentrations on Plate Count Agar supplemented with 3% NaCl. The colonies were phenotypically characterized as described by Bjørkevoll, Olsen, and Skjerdal (2003) and internally compared.

## 3. Results and discussion

### 3.1. Cod salting

The total, water and NaCl cod weight ($M$) changes, determined with Eqs. (2)–(4) (at sampling time $t$ and 0), and the cod composition at the end of the salting period depended on the cod ice-storage time (Table 2), indicating that important process parameters like yield were strongly influenced by the freshness of the raw material.

$$\Delta M_t^{\mathrm{o}} = \left(\frac{M_t^{\mathrm{o}} - M_0^{\mathrm{o}}}{M_0^{\mathrm{o}}}\right) \quad (2)$$

Table 2
Total, water and NaCl weight changes in the salting step ($\Delta M_t^o$, $\Delta M_t^w$ and $\Delta M_t^{NaCl}$), water and NaCl weight fraction of the salted cod ($x^w$ and $x^{NaCl}$), and NaCl concentration in the cod liquid phase ($z^{NaCl}$) at the end of the salting period for the different raw materials (SD: standard deviation)

| Storage time (days) | $\Delta M_t^o \pm SD^{***}$ | $\Delta M_t^w \pm SD^{***}$ | $\Delta M_t^{NaCl} \pm SD^{**}$ | $x^w \pm SD^{***}$ | $x^{NaCl} \pm SD^{**}$ | $z^{NaCl} \pm SD^{n.s.}$ |
|---|---|---|---|---|---|---|
| 0 | $-0.29 \pm 0.02^a$ | $-0.42 \pm 0.02^a$ | $0.13 \pm 0.01^a$ | $0.533 \pm 0.006^a$ | $0.185 \pm 0.005^a$ | $0.258 \pm 0.004^a$ |
| 7 | $-0.15 \pm 0.03^b$ | $-0.33 \pm 0.02^b$ | $0.17 \pm 0.01^b$ | $0.559 \pm 0.000^b$ | $0.205 \pm 0.009^b$ | $0.268 \pm 0.008^{ab}$ |
| 12 | $-0.10 \pm 0.04^b$ | $-0.29 \pm 0.02^c$ | $0.19 \pm 0.01^b$ | $0.567 \pm 0.002^c$ | $0.210 \pm 0.006^b$ | $0.270 \pm 0.005^b$ |

Means in a column with different letters are significantly different; n.s.: non significant.
** $P < 0.01$.
*** $P < 0.001$.

$$\Delta M_t^w = \left( \frac{M_t^o \cdot x_t^w - M_0^o \cdot x_0^w}{M_0^o} \right) \quad (3)$$

$$\Delta M_t^{NaCl} = \left( \frac{M_t^o \cdot x_t^{NaCl} - M_0^o \cdot x_0^{NaCl}}{M_0^o} \right) \quad (4)$$

A decrease in the weight loses is observed when storage time increases, in agreement with the results obtained by Gudmundson and Arason (1992), Akse and Joensen (1996a) and Lauritzen et al. (2004) as a consequence of the lower water loss and the higher NaCl uptake when the storage time increases.

The main differences in the weight changes between the different raw materials were observed in the pre-rigor raw material (0 storage days), being significantly lower than those stored for 7 and 12 days. There were no significant differences for total weight changes between the cods stored for 7 and 12 days. It should be taken into account that the pre-rigor raw material goes into rigor during the salting process, favoring sample dehydration due to muscle contraction, as was observed by Sørensen, Helgason, and Brataas (1997) during lightly salted cod manufacture.

Another reason that might explain the reduction in the cod weight loss as a function of storage time could be the changes in the cod structure throughout the storage period due to enzymatic reactions that would disrupt the cod structure (Ólafsdóttir et al., 1997), thereby, improving the mass transfer kinetics. The mass transfer improvement might be the reason why the NaCl uptake increases while the water loss decreases. In the osmotic dehydration processes, the factors improving the global mass transfer kinetics usually increase the transport of the component with higher resistance (Barat, Chiralt, & Fito, 2001; Lazarides, Katsanides, & Nicolaides, 1995; Skjerdal et al., 1995). The $Na^+$ and $Cl^-$ ions components have a higher resistance to transport than water as can be seen when comparing their reported diffusivity values in different salting processes (Gou & Comaposada, 2000).

Finally, it can be stated that the higher process yield would be achieved when working with the cod stored for 12 days, having a clear influence on the economic benefits.

