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# **PHYSICAL AND SENSORY CHANGES IN HEADED AND GUTTED BALTIC HERRING DURING IMMERSSED SALTING IN BRINE WITH THE ADDITION OF ACETIC ACID PART 1. WEIGHT LOSSES, COLOR OF FLESH AND ITS SENSORY PROPERTIES**

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## **ABSTRACT**

Headed and gutted Baltic herring were immersed in 16 % brine containing 0, 1, 2, 3, 4, 5, 6 or 7 % acetic acid. Weight ratio of fish to brine was 1:1. Samples were stored for two weeks at a temperature of  $8 \pm 1^\circ\text{C}$ . Changes were investigated in fish weight, weight and volume of brine, pH of flesh and brine, color parameters of flesh and its sensory properties after one and two weeks of maturation. It was demonstrated that fish brined in a 16 % solution of NaCl with an addition of 1% acetic acid were of the best quality. In the flesh of these fish, no sour ("briny") flavor could be detected, and the delicate, slightly elastic, texture was evaluated as very desirable. The addition of acetic acid into the brine improved the lightness of flesh substantially; at the same time, however, it increased weight losses of fish after brining, mainly on account of a decrease in the water content in fish flesh.

**Key words:** Baltic herring, immersed salting, acetic acid addition, physical and sensory changes

## INTRODUCTION

The addition of acids during salting of fish has been described in literature—particularly, hydrogen chloride [17] glutamic and lactic acids [7-8] and ascorbic acid [20]. These acids are mainly added to fish along with salt during dry or combined salting; they are more seldom used as solutions for dipping fresh fillets before salting for the purpose of the removal of a fishy odor [2] or the improvement in the shelf-life of lightly salted fish [13].

A 1% (v/v) addition of propionic acid to saturated brine during the preparation of salted-pressed fish was applied by Chakraborti et al. [1]. Shimomura and Matsumoto [18] examined changes in texture and proteins during acid (4%)-salt (2%) curing of mackerel flesh; however, the conditions applied were rather little typical of practical brine salting, and more typical of marinating. In the process of marinating of fish, acetic acid is widely used, where, apart from the preservative function, it is a regulator of pH for tissue cathepsin activity and an agent lightening fish flesh [10, 16]. The preservative action of acetic acid is attributable not only to lowered pH, but also to specific bacteriostatic activity [12, 14, 21].

The addition of acetic acid during the fast curing process of fish is also recommended by some factories producing salinats. In literature, however, there is not enough data about the influence of the acetic acid addition into brine upon the physical and sensory properties of flesh of brined fish. It is for this reason that these issues are the subject of this paper.

## MATERIALS AND METHODS

### Fish

Baltic herring (*Clupea harengus membrans*) were caught in Pomeranian Bay in March, stored in ice, and delivered to the laboratory while rigor mortis was still present. The herring specimens were classified as grades “D” and “S” (18–26 cm in total length), with gonads at maturity stages III–V on Mayer’s scale. The fish were deiced, headed and gutted, cleaned and drained.

### Sample preparation

Headed and gutted herring (sample weight: 750 g, in three repetitions) were immersed in a 16 % NaCl solution containing 0, 1, 2, 3, 4, 5, 6, or 7 % acetic acid, so that the weight ratio of fish to brine was 1:1. The samples were stored in glass jars 1.5 liters in volume, with a tight lid, in a cooling chamber at a temperature of 8°C for two weeks.

The samples were carefully removed from the jars without a loss in brine, placed on a filter of dense gauze in a funnel, and left for 20 min at 8°C to drain the brine.

### Fish weight and brine volume

The weight of headed and gutted fish after 1 and 2 weeks of salting was determined to 0.1 g by weight method using the WS 21 balance (Mera-Wag, Gdańsk). The volume of brine, after draining it through dense gauze, was measured to 5 ml in a measuring cylinder 1 l in volume.

### Water, fat and total protein determination

Samples of minced skinless fillets (5 g, triplicates) were dried in an oven at 105°C for 6 h, cooled and reweighed. Subsequently, these samples were taken for the determination of fat by “batch method” [23] based upon the difference in their weight before and after extraction with ethyl ether in the Soxhlet apparatus. Total nitrogen (samples of mince 1 g each, triplicates) was determined by Kjeldahl’s method in the Kjeld-Tec apparatus and recalculated into total protein using the conversion factor of 6.25.

### pH value

pH value was measured by using the N 517 OE numerical pH meter equipped with a slab electrode (TEL-EKO S.A., Wrocław, Poland).

