

Sveriges lantbruksuniversitet Swedish University of Agricultural Sciences

Faculty of Natural Resources and Agricultural Sciences

Technical and sensory improvements of a product containing pickled herring in thick sauce

Tekniska och sensoriska förbättringar av inlagd sill i en krämig sås

Charlotte Svedberg

Independent Project in Food Science • Master Thesis • 30 hec • Advanced A2E Publikation/Sveriges lantbruksuniversitet, Institutionen för livsmedelsvetenskap, no 438 Uppsala, 2016

Technical and sensory improvements of a product containing pickled herring in thick sauce

Tekniska och sensoriska förbättringar av inlagd sill i en krämig sås

Charlotte Svedberg

Supervisor:	Jana Pickova, Swedish University of Agricultural Sciences, Department of Food Science
Examiner:	Maud Langton, Swedish University of Agricultural Sciences, Department of Food Science

Credits: 30 hec Level: Advanced A2E Course title: Independent project/degree project in Food Science - Master's thesis Course code: EX0425 Programme/education: Agricultural Programme - Food Science

Place of publication: Uppsala Year of publication: 2016 Title of series: Publikation/Sveriges lantbruksuniversitet, Institutionen för livsmedelsvetenskap Serie no. 438 Online publication: http://stud.epsilon.slu.se

Keywords: product development, clupea harengus, sauce consistency, sensory analysis, rheology, xanthan gum, hydrocolloid

Sveriges lantbruksuniversitet Swedish University of Agricultural Sciences

Faculty of Natural Resources and Agricultural Sciences Department of Food Science

Abstract

Herring aimed to be pickled is first marinated in a salt and acidic brine. The marinating process is crucial for preservation and for development of the flavor characteristic for pickled herring. Yet, a strong taste of salt and acid itself is not desired within the final product. When presented to the consumer, the herring pieces lie within a sweet and flavored cover brine or thicker sauce. In the latter case, the consistency of the sauce becomes an important matter, not only to the consumer but also from production perspective. A slimy and rubbery texture causes difficulties when the sauce is to be filled up in jars. In addition, such a consistency is typically rejected by the consumers. The aim of this project was to find out what alteration actions can be done in order to improve taste- and consistency properties of a product containing pickled herring in thick sauce. Four ingredients of the original recipe; water, sugar, oil and thickening agent, were identified as parameters possibly involved in undesired properties of a product. A test series of samples with varying amounts of these four parameters was made up. Consistency of the test samples was evaluated through rheological measurements with the original sample and a competing product as references. The salt and acid content of the herring pieces in each sample were measured and then compared within the test sample series and to the original sample. In addition, a sensory test was set up in order to evaluate whether the taste intensity of salt and acid correlated with the real salt and acid content. Concentration of oil, water and thickening agent was indicated to have a strong impact on sauce consistency while oil influenced the salt content. The flavor was dependent on both oil and sugar. Further research on how single parameters affect certain properties as well as how one parameter influences the effect of another is needed.

Keywords: product development, clupea harengus, sauce consistency, sensory analysis, rheology, xanthan gum, hydrocolloid