As regards the cod water and NaCl weight fraction ($x^w$ and $x^{NaCl}$, respectively), their values increase with increasing storage time prior to salting, while the estimated NaCl concentration in the cod liquid phase remains practically constant and around to the concentration of a saturate NaCl brine (0.263 w/w). The $z^{NaCl}$ value indicates that the cod liquid phase at the end of the salting period is in equilibrium with the surrounding salting medium, as reported by Barat et al. (2002) and Barat et al. (2004b). The slight increase in the $z^{NaCl}$ depending on the cod freshness, which is above the concentration of a saturated brine for the cod stored for 12 days, could be due to an increase in the amount of $Na^+$ and $Cl^-$ ions interacting with the cod proteins (Offer & Trinick, 1983). Offer and Trinick (1983) stated that the $Cl^-$ ions during salting were retained on the protein surface due to charge attractions (usually the total charge of the proteins is positive). The action of the cod proteolytic enzymes on the muscle proteins throughout ice storage time could contribute to increase the protein surface being susceptible to interact with the chloride ions, which could be the reason for the observed increase in the $z^{NaCl}$ value.

### 3.2. Cod drying

The cod composition at the end of the drying process and the total, water and NaCl weight changes, depending on the cod storage time, can be seen in Table 3. The moisture of the dried cod increases with increasing storage time of the raw material, while the NaCl weight fraction is lowest for the freshest raw material. The $z^{NaCl}$ values being 0.26 w/w (the value corresponding to the NaCl brine saturation concentration), indicates the existence of precipitated salt crystals. The NaCl weight fraction corresponding to dissolved and precipitated salt can be estimated by means of the Eqs. (5) and (6), with the dissolved NaCl weight fraction ($x^{NaCl\ solution}$) being 0.15, 0.15 and 0.16 for 0, 7 and 12 days, respectively.

$$x^{NaCl} = x^{NaCl\ solution} + x^{NaCl\ crystal} \quad (5)$$

$$z^{NaCl} = \frac{x^{NaCl\ solution}}{x^{NaCl\ solution} + x^w} \quad (6)$$

Table 3
Total, water and NaCl weight changes in the drying step ($\Delta M_t^o$, $\Delta M_t^w$ and $\Delta M_t^{NaCl}$), water and NaCl weight fraction of the dried cod ($x^w$ and $x^{NaCl}$), and NaCl concentration in the cod liquid phase ($z^{NaCl}$) after the drying step (SD: standard deviation)

| Storage time (days) | $\Delta M_t^o \pm SD^{***}$ | $\Delta M_t^w \pm SD^{n.s.}$ | $\Delta M_t^{NaCl} \pm SD^{**}$ | $x^w \pm SD^{***}$ | $x^{NaCl} \pm SD^{**}$ | $z^{NaCl} \pm SD^{*}$ |
|---|---|---|---|---|---|---|
| 0 | $-0.26 \pm 0.03^a$ | $-0.22 \pm 0.01^a$ | $-0.04 \pm 0.01^a$ | $0.43 \pm 0.00^a$ | $0.20 \pm 0.01^a$ | $0.32 \pm 0.01^a$ |
| 7 | $-0.24 \pm 0.03^b$ | $-0.22 \pm 0.01^a$ | $-0.02 \pm 0.01^b$ | $0.44 \pm 0.00^b$ | $0.24 \pm 0.00^b$ | $0.35 \pm 0.00^b$ |
| 12 | $-0.25 \pm 0.02^c$ | $-0.22 \pm 0.01^a$ | $-0.03 \pm 0.00^a$ | $0.46 \pm 0.00^c$ | $0.24 \pm 0.01^b$ | $0.34 \pm 0.01^b$ |

Means in a column with different letters are significantly different; n.s.: non significant.
* $P < 0.05$.
** $P < 0.01$.
*** $P < 0.001$.

It is interesting that the total weight and water loss in the drying process are nearly the same, regardless of the storage time of the raw material. This could be explained by the protein matrix, with respect to water binding capacity, being similar due to the strong denaturizing effect of the high NaCl concentrations in the cod liquid phase, which would imply that the initial differences in the raw material have been smoothed out during the salt-curing step. It should be noted that all the samples had the same $a_w$ value at the beginning of the drying step (≈0.75), which corresponds to the $a_w$ value of a saturated NaCl brine (Barat, Rodrıguez-Barona, Andres, & Fito, 2003), as all of them had the same $z^{NaCl}$ value (≈0.26). Since the driving force of the process is the difference in the $a_w$ between the air and the cod surface (Wesselingh & Krishna, 1990), it could be expected, as was observed, that all the samples, regardless of the raw material storage time, would have the same water loss and consequently, the same total weight loss.