## Color assessment

The color parameters were measured with the HunterLab colorimeter, type D25-D2, based on a white standard tile ( $L = +92.8$ ,  $a = -1.1$ , and  $b = +0.4$ ) [3, 22]. 25 g of minced skinless fillets of slated herring was put in a sample cup 8 cm in diameter, and pushed tight by hand. The color of the sample was described as  $L$  (lightness),  $a$  (“+” red, “-” green), and  $b$  (“+” yellow, “-” blue).

Color differences of samples were also explained in terms of the white index (W.I.) by using the following equation [4]:

$$\text{W.I.} = 100 - [(100 - L)^2 + a^2 + b^2]^{1/2}$$

## Sensory assessment

Seven panelists were selected from among the laboratory staff. They were trained in the basic concepts of descriptive analysis and terminology. The following techniques of assessment were applied: the texture profile on a 5-point intensity scale for each of the following properties: fibrous, hard, soft, watery, elastic, juicy.

## RESULTS

### Chemical composition of fish flesh

Baltic herring used in the tests contained relatively little fat in muscle tissue (Table 1), and as pre-spawning non-feeding herring, were characterized by a low activity of digestive enzymes, and a moderate activity of proteolytic lysosomal enzymes (unpublished data). These fish could therefore be evaluated as material typical of the beginning of the fishing season for Baltic herring of medium salting value [6].

Table 1. Chemical composition of muscle tissue of Baltic herring examined

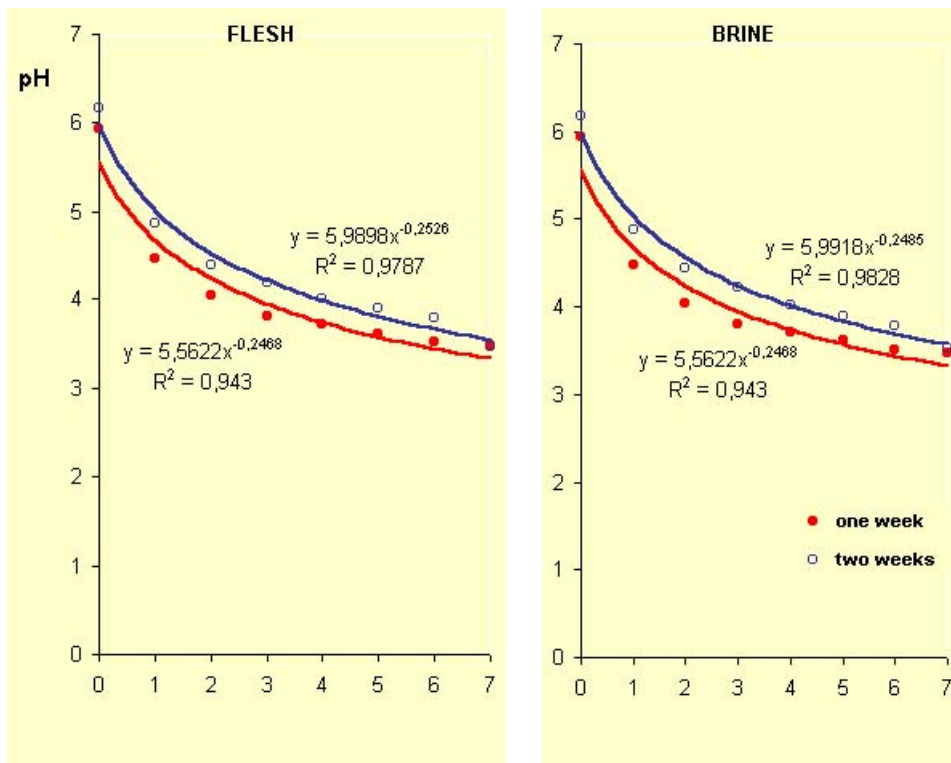
Parameters	[%]	
	$\bar{x}$	SD
Water	78.63	0.77
Lipids	4.50	0.182
Crude protein (total N * 6,25)	16.78	0.307
Pure protein <sup>x/</sup>	14.48	-
Nonprotein nitrogen	0.368	0.028

\*from a difference between total nitrogen and nonprotein nitrogen, multiplied by 6.25

### Changes in pH during salting

After one week of salting, herring flesh in the control sample (salted in a 16% NaCl solution, without acetic acid addition) had a pH of 5.8, whereas fresh herring flesh-a pH of 6.7. The addition of acetic acid to the NaCl solution (in the amount from 1 to 7%) gradually reduced pH of herring flesh, down to 3.75 at the highest concentration of the additive (Fig. 1). The relationship between the acetic acid concentration in brine and pH of flesh or brine could be described very accurately with an exponential regression equation. After the first week of salting, pH of flesh was slightly higher than pH of brine (by 3-5%), and after two weeks, it was almost identical. This indicates that a certain state of balance in the diffusion of the acid between brine and flesh was reached.