Sammanfattning

Inlagd sill marineras i en salt- och ättikslake innan den läggs i glasburkar tillsammans med en sötad och smaksatt sås eller lake. Marineringsprocessen är viktig för sillens hållbarhet men också för att sillens karaktäristiska smak och arom skall komma fram. En stark smak av just salt och ättika är dock inte önskvärd i slutprodukten. Då sillen läggs i en tjock sås spelar såskonsistensen en viktig roll, både för konsument och produktion. En seg och klistrig sås är svår att fylla upp i glasburkar och ogillas dessutom oftast av konsumenterna. Målet med det här projektet var att ta reda på vad som kan göras för att förbättra smak- och konsistensegenskaper hos en produkt bestående av inlagd sill i tjock sås. Med hjälp av litteraturstudier kunde fyra ingredienser i orginalreceptet; vatten, socker, olja och förtjockningsmedel, antas bidra till de oönskade egenskaperna hos produkten. Följaktligen gjordes en serie med prover där mängden av dessa ingredienser skiftade. Konsistensen hos såserna i testserien utvärderades genom reologiska mätningar där orginalprovet samt en konkurrerande produkt utgjorde referenser. Salt- och syrainnehållet hos sillbitarna i några av testproverna mättes instrumentellt och jämfördes sinsemellan samt mot orginalreceptet. Proverna jämfördes även sensoriskt av en testpanel för att kunna fastställa huruvida smakupplevelsen av salt och syra korrelerade med det verkliga innehållet. Mängden olja, vatten och förtjockningsmedel visade sig ha stor inverkan på såskonsistensen medan oljekoncentrationen spelar roll för sillbitarnas salthalt. Smaken påverkades av både oljan och sockret. Ytterligare studier om hur enskilda parametrar inverkar på specifika egenskaper samt hur mängden av en parameter påverkar effekten av en annan behövs.

Nyckelord: produktutveckling, clupea harengus, såskonsistens, sensorisk analys, reologi, xantangummi, hydrokolloid

Table of contents

Abb	reviations	7
1	Introduction	8
1.1	Aim	8
2	Literature review	10
2.1	Features of pickled herring in thick sauce	10
2.2	Effects of brining on the final product	10
2.3	Oil as an ingredient of sauces	11
2.4	Hydrocolloids for thickening and stabilization	11
2.5	Parameters influencing the effect of hydrocolloids	12
2.6	Xanthan gum	12
3	Materials and Methods	13
3.1	Project initialisation	13
3.2	Literature review	13
3.3	Raw material	14
3.4	Sauce production	14
3.5	Recipes	14
3.6	Rheology measurements	15
3.7	Salt and acid measurements	15
	3.7.1 Salt content	15
	3.7.2 Titratable acidity	16
3.8	Sensory analysis	16
3.9	Data analysis	16
4	Results	17
4.1	Rheology measurements	17
4.2	Salt and acid measurements	19
4.3	Sensory analysis	21
5	Discussion	22
5.1	Altering one parameter changes the whole formula	22
5.2	Choice of method for evaluation of consistency	22
5.3	Procedure of rheology measurements	22
5.4	Use of references	23
5.5	Outcome of rheology measurements	23
	5.5.1 Increase of both water and oil gives higher viscosity	23

	5.5.2	Decrease of oil lower the viscosity	24
	5.5.3	Xanthan gum affects viscosity	24
5.6	Salt a	nd acid content by measurements and sensory analysis	24
	5.6.1	Titratable acidity as measure of acid content	24
	5.6.2	Oil influence the diffusion of salt	25
	5.6.3	Oil contributes to a milder taste experience	25
	5.6.4	Sugar decrease the sharp taste	26
	5.6.5	Choice of assessors and vocabulary	26
6	Concl	lusion	27
-	Concl ences	lusion	27 28
Refer	ences	ements	
Refero Ackno	ences owledg		28
Refere Ackno Apper	ences owledg ndix 1	ements	28 31

Abbreviations

o/w emulsion	Oil-in-water emulsion
Pa·s	Pascal-second, SI unit of viscosity
s ⁻¹	Reciprocal- or inverse seconds, SI unit of shear rate
w/o emulsion	Water-in-oil emulsion

1 Introduction

Pickling is an ancient but still popular way of preserving herring, especially within the Nordic countries. The pickling process starts with the herring being stored in a salt and acid brine to lower pH and water activity of the fish. The brining procedure also causes a maturation of the herring flesh which is necessary for development of its characteristic flavor and texture. After brining, the fish is transferred to glass jars together with a clear brine or a thick sauce that contains sugar and spices in order to balance the sharp taste of salt and acid obtained from brining (Szymczak *et al.*, 2013; Sampels, 2015). Clear cover brine was originally the only type of accompaniment for pickling herring but thick sauces are now gaining popularity (TT, 2015). In the case of thick sauces, texture and consistency are of uttermost importance since this type of sauce adheres to the fish piece and thus belongs to the edible part of the product, as oppose to clear brine which drips of the fish prior to consumption. A thick and smooth sauce that adheres to the herring is desirable. To achieve this, the sauce formula combines an oil-in-water (o/w) emulsion with an emulsifier and some kind of thickening agent (Mandala *et al.*, 2004).