A small NaCl loss can be observed during the drying process, corresponding to the NaCl crystals formed on the cod surface, which fall into the trays of the dryer as a result of mechanical factors. The NaCl loss ranged from 2% to 4% (determined by means of a mass balance) of the initial weight of the cod in the drying period.

### 3.3. Cod desalting

#### 3.3.1. Mass balance applied to the cod desalting operation

The main components transferred in the salting step between the cod and its surroundings are water and NaCl (Barat, Rodrıguez-Barona, Andrés, & Ibáñez, 2004b). As such, the total weight changes ($\Delta M_t^o$) will be equal to the sum of the water and NaCl weight changes ($\Delta M_t^w$ and $\Delta M_t^{NaCl}$).

The experimental $\Delta M_t^o$ values corresponding to the desalting processes at the analyzed sampling times for the cods stored at different periods of time were plotted against the sum of the $\Delta M_t^w$ and $\Delta M_t^{NaCl}$ (Fig. 1). It can be observed that the plotted points are very close to the diagonal of the figure, supporting the previously considered hypothesis. In some cases, particularly for the freshest raw material, the experimental points were located slightly above the diagonal, which indicates that other components such as soluble proteins or tiny cod fragments could be overlooked. The alignment of the experimental points with the diagonal is also indicative of the consistency of the experimental results.

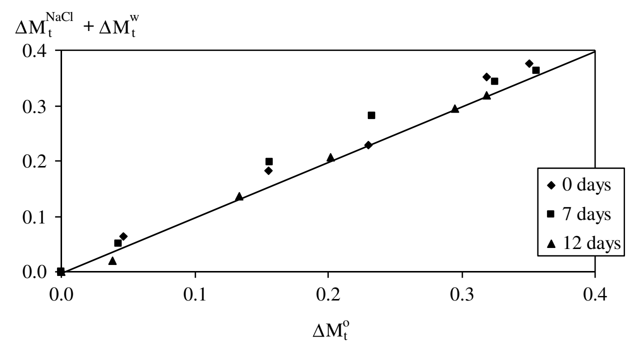

Fig. 1. Mass balance of samples ice stored for 0, 7 and 12 days, at the different sampling points in the desalting experiments.

Most of the 12-day points were nearly on the line while 0-days and the majority of 7-days points were nearly always above it. Thus, it appears that the influence of factors besides salt and water on the mass transfer was more pronounced for the two freshest raw materials than for the oldest. This could be explained by changes in protein or matrix status during storage prior to salting (changed resistance for NaCl transport, degrading of membranes, loss of soluble compounds that protect the bound protein water from "invasion" of ions (for further comments on bound water see below)). This behavior was also observed by Lauritzen et al. (2004).

#### 3.3.2. Desalted cod weight changes and composition

The desalted cod composition after 30 h of desalting without water changes can be seen in Table 4. It is seen that the cod moisture is nearly the same regardless of the type of raw material employed, while the NaCl weight fraction increases with raw material storage time. Consequently, the $z^{NaCl}$ concentration of the desalted cod increases with storage time.

Concerning weight changes during the desalting step, no clear pattern was observed, even though the NaCl

Table 4
Total, water and NaCl weight changes, and water and NaCl weight fraction of the desalted cod, and NaCl concentration in the cod liquid phase after the desalting process (SD: standard deviation)

| Storage time (days) | $\Delta M_t^{o\,n.s.}$ | $\Delta M_t^{w\,**}$ | $\Delta M_t^{NaCl\,***}$ | $x^w \pm SD^{n.s.}$ | $x^{NaCl} \pm SD^*$ | $z^{NaCl} \pm SD^*$ |
|---|---|---|---|---|---|---|
| 0 | 0.35 ± 0.03[a,b] | 0.55 ± 0.02[b] | −0.173 ± 0.001[c] | 0.73 ± 0.01[a] | 0.022 ± 0.000[a] | 0.029 ± 0.001[a] |
| 7 | 0.36 ± 0.03[b] | 0.57 ± 0.03[b] | −0.204 ± 0.001[a] | 0.74 ± 0.01[a] | 0.026 ± 0.001[b] | 0.033 ± 0.002[ab] |
| 12 | 0.32 ± 0.04[a] | 0.52 ± 0.03[a] | −0.200 ± 0.001[b] | 0.74 ± 0.01[a] | 0.028 ± 0.001[b] | 0.036 ± 0.001[b] |

Means in a column with different letters are significantly different; n.s.: non significant.
* $P < 0.05$.
** $P < 0.01$.
*** $P < 0.001$.

weight changes, which were higher for the cod stored for 7 and 12 days. A clearer picture of the influence of raw material storage time on the total weight changes can be seen when comparing the total weight changes throughout the whole process (salting, drying and desalting) referred to the initial weight of the raw material (Fig. 2). It can be seen that the total weight changes are different for all the raw material following the salting process, but when the drying and desalting steps are done, the differences between the cod stored for 7 and 12 days disappear, the only remaining differences being between the fresh raw material and those stored for 7 and 12 days.