**Fig. 1. Effect of acetic acid concentration in brine on changes in pH of flesh and brine**

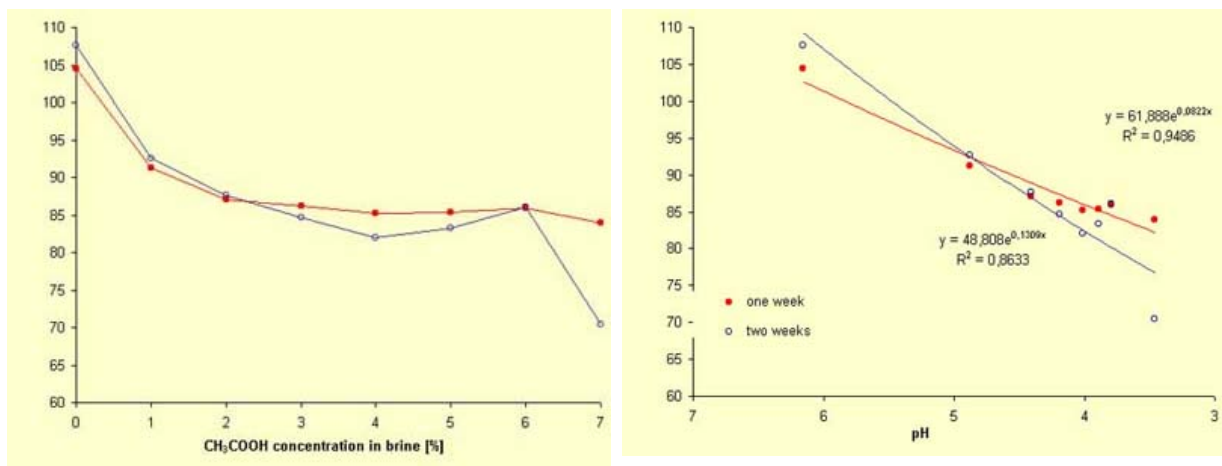


In the period between the first and the second week of salting, an increase in pH of flesh and brine was observed, which was probably caused by progressing enzymatic hydrolysis of protein. The largest increase in pH (by 0.37-0.40 unit in flesh, and by around 0.41 unit in brine) occurred in samples with a small addition of acetic acid, whereas, in the sample with the largest acetic acid addition (7%), such an increase was not detected at all.

**Changes in the weight of headed and gutted fish and the water and lipid content in flesh**

Salting in the solution of sodium chloride alone brought about an increase in the weight of headed and gutted herring by 5 and 7.5% after one and two weeks of storage, respectively (Fig. 2a). These changes resulted almost exclusively from diffusion of sodium chloride into tissue, as the water content in flesh decreased during salting (Fig. 3).

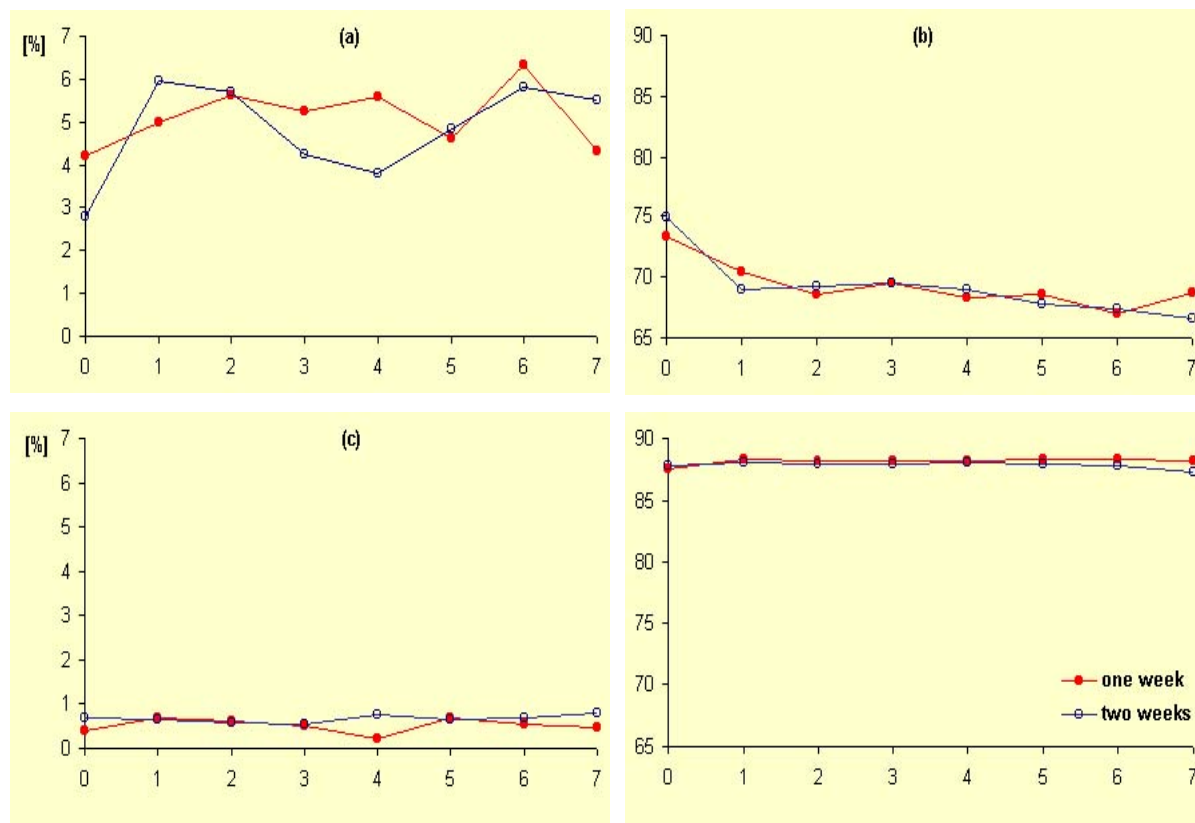
**Fig. 2. Effect of CH<sub>3</sub>COOH concentration and pH on changes in weight of headed and gutted Baltic herring after one and two weeks of salting**



