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Influence of mono- and divalent salts on water loss and properties of dry salted cod fillets

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A B S T R A C T

Salted cod is a product highly appreciated by consumers, especially in Southern Europe and Latin America. In recent years there has been increasing consumer demand for products with low sodium content, and this has led the salting industry to seek new salt mixtures to help to reduce Na^+ levels without producing alterations in the properties of the final product. In this study, Atlantic cod (*Gadus morhua*) was initially brined with various mixtures of salts based on NaCl, at various pH levels and including KCl, $MgCl_2$ and/or $CaCl_2$. After subsequent dry salting with NaCl, the Na^+, K^+, Ca^{2+} and Mg^{2+} cation contents were evaluated, and also their effect on water loss, salt uptake, entry of chloride, water holding capacity (WHC), water extractable protein (WEP) and hardness of the end product. A greater presence of K^+ in muscle was associated with greater water loss, salt uptake and hardness of the dry salted product. Moreover, incorporation of Ca^{2+} and Mg^{2+} negatively affected water holding capacity. These changes were not dependent on brine pH and might significantly alter the acceptability of the final product.

1. Introduction

Salting played a fundamental part in human nutrition in the course of history until well into the twentieth century. Initially, the aim of salting was the preservation of fish. Now, despite the development of other preservation methods, its low production cost, the simplicity of the process and demand for the product have meant that salted products, and in particular salted fish (especially cod) continue to be sold in high quantities. Nowadays, the main countries that produce salted cod are Iceland and Norway (Thorarinsdóttir, Bjørkevoll, & Arason, 2010), whereas the main consuming countries are those of southern Europe (mainly Portugal and Spain) and some Latin American countries, such as Brazil.

The typical salting process is dry salting or "kench salting", where the fish is filleted or "butterfly" split and stacked with alternating layers of salt (Thorarinsdottir, Arason, Bogason, & Kristbergsson, 2004). In recent years, presalting followed by dry salting has become the most popular production method (Brás & Costa, 2010; Gudjónsdóttir, Arason, & Rustad, 2011; Martínez-Alvarez & Gómez-Guillén, 2006; Thorarinsdottir et al., 2004). The aim of presalting is to increase both the water holding capacity and the yield of the salted product. Presalting can be carried out by brine injection and/or immersion in brine (Thorarinsdottir, Arason, Sigurgisladottir, Valsdottir, & Tornberg, 2011; Thorarinsdottir, Arason, Thorkelsson, Sigurgisladottir, & Tornberg, 2010). Salting by injection consists in injecting a saline solution into the muscle, thus reducing the salting time, which in turn favours rapid, homogeneous distribution of salt in the muscle. Brining, on the other hand, consists in immersing the fish for 1–4 days in a solution of salt and water (brine). The final product, lightly salted cod (approx. 2 g NaCl/100 g of product), can be marketed as it is (Gudjonsdottir et al., 2010; Lauzon, Magnússon, Sveinsdóttir, Gudjónsdóttir, & Martinsdóttir, 2009; Thorarinsdóttir, Bjørkevoll, et al., 2010), although usually it is then dry salted, losing water and gaining salt until an equilibrium is reached, and at the same time acquiring its characteristic organoleptic characteristics. The dry salted product may be subjected to a drying process prior to distribution, finally being rehydrated by the consumer before consumption. The advantages of a prior brining step are that the final product is less hard (Brás & Costa, 2010), salting is quicker and the yield is greater (Brás & Costa, 2010; Thorarinsdottir et al., 2004), although during the first 4–5 days of brining there is a loss of water accompanied by soluble protein (Del Valle & Nickerson, 1967; Martínez-Alvarez & Gómez-Guillén, 2005).

During brining there is an increase in the salt content of the muscle, owing to diffusion of the NaCl present in the brine solution. There is also diffusion of water into the brine, brought about by the difference in NaCl concentration between the muscle and the

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surrounding brine/salt (Thorarinsdottir, Arason, et al., 2010). When the salt concentration in the muscle is slightly higher than the physiological ionic strength (>0.15 mol), the inter-fibrillar spaces become larger owing to electrostatic shielding effects from salt ions binding to charged parts of the filaments, increasing the water absorption capacity of the proteins (Barat, Rodríguez-Barona, Andrés, & Fito, 2002; Offer et al., 1989; Offer & Trinick, 1983). At concentrations >0.5 mol, the thick filaments depolymerise, which leads to a significant swelling of myofibrils, reaching a maximum at salt concentrations of 0.8–1 mol, in a process known as "salting in" (Fennema, 1990; Offer & Knight, 1988). At higher concentrations (>1 mol), the muscle proteins begin to aggregate irreversibly, and this causes a lateral contraction of the myofibrillar compartment. As a result, the muscle hardens and retracts. The water holding capacity of the cells decreases and the muscle begins to lose water, in a process known as "salting out" (Kelleher & Hultin, 1991; Stefansson & Hultin, 1994). During the dry salting process, the entry of salt into the muscle increases as a result of a diffusion mechanism, and extraction of water from the tissues increases, which leads to dehydration of the fish, resulting from the greater difference in concentrations between the sample and the medium, the pressure effect due to the weight of the salt, and the capillary effect in the salt bed (Barat, Rodrıguez-Barona, Andrés, & Fito, 2003). This water loss affects the conformation of muscle proteins, causing denaturation and aggregation, and therefore changes in functional properties.