The ANOVA analysis indicated that 7 and 12 days stored cods were a homogeneous group after the salting ($P < 0.001$), drying ($P < 0.001$) and desalting ($P < 0.01$) operations.

Fig. 3 depicts changes in the cod liquid phase NaCl concentration ($z^{NaCl}$) and the desalting solution ($y^{NaCl}$) throughout the desalting process. The study of those changes allow to understand how is the desalting process progressing as regards the NaCl concentration, and in which way the cod samples approaches to the equilibrium with the desalting solution from the NaCl concentration point of view. It can be seen that these values are very close for the different raw materials (the ANOVA indicated that 0 and 7 days stored cods were a homogeneous group, and 7 and 12 days were another homogeneous group, with a $P$ value lower than 0.05). The $z^{NaCl}$ value decreases and the $y^{NaCl}$ increases, reaching a similar value at the end of the desalting experiment (30 h). The experimental $z^{NaCl}$ and $y^{NaCl}$ values can be compared at the end of the desalting experiment with the theoretical equilibrium values ($z_e^{NaCl}$ and $y_e^{NaCl}$), which can be obtained if the initial salted cod (SC): desalting solution (DS) ratio ($M_0^{SC}/M_0^{DS}$) and the initial composition of both elements (NaCl and water weight fraction in the cod—$x_0^{NaCl}$ and $x_0^w$—and in the desalting solution—$y_0^{NaCl}$ and $y_0^w$, respectively) are established using a mass balance (Barat et al., 2004b) (Eq. (7)):

$$z_e^{NaCl} = y_e^{NaCl} = \frac{\frac{M_0^{SC}}{M_0^{DS}} \cdot x_0^{NaCl} + y_0^{NaCl}}{\frac{M_0^{SC}}{M_0^{DS}} \cdot (x_0^w + x_0^{NaCl}) + (y_0^w + y_0^{NaCl})} \quad (7)$$

The $z_e^{NaCl}$ values for the desalted cods derived from raw material stored at 0, 7 and 12 days and calculated by means of Eq. (7) were 0.021, 0.025 and 0.024 respectively, and the experimental $z^{NaCl}$ values at the end of the desalting stage were 0.029, 0.033 and 0.036, the difference between them being very slight.

If the cod liquid NaCl phase concentration ($z^{NaCl}$) is compared to the desalting liquid NaCl concentration ($y^{NaCl}$) for all the sampling points of the desalting operation except for time 0 (Fig. 4), a linear relationship is observed with a good correlation coefficient, although

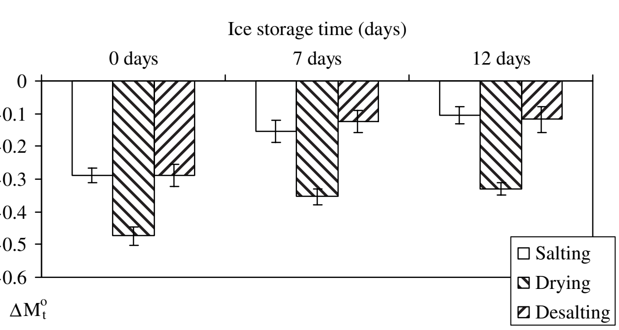


Fig. 2. Total weight changes at the end of the salting, drying and desalting stages with reference to the initial raw cod weight.