1.1 Aim

The aim is to identify parameters that can be altered in order to improve the recipe of a pickled herring product by means of sauce consistency and herring taste.

A private-label product containing pickled herring in thick sauce will be subjected to improvements within this product development project. Specific inquiries have been made by the customer regarding sauce consistency and taste of herring pieces. A sauce with less slimy consistency and herring pieces with a less distinctive taste of acid and salt is desirable.

Parameters expected to contribute to the undesired properties will be identified and a series of samples with alterations of these parameters shall be prepared based on this knowledge. The sample series will be evaluated instrumentally and sensorially whereupon the results are going to be compared to reference samples in order to state whether any of the alterations have had positive effects on taste or consistency (Laaman, 2011).

2 Literature review

2.1 Features of pickled herring in thick sauce

The product has to satisfy the consumer by taste and texture but it also has to stay stable over time (Mandala *et al.*, 2004) and not least, fit the production line. Pickled herring in thick sauce is a complex food product consisting of two different phases (i.e. herring and sauce) with a number of different features that has to be taken into account in order to succeed with recipe formulation. The sauce has to fulfill certain demands even to get produced. A too viscous sauce with rubbery consistency causes problems when to be filled in jars and should be avoided (Lorenzo *et al.*, 2008). Additionally, this texture is typically rejected by the consumers. One of the factors affecting the viscous properties is the choice of thickening agent (Saha & Bhattacharya, 2010). Presently, Xanthan gum is commonly used as a thickening agent in thick herring sauces since it is stable even at a low pH (Barbara Katzbauer, 1997).

Marinating the fish is crucial for enzymatic maturation that gives the characteristic taste and texture of pickled herring. It also lowers the pH which preserves the product and prevents it from getting affected by *Clostridium botulinum*. Nevertheless, this preservation method has to be taken into account when processing the product further. A concentrated flavor of salt and acid within the herring pieces will not be appreciated by the consumers (Sikorski, 1990). As already mentioned, the low pH also influences the choice of thickening agent.

2.2 Effects of brining on the final product

For preservation and safety, pickled herring has to keep a pH below 5.0. This is obtained by the marinating process as salt and acid diffuse into the fish when stored in marinating brine (Rodger *et al.*, 1984). Within one to three weeks of mar-

inating, salt and acetic acid reaches an equilibrium state (Sampels, 2015). The decreased pH promotes proteolytic activity which lowers the water holding capacity and causes nitrogen leakage from herring to brine. This in turn leads to weight loss and enhanced hardness of the flesh (Szymczak & Kołakowski, 2012). Denaturation of muscle proteins is reduced by fat which implies that herring pieces with high fat content keep a more tender texture compared to leaner fillet pieces (Szymczak et al., 2013). The concentrated content of salt and acetic acid within the fish is by flavor reasons not desirable within the final product (Sikorski, 1990). Sugar is known to neutralize sour taste without changing the pH and is added to the pickled herring product by being a part of the covering brine or sauce (Savant, 2001). A migration of sugar molecules to the herring flesh and a simultaneous transfer of salt and acid from meat to cover sauce is desired to decrease the salt and acidic taste of the herring. A successful transfer of molecules is dependent on water activity and chemical potential of the substances involved. The water activity of a two-phase system strives towards becoming equal in both phases. The water activity is in turn dependent on the solids dissolved in the water that similarly strives towards reaching equal chemical potential on both sides of the membrane (Hill et al., 1998).