Salting in the sodium chloride solution with the acetic acid addition brought about a loss in the weight of gutted and headed herring, mainly on account of a decrease in the water content in flesh. The weight of fish decreased along with an increase in the acetic acid concentration in brine, irrespective of the time of salting (1 or 2 weeks). The relationship between the weight of herring and pH of flesh was close to exponential after one week of salting and almost linear after two weeks of salting (Fig. 2b). The value of the coefficient  $b$  in the linear regression equation was -8.77, which indicates that a reduction in pH by one unit brings about a decrease in the weight of gutted and headed fish by around 9%, relative to their initial weight. Along with an increase in the acetic acid concentration in the solution, there was a decrease in the water content in flesh with a simultaneous increase in the water content in brine (Fig. 3b and 3d). However, the curves of an increase in the water content in brine along with increasing acid concentration are not so clear as the curves of a decrease in the water content in flesh, for, apart from water, also the products of the hydrolysis of flesh diffused into brine. This fact can be additionally confirmed by a lower water content in brine after two weeks of salting than after one week.

The lipid content in flesh and brine did not form a regular relationship with the acid concentration in the solution. An upward trend could, however, be observed in the lipid content in flesh within the range of the acid concentration from 1 to 2% and from 5 to 7%, and a downward trend—within the range of 2 to 4% (Fig. 3a and 3c).

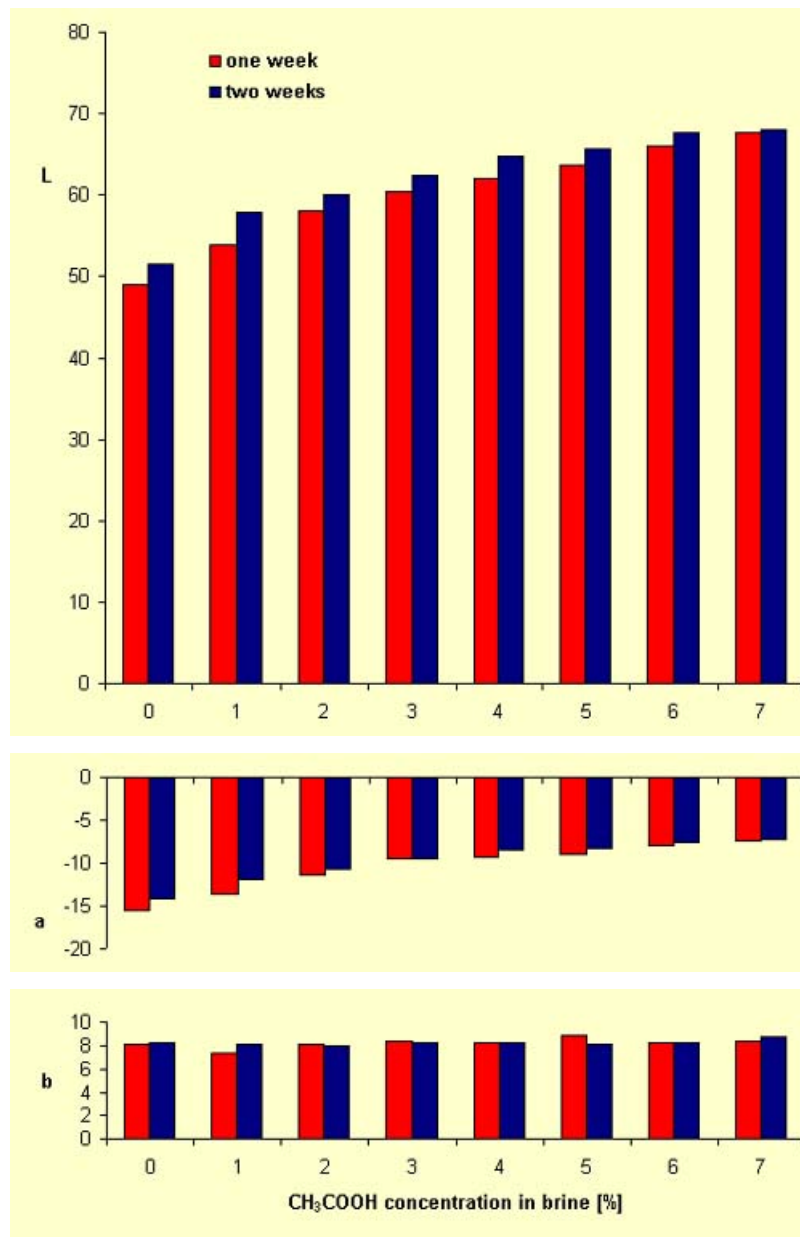
**Fig. 3. Effect of CH<sub>3</sub>COOH concentration in brine on changes in fat (a) and water (b) content in flesh and fat (c) and water (d) in brine after one and two weeks of immersed salting of headed and gutted Baltic herring**