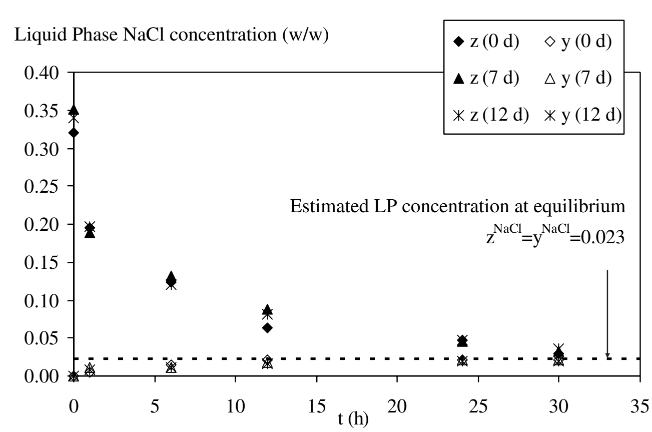


Fig. 3. Changes in the cod liquid phase NaCl concentration ($z^{NaCl}$) and the desalting solution ($y^{NaCl}$) throughout the desalting process for cod stored for 0, 7 and 12 days (the dotted line corresponds to the average $z_e^{NaCl}$ value of 0.023 as calculated by the means of Eq. (7)).

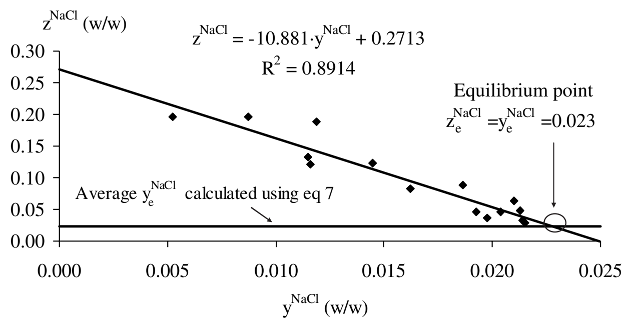


Fig. 4. Fitting of the NaCl cod liquid phase concentration ($z^{NaCl}$) and the desalting liquid NaCl concentration ($y^{NaCl}$) for all the sampling points of the desalting operation except for time 0.

the NaCl concentration of the desalting water changes over a narrow range of values. This excellent correlation would enable the indirect estimation of the $z^{NaCl}$ value of the cod during the desalting operation by measuring the NaCl concentration of the desalting solution. It can be seen that after 30 h of desalting, the cod liquid phase has almost achieved the average $z^{NaCl}$ equilibrium concentration calculated by means of Eq. (7).

### 3.3.3. Cod desalting kinetics

The changes in water, NaCl and total weight is shown in Fig. 5. A certain tendency can be observed, as those cod samples coming from cod stored for 7 days having a higher water gain, and the cod samples stored for 0 days having a lower NaCl loss probably due to the lower NaCl gain during the salting stage. The ANOVA analysis indicated that at the end of the desalting process the only statistically significant differences ($P < 0.001$) corresponded to the NaCl weight changes.

It is interesting that the cod samples are still gaining weight at the end of the 30 h of desalting, while the $z^{NaCl}$ value has almost reached equilibrium (see Fig. 3), as has been reported in other studies (Barat, Rodrıguez-Barona, Andrés, & Visquert, 2004c). It seems that for the size of the cod samples employed, the rehydration equilibrium is reached later than the desalting equilibrium. This observation illustrates that desalting and rehydration not necessarily occurs at the same velocity. The explanation for this could be that changes in the bound water, i.e., the protein hydration water, are slower than in the transport of free water (Cayley, Lewis, Guttman, & Record, 1991).

The weight changes were calculated according to Eq. (8). A mathematical model for the weight changes throughout time was fitted to the experimental data, supposing that the weight changes were related to the square root of time, supposing a pseudo-diffusional transportation. Very good correlations were found for all the raw materials. The equation coefficients and the fitting correlation factors are shown in Table 5. Although very good correlations are obtained, there was a tendency for the fitted slope to deviate from the experimental points at 24 and 30 h of desalting, coinciding with results obtained in another study in which a change in the mass transfer kinetics was observed around that same time period (Barat et al., 2004b). Again, the parameters of the fitted equation are very close with no differences due to cod storage time.

$$\Delta M_t^{i} = 1 + k_1 + k_2 \cdot t^{0.5} \quad (8)$$

When the $\Delta M_t^{o}$ values were plotted against the $z^{NaCl}$ values (Fig. 6), a similar behavior to that reported by Barat et al. (2004b) was noticed. The initial fast $z^{NaCl}$ value decrease with very low total weight increase could be explained by the dilution of the superficial NaCl crystals. In the other two time periods the relationship between the $\Delta M_t^{o}$ and $z^{NaCl}$ values was linear, with the slope of the adjusted line increasing when the desalting process progressed, which meant that the last time period was more favorable to water gain than the previous one, probably as a result of the uptake of water due to changes in the hydrodynamic mechanism during protein matrix rehydration. The change in the slope could also