In recent years, the relationship between excessive consumption of sodium and hypertension (Winter, Tuttle & Viera, 2013) has increased demand for low-salt products, and this has encouraged the food industry to reduce the sodium content in processed products. The alternatives to salting of fish include partial substitution of NaCl by KCl, the incorporation of other salts such as calcium chloride or magnesium chloride, or the use of salt solutions with a different pH during brining (Aliño, Fuentes, Fernández-Segovia, & Barat, 2011; Braschi, Gill, & Naismith, 2009; Lee, 2011; Martínez-Alvarez, Borderías, & Gómez-Guillén, 2005; Rodrigues, Ho, López-Caballero, Bandarra, & Nunes, 2005). However, the incorporation of KCl or divalent salts in the salt mixtures used could cause changes in the sensory properties of the product (Arganosa & Marriott, 1990; Gelabert, Gou, Guerrero, & Arnau, 2003; Lauritzsen & Akse, 1995; Reddy & Marth, 1991). Also, these salts could alter the functional properties of muscle proteins (Kinsella, 1982; Morrissey, Mulvihill, & O'Neill, 1987), affecting the quality of the final product to a greater or lesser extent. Thus, the replacement of NaCl with other salts such as KCl, $MgCl_2$ or $CaCl_2$ may have a negative effect on water holding capacity (Weinberg, Regenstein, & Baker, 1984), and/or on texture (Martínez-Alvarez et al., 2005). The effect of salts on the conformational stability and solubility of proteins is a strong function of the ionic species present (Baldwin, 1996; Zhang & Cremer, 2006). Thus, interactions of protein with water are correlated with the size of the hydrated radius of the ion, so that the greater the radius, the greater the dehydration caused in the protein and vice versa. It is likely that these effects are influenced by surface load intensity, which is in turn influenced by atomic radius (Eagland, 1975; Kinsella, 1982). In general, in accordance with the Hofmeister series, cations determine effectiveness in protein hydration, at a given (low) ionic strength, in the following decreasing order: $Ca^{2+} > Mg^{2+} > Li^{+} > Cs^{+} > Na^{+} > K^{+} > NH_4^{+}$ (Baldwin, 1996; Morrissey et al., 1987; Von Hippel & Wong, 1964). During the salting of the fish, the entry of salts causes conformational changes in the proteins, which give rise to changes in solubility to a greater or lesser extent, depending on the salts used, the pH of the brine and the degree of salting achieved, among other factors. Furthermore, the pH of the medium can also cause changes in the functional properties of the muscle proteins in the salted product. Alteration of the net load of the protein molecule may increase or reduce protein–water and protein–protein interactions (Stefansson & Hultin, 1994), consequently affecting protein functionality (Lauritzsen, Akse, Gundersen, & Olsen, 2004).

The aim of this study was to relate muscle Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} contents with parameters such as water loss, salt uptake and chloride content, and with physical and physicochemical properties, such as hardness, water-holding capacity (WHC) and water-extractability protein (WEP) of dry salted cod fillets (*Gadus morhua*).

2. Materials and methods

Following capture off the coast of Iceland by a commercial fishing boat, cod (*G. morhua*) specimens were headed, gutted, washed and placed in bins, covered with ice. The bins were immediately transported to the Icelandic Fish Processing School. Cod specimens were cut lengthwise into two parts, each weighing between 500 and 900 g, and salted by immersion in brine for 36 h: fish/brine ratio 1/1.4, temperature 4 °C. The salt concentration in all brines was the same (18 g of salt in 100 mL of water). The brines consisted of distilled water and a mixture of salts containing variable quantities of sodium chloride, potassium chloride, calcium chloride and magnesium chloride (Table 1). The initial pH of the brines was adjusted to the level shown in Table 1 by addition of citric acid (19.2 g/L) or sodium hydroxide (4 g/L). Sodium chloride (NaCl) was supplied by Supreme Salt Co., Ltd.; potassium chloride (KCl) was supplied by Saltkaup Ltd.; magnesium chloride ($MgCl_2$) hexahydrate and calcium chloride ($CaCl_2$) dehydrated were supplied by Merck.

The fillets were then dry salted for 25 days by covering in Torrevieja salt (99.4 g NaCl/100 g of Torrevieja salt, max. 0.1 g Ca^{2+}/100 g, max. 0.09 g Mg^{2+}/100 g, max. 0.45 g sulphate/100 g) from Unión Salinera de España (Barcelona, Spain). The temperature throughout the process was 4 °C. The fillets were then shipped to Spain by refrigerated transport. The final water content of the dry salted samples was 53.82–57.46 g/100 g of sample. Protein content was 20.88–23.66 g/100 g, and ash content was 19.69–23.08 g/100 g. The dorsal part of each skinless fillet was chopped into 150–200 g portions (approximate dimensions: length 9 ± 2 cm, width 5 ± 1 cm, and thickness 3 ± 1 cm). All these portions were then mixed together and stored at low temperature until used.

2.1. Determination of water loss

Moisture of samples before and after brining or dry salting was firstly determined on approximately 5 g of minced muscle, by oven drying at 110 °C to constant weight, following technique 950.46 (AOAC, 2000). Results were expressed as water loss (g/100 g) in brined (WLb) and salted (WLs) fillets.

$$\begin{aligned}\text{WLb} &= \text{Mb} - \text{Mr}, \text{where Mb} \\ &= \text{Moisture of brined sample and Mr} \\ &= \text{Moisture of raw sample.}\end{aligned}$$

$$\begin{aligned}\text{WLs} &= \text{Ms} - \text{Mb}, \text{where Ms} \\ &= \text{Moisture of dry salted sample and Mb} \\ &= \text{Moisture of brined sample.}\end{aligned}$$

2.2. Determination of ions: sodium, potassium, calcium and magnesium

Approximately 5 g of muscle was reduced to ashes and homogenised in 5 mL suprapure nitric acid diluted with Milli-Q water