### Changes in flesh color

An increase in the acetic acid concentration did not bring about considerable changes in the yellow hue of the color ( $b$ ); at the same time, it increased the lightness of the color ( $L$ ) noticeably. The relationship between  $L$  and the acid concentration was close to exponential (Fig. 4). This means that even a slight addition of acid to the sodium chloride solution has a clear lightening effect on the color of herring flesh. For example, after one week of salting, the lightness of the color of herring flesh increased by more than 10% in samples with a 1% acetic acid addition, and by more than 18.5% in samples with a 2% acetic acid addition.

**Fig. 4. Effect of acetic acid concentration in brine on flesh color of salted Baltic herring after one and two weeks of ripening**

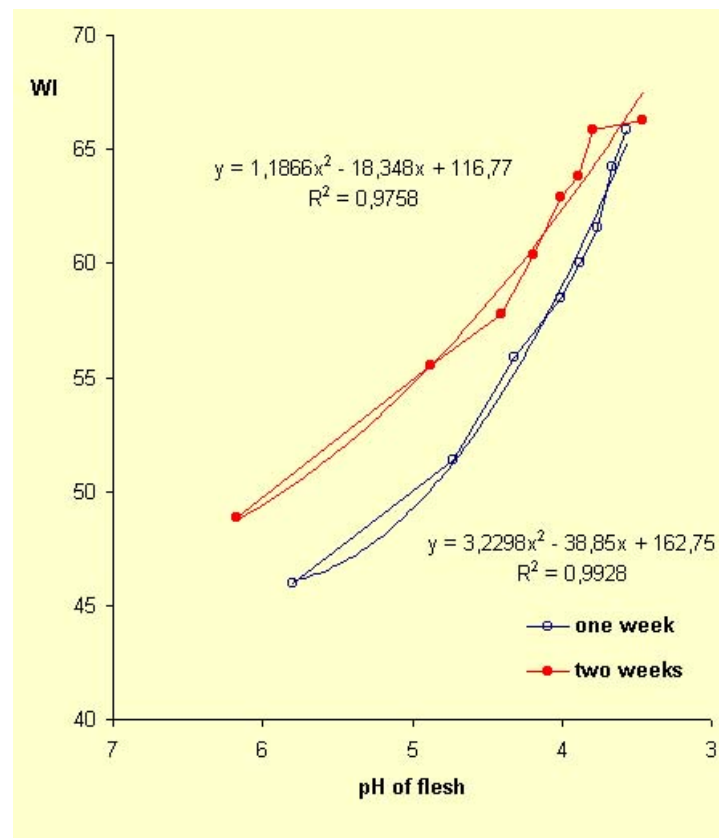
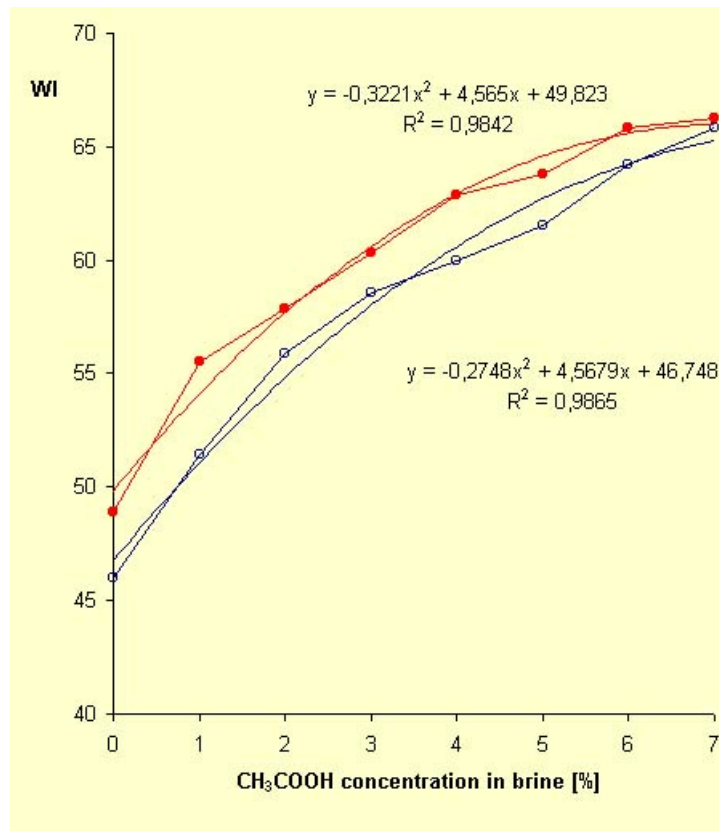