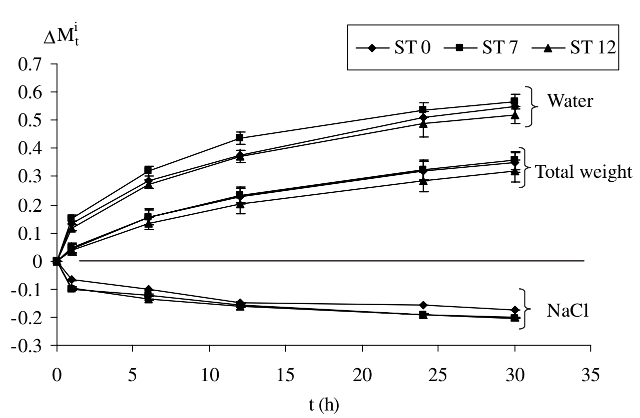


Fig. 5. Total, water and NaCl weight changes of cod throughout the desalting experiments (ST: storage time).

Table 5
Kinetic parameters for total weight changes adjusted to Eq. (8)

| | Storage time (days) | $k_1$ | $k_2$ | $R^2$ | SE[a] |
|---|---|---|---|---|---|
| $\Delta M_t^{o}$ | 0 | −0.0146 | 0.0679 | 0.95 | 0.026 |
| | 7 | −0.0196 | 0.0700 | 0.95 | 0.026 |
| | 12 | −0.021 | 0.0626 | 0.94 | 0.028 |
| $\Delta M_t^{w}$ | 0 | 0.0465 | 0.0935 | 0.99 | 0.019 |
| | 7 | 0.0818 | 0.0925 | 0.97 | 0.029 |
| | 12 | 0.0418 | 0.09 | 0.97 | 0.028 |
| $\Delta M_t^{NaCl}$ | 0 | −0.0484 | −0.0233 | 0.94 | 0.010 |
| | 7 | −0.0716 | −0.0241 | 0.99 | 0.005 |
| | 12 | −0.0776 | −0.0232 | 0.99 | 0.004 |

[a] SE: Standard error.

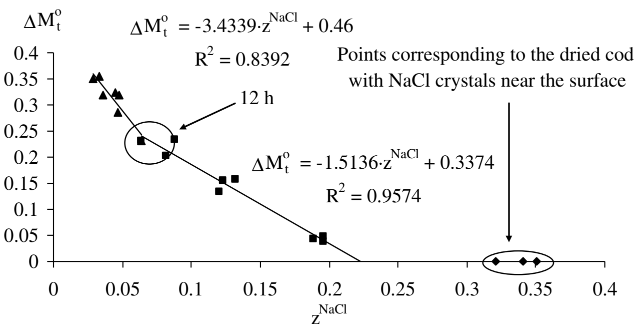


Fig. 6. Plot of the $z^{NaCl}$ and $\Delta M_t^o$ experimental data during the desalting experiments.

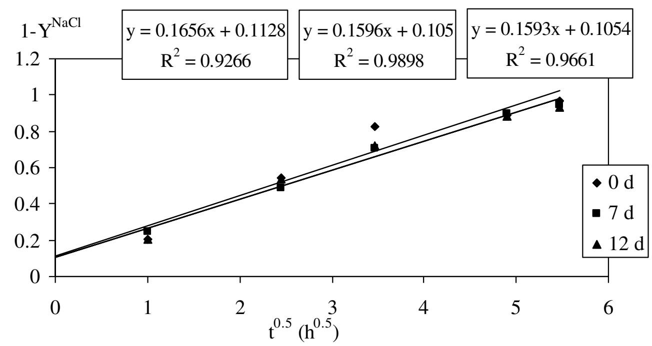


Fig. 7. Reduced driving force $(1 - Y_T^{NaCl})$ versus $t^{0.5}$.

be related to the importance of the mass transfer mechanisms in the total weight change due to activity or pressure gradients (Barat et al., 2004c).

The changes in the $z^{NaCl}$ and $y^{NaCl}$ values throughout the time scale were used to determine the effective diffusion coefficient of the cod samples by using the integrated solution of Fick's equation for a semi-infinite slab (Eq. (9)) (Crank, 1975) with the inclusion of an independent term $K$ that would allow for correction of any effect of hydrodynamic mechanisms on the deviation of the adjusted equation from the co-ordinate's origin or any other mass transfer phenomena occurring at the very beginning of the process (Barat et al., 2004b). $l_i$ is half the thickness of the slab (1 cm in our experiments), as no additional resistance in the skin covered surface was considered due to its very low fat content (Burgess et al., 1987) and $Y_T^{NaCl}$ is the reduced driving force between the cod liquid phase and the desalting solution. The $z_0^{NaCl}$ employed value in Eq. (9) was 0.26 (corresponding to saturated brine) instead of the calculated $z^{NaCl}$ value reached when taking into account all the NaCl of the cod (see Table 3). It was observed in a previous study that the excess of NaCl located near the cod surface was lost at the very beginning of the process (Barat et al., 2004c). The substituted $z_e^{NaCl}$ value in Eq. (9) was obtained by applying the mass balance (Eq. (7)).

$$1 - Y_T^{NaCl} = 1 - \left(\frac{z_t^{NaCl} - y_t^{NaCl}}{z_e^{NaCl} - z_0^{NaCl}}\right) = 2 \cdot \left(\frac{D_e \cdot t}{\pi \cdot l^2}\right)^{0.5} + K \qquad (9)$$

Eq. (9) was matched to the experimental data (Fig. 7) and the $D_e$ and $K$ parameters obtained are given in Table 6.

All the kinetic parameters were quite similar, and no significant differences depending on the raw material storage time were observed, being in the same range as the $D_e$ value reported in another cod desalting study (Barat et al., 2004b). The $K$ parameter's average value was 0.108, indicating an initial weight increase due to the fast initial water gain due to the hydrodynamic mechanism. A combined equation for routine use can be employed with the average $D_e$ and $K$ values shown in Table 6.

Table 6
Kinetic parameters ($D_e$ and $K$ values) obtained from fitting Eq. (9) to the experimental data

| Storage time (days) | $D_e$ (m²/s) | $K$ (–) | SE[a] |
|---|---|---|---|
| 0 | $5.98 \times 10^{-10}$ | 0.113 | 0.082 |
| 7 | $5.56 \times 10^{-10}$ | 0.105 | 0.031 |
| 12 | $5.54 \times 10^{-10}$ | 0.105 | 0.052 |
| Average values | $5.69 \times 10^{-10}$ | 0.108 | 0.058 |

[a] SE: Standard error.

### 3.3.4. Sensory and microbial effects

Based on the mass transfer results obtained, it could be concluded that the freshest raw material gave a lower yield during salting than the other raw materials, and that this difference remained during drying and desalting. Therefore, from an economic point of view, it seems that stored raw material could be recommended for use in salting and drying. This is in accordance with Burgess et al. (1987) and Akse and Joensen (1996b). To offer a more holistic recommendation, the effect of raw material freshness for salting on sensory and microbial quality was examined.

### 3.3.5. Sensory quality

The results of the sensory analyses are presented in Fig. 8 (PCA plot). The typical texture attributes flakiness ($P < 0.001$), cohesiveness, hardness and fibrousness (all $P < 0.05$) were significantly different for the samples. The freshest raw material tended to lead to a harder desalted fish, while the oldest raw material gave a higher flakiness, probably due to more proteolytic degradation of the muscle prior to salting. Thus, freshness seemed to influence the sensory quality of the product. However, it could not be concluded which raw material gave the best sensory quality. It has been reported that the texture and taste are the most important parameter for sensory

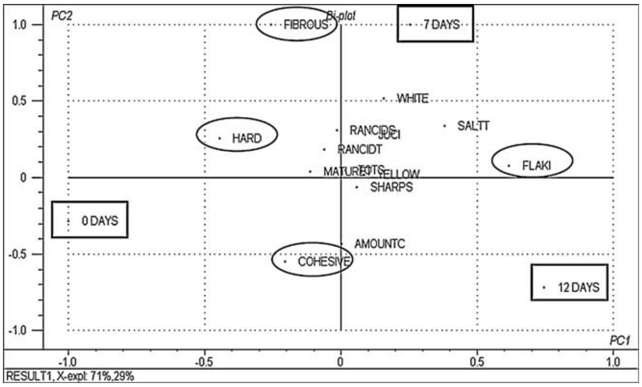


Fig. 8. Results of sensory analysis as a function of the evaluated sensorial parameters (the marked attributes had significant differences).

ranking of cooked samples of desalted cod among consumers familiar with traditionally desalted cod. (Skjerdal et al., 1999), but the study did not describe which kind of texture the consumers preferred. To our knowledge, consumer studies of desalted cod in different markets related to freshness of the raw material have not been reported.