The redness of the color of herring flesh was low, which was confirmed by minus values of the chromatic coefficient  $a$ ; nonetheless, an upward trend of this coefficient along with an increase in the acetic acid concentration was noticeable, at least within the concentration range of 1–3% (Fig. 4).

The white index (W.I.) of herring flesh increased along with an increase in the acid concentration in brine, at a rate close to exponential, from around 46–48 to around 65. However, a precise description of this relationship was possible only by means of a second-power equation (Fig. 5a). A unit increment in the W.I. was clearly larger within the initial concentration range than within the whole range of the acetic acid concentration in brine. For example, within the range of 0-1, it amounted to 5.39, in the 1-2 range—to 4.48, and within the whole range (0-7 %) of the acetic acid concentration—barely to 2.64 after one week of fish salting. After two weeks of salting of fish, these values were equal to 6.67, 2.29 and 2.47, respectively. This means that even a slight addition of acid to brine has a clear whitening effect on herring flesh.

The W.I. value was obviously strictly dependent on pH of flesh. An exponential increase in the W.I. was observed along with a decrease in pH of flesh (Fig. 5b).

**Fig. 5. Relationship between W.I. and CH<sub>3</sub>COOH concentration in brine and pH of flesh after one and two weeks of imersed salting of headed and gutted Baltic herring**

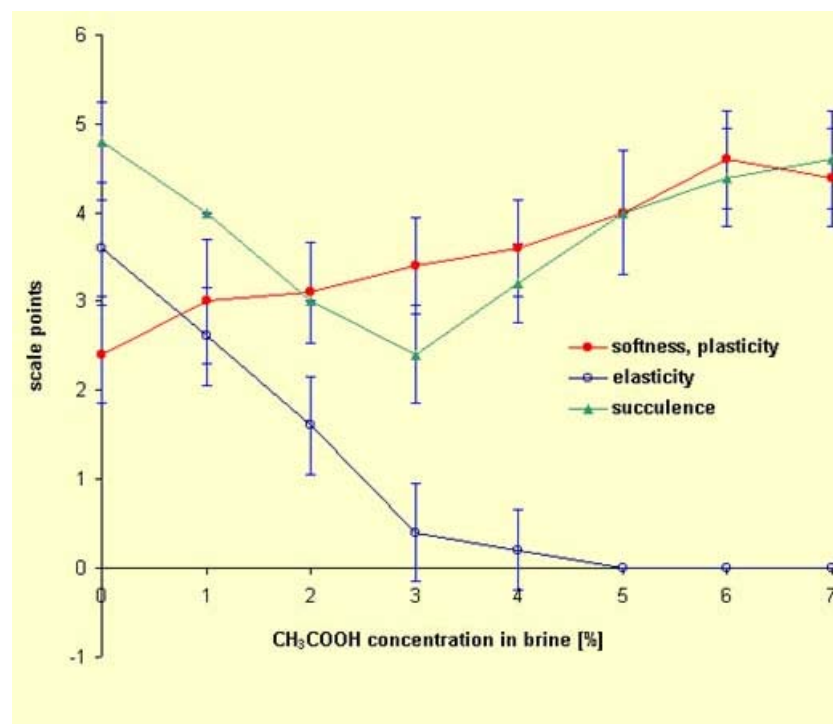


## Changes in texture

Only those features of the skinless fillets texture are discussed that turned out to be the most important for evaluating the maturation of fish flesh during salting.

Baltic herring flesh, salted in the solution of sodium chloride alone, was characterized by substantial elasticity, which, on the one hand, resulted from its relatively large water absorption, and on the other, from incomplete maturity. The acid addition to the brine reduced the elasticity of flesh noticeably, so that at a 4%  $\text{CH}_3\text{COOH}$  concentration it was hardly perceptible. Along with an increase in the acid concentration within the range of 1-3%, a decrease in flesh succulence was also observed; its consistency was defined as “dryish”, or slightly “fibrous”. The smallest succulence of flesh was observed at a 3%  $\text{CH}_3\text{COOH}$  concentration in brine, which corresponded to a pH of around 4.0. A further increase in the acid concentration within the range of 3 to 7% clearly improved flesh succulence, which increased almost to its initial level (Fig. 6).

**Fig. 6. Effect of  $\text{CH}_3\text{COOH}$  concentration in brine on changes in texture parameters of flesh of headed and gutted Baltic herring after one week of salting**



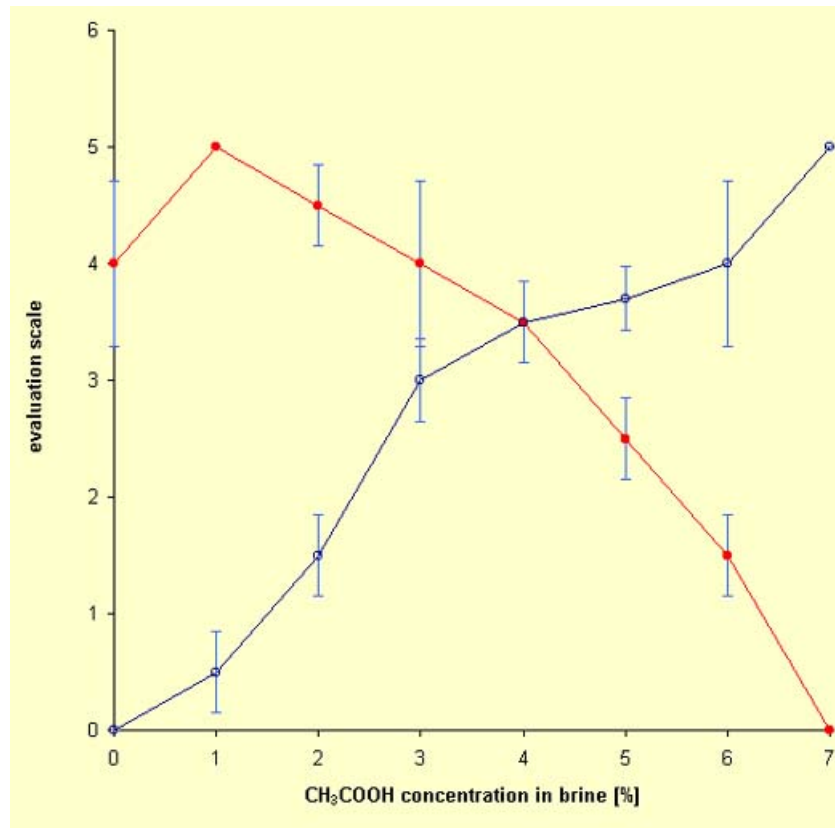
With regard to flesh texture, the following two product groups could be distinguished: a) with flesh relatively elastic and little plastic (acid concentration in the solution 1-2%), b) with flesh relatively plastic and succulent, but almost lacking in elasticity (acid concentration 4-7%). The latter group of properties was typical of marinated fish rather than salted fish.

## Flavor of flesh

Acetic acid at a concentration of 1% in the sodium chloride solution enhanced the perception of a salty flavor of flesh noticeably. In comparison with the control sample (without the acetic acid addition), flesh had a more salty flavor, sharper and slightly bitter, while “sourness” was not perceptible at all. At a 2% acetic acid concentration in the solution, the sourness of flesh was already slightly perceptible; however, the strong (stronger than in the control sample) salty flavor was still dominant (Fig. 7). Both the above groups of fish were classified as “salted fish”. An increase in the acetic acid concentration to 3% gave the flesh a salty-sour flavor and an increase to 4%-a sour-salty flavor, typical of fish marinades rather than salted fish. The perceptibility of sourness increased along with an increase in the acetic acid concentration in the solution. With an increase in the acid concentration to 6%, sourness was so strong that the saltiness of flesh was little perceptible, and at a 7% acetic acid concentration, the saltiness of flesh was not perceptible at all.