### 3.3.6. Microbial quality

The total viable counts (TVC) in the fish prior to salting, after drying, desalting and 6 days of chilled storage at 4 °C are shown in Fig. 9. The bacterial content varied widely in the raw material, but the difference was smoothed out during salting and drying. This is in accordance with previous studies (e.g., Skjerdal et al., 1997), and was due to that the bacteria had become prevalent in fresh fish during chilled storage were eliminated during salt-curing and drying. During desalting and subsequent storage, the bacterial growth was similar in the products from all raw materials (Fig. 9), and *Psychrobacter* sp was dominating in all samples. Shortly after desalting, these bacteria represented more than 99% of the total count in the fish from the two oldest

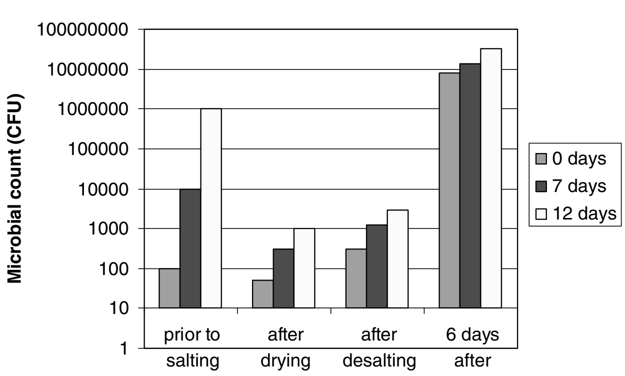


Fig. 9. Total viable count in the fish for the different process steps. The presented data represent the average of 3 samples, measured in duplicate. The standard deviation is in all cases app 0.5 log units.

old raw materials, and app 60% in the fish from the freshest (results not shown). After 6 days of chilled storage, however, *Psychrobacter* sp represented 95–100% of the total count in all samples, and a musty odor had developed. *Psychrobacter* sp have been shown to be major spoilage bacteria in desalted cod, causing a musty off-odor being sensory detectable at approximately $10^6$–$10^7$ cfu/g of fish (Bjørkevoll et al., 2003; Skjerdal et al., 2002). These bacteria are predominant in most fresh cod, but are able to survive as non-growing cells during salting and drying, and recover during desalting (Bjørkevoll et al., 2003). Based on the obtained results, it could be concluded that the freshness of the raw material have no significant effect on the storage stability of desalted cod products.

The main difference between the raw materials concerning microbial status of the desalted product was observed to be a higher diversity of the microbiota in the desalted fish from the freshest raw material. The morphology of all the salt-tolerant strains was for the 7 and 12 day old raw materials similar to that of *Psychrobacter* sp, but varied more for the freshest raw material. In order to investigate whether the additional strains originated from the fresh fish, the salt tolerance of isolated strains from the respective raw materials was tested, and the strains characterized and compared with isolates from the desalted cod immediately after desalting. For the freshest raw material, 10 of the approximately 30 tested strains grew in salt concentrations up to app 8%, and survived in 20–25% NaCl for at least 3 days, indicating that they could survive both at high and low salt concentrations. The corresponding numbers for the 7 and 12-day-old raw materials were 4 and 5 strains. Analyses of sterile desalted samples confirmed that the number of different strains in desalted fish was highest for the freshest raw material (results not shown). Most of the salt tolerant strains were isolated from the skin mucus of the fresh fish. The higher diversity of bacteria in desalted cod from the freshest raw material could therefore probably be explained by the higher amount of skin mucus on the freshest raw material. The results suggest that use of very fresh raw material for salt-curing could lead to a more unpredictable spoilage pattern of desalted fish, as local salt-tolerant bacteria with spoilage potential are likely not to be diminished during the salting and drying step.

## 4. Conclusions

The influence of cod freshness on the salting, drying and desalting stages was studied. A very important influence of cod freshness on the process yield during the salting step was observed, probably due to the influence of the rigor state in the 0 day stored cod and the modification of the cod tissue as a consequence of proteolytic enzymes, resulting in changes in the mass transfer coefficients, improving NaCl diffusion and consequently reducing the water loss, with a resulting process yield increase.

The subsequent drying and desalting stages are very similar for the different raw materials, although the differences in the total weight changes between the 0 day stored fresh raw material, and those stored for 7 and 12 days remain.

The measure of the NaCl concentration of the desalting water has been proposed as a possible way to estimate the NaCl concentration in the cod liquid phase throughout desalting and at equilibrium. The cod desalting experimental data fitted properly to a model previously proposed.

The freshness of the raw material for salting seems to influence the sensory quality of the desalted products, as the freshest raw material leads to a harder and less flaky desalted product.

The results obtained in the study of the microbial quality indicated that the desalted product obtained from the 7-day-old raw material was just as microbial stable as the achieved when using fresher raw material.

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