**Fig. 7. Effect acetic acid concentration in brine on the perceptibility of a salty and sour flavor in flesh of salted Baltic herring (skinless fillets were evaluated)**



## DISCUSSION

The effect of the acetic acid addition to brine on the physical and sensory properties of immersed salted Baltic herring depends upon both the acid concentration and the type of qualitative feature under consideration.

As far as the flavor and texture of flesh are concerned, two ranges of the acid concentration can be distinguished. Within low acid concentrations (1-2%), fish can be regarded as “salted”, and within higher concentrations (4-7%)-as “marinated”.

The acetic acid concentration in brine imperceptible with regard to flesh flavor and aroma does not exceed 1%. A 2% concentration still allows the classification of fish as salted, but with a sour flavor perceptible. Fish salted in 16% NaCl with a 4-5% CH<sub>3</sub>COOH addition were classified as “sour-salty”, resembling typical marinades of relatively good sensory desirability.

High acetic acid concentrations (6-7%) had an inhibitory effect on the perceptibility of the salty flavor in flesh, so that, at the highest concentration, it was not perceptible at all. Flesh was, however, evaluated as too sour, even in comparison with the flavor of classic cold herring marinades.

It should therefore be accepted that the allowable acetic acid concentration in brine used for immersed salting of fish should not exceed 1%. The presence of 1% acetic acid in brine improves the lightness and texture of Baltic herring flesh substantially. A decrease in flesh elasticity is accompanied by an increase in its softness/plasticity, which was perceived in the oral evaluation as a clearly desirable feature. A slight reduction in flesh succulence occurring at this acid concentration was not evaluated as a disadvantage, although at a 3% acetic acid concentration in brine the deterioration in flesh succulence was considerable, and part of the evaluating panelists stressed the “dryishness” of flesh, and even its slight “fibrousness”. Increasing succulence of fish flesh slated in brine at an acid concentration higher (4-6%) than a 3% concentration considered as critical was surprising (Fig. 7). This may indicate that proteolysis, rising along with a decrease in pH, not only increases the plasticity of flesh, but also inhibits the perception of its dryness, as these changes were not accompanied by a real increase in the water content in flesh (Fig. 3b).

The addition of acetic acid to brine is very effective in reducing pH of salted herring flesh, for the very process of salting (without the acid addition) brings about a substantial decrease in pH of flesh (down to around 5.8 after one week of salting). For instance, during salting in a 16% NaCl solution containing 3% CH<sub>3</sub>COOH, pH of Baltic herring flesh decreased to around 4.1 (Fig. 1) - that is, down to the value that is reached by Baltic herring marinated in a 7% NaCl and 4.5% CH<sub>3</sub>COOH solution [9].

A decrease in pH of herring flesh during salting can be explained through progressing protein hydrolysis, since a procedure is known in which protein digestibility is calculated from the drop in pH obtained after in vivo digestion of the substrate [15]. Nonetheless, although pH drop can be used to follow the cause of hydrolysis of a single substrate, and in spite of a demonstrated correlation between pH drop and in vivo protein digestibility, pH drop alone cannot serve as a measure of the extent of protein hydrolysis for the comparison of different substrates [11].

Ito et al. [5] demonstrated that an increase in gel strength of Alaska pollock meat soaked in NaCl solution was accompanied by the formation of a cross-linked myosin heavy chain in it. These changes were very similar to the case of salted meat paste induced by setting in a process of production of kamaboko gel.

The only negative result of the presence of acetic acid in brine was lower yield of fish after salting. Fish salted in the brine alone exhibited a weight increment after salting up to around 107%, and fish salted in brine with a 1% acetic acid addition-of barely 93% relative to their initial weight. Since the weight of headed and gutted fish decreased almost linearly along with a decrease in pH of flesh, it should be assumed that the main reason for this drop was decreasing water absorption resulting from protein denaturation. Muscular fish proteins exhibit the smallest water absorption at a pH of around 4 [19]. A certain compensation for the reduced product yield is an improvement in the lightness of salted Baltic herring flesh, which is noticeable even at the lowest acetic acid concentration in the solution (1 %).

## CONCLUSIONS

1. Headed and gutted Baltic herring, after 1-2 weeks ripening in 16% NaCl solution with low acetic acid concentrations (1-2%), can be regarded as "salted", and within higher concentrations (4-7%) as "marinated".
2. High acetic acid concentration (6-7%) in the brine had an inhibitory effect on the perceptibility of the salty flavour in flesh, so that, at the highest concentration, it was not perceptible at all.
3. Higher addition of acetic acid into brine improved the lightness of the herring flesh substantially, but increased weight losses of fish after brining, mainly on account of a decrease in the water content in fish flesh.
4. Allowable acetic acid concentration in 16% NaCl solution used for immersed salting of headed and gutted Baltic herring, at temperature  $5 \pm 1$  °C, should not exceed 1%.

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