2.3 Oil as an ingredient of cold sauces

Fat is known to increase creaminess and encapsulate flavors which makes it a popular ingredient in all kind of food products. Vegetable oils have higher viscosity than water within the temperature range 0-20°C which also could influence the consistency of liquid and semi-solid foods aimed to be consumed at low temperatures. When used in sauces, oil has to be accompanied by an emulsifier not to get separated from the water phase. A surface active component such as egg yolk or lecithin can be used. Emulsions are thermodynamically unstable and will eventually separate even when an emulsifying protein is present. One way of preventing products with long expiry date from separating is to add a stabilizing hydrocolloid (Phillips & Williams, 2009). Except for long term stabilization of the emulsion, the hydrocolloid also helps herbs and vegetable pieces to stay evenly distributed within the jar.

2.4 Hydrocolloids for thickening and stabilization

Hydrocolloids are polymers of saccharides or proteins often employed within the food industry for product improvement, especially by means of viscosity or texture (Saha & Bhattacharya, 2010). The ability of hydrocolloids to bind with water and swell provides increased viscosity to a solution. In addition, texture of a liquid or

semi-solid products are dependent on hydrocolloids in order to remain over time. This is defined by the product stability which in other words can be described as lack of negative effects (Laaman, 2011). Features common to all hydrocolloids are their ability to dissolve and disperse in water (Li & Nie, 2016). However, how and to what extent this occurs among different types of hydrocolloids makes them differently suitable depending on the product.

2.5 Parameters influencing the effect of hydrocolloids

Hydrocolloids differ from each other in what properties they show and the conditions required for optimal development. Common to all hydrocolloids is their need of getting hydrated in order to exhibit their functions properly. The extent to which a hydrocolloid is hydrated depends not just on the amount of water but also on other solvents present. Acid, salt and sugar decrease water activity which gives poorer solving capability than pure water. It is recommended to add such ingredients after the hydrocolloid has been hydrated to lower the negative effects on the hydration process (Laaman, 2011). To serve as a thickening agent, the hydrocolloid has to reach a certain concentration level called overlap concentration (C*). Below this concentration, the flow behavior is newtonian (Saha & Bhattacharya, 2010). Too high concentration of hydrocolloid may cause overstabilization that can result in a firm or gummy texture (Laaman, 2011).

2.6 Xanthan gum

Xanthan gum is an extracellular polysaccharide naturally produced by *Xanthomonas campestris*, a bacterium found on cabbage plants. The polysaccharide is commercially produced through aerobic fermentation by pure cultures with desired properties. The molecular backbone of Xanthan gum consists of a straight chain of glucose units similar to cellulose. Every second glucose unit is connected to a trisaccharide side chain with two mannose units, one connecting the side chain to the backbone and the other terminal. In between the two mannose units there is a glucuronic acid. The mannose units connected to the backbone contains an acetyl group while about half of the terminal mannose residues are linked to pyruvic acid which makes the xanthan gum molecule anionic (Garcia-Ochoa *et al.*, 2000; Phillips & Williams, 2009).

3 Materials and Methods

3.1 Project initialisation

A private-label product containing pickled herring in thick sauce is to be improved within this project. Specific inquiries regarding sauce consistency and taste of the herring pieces was made by the customer. These inquiries made up the base for the improvement work. The customer considered the sauce consistency too rubbery and slimy and described the texture as almost snotty. This became apparent when pouring the sauce off from a spoon. It then became very long instead of falling down in one piece. A sauce with "shorter" and creamier structure was desired by the customer. There is one similar competing product on the market with a sauce consistency that fulfilled the customer's idea of what the consistency should be like. It was decided to use this competing product as a reference for establishing whether any progress is made regarding sauce consistency. The taste of the fillet pieces was described as sharp of salt and acetic acid; a milder taste experience was requested by the customer.

3.2 Literature review

Literature studies were conducted in order to identify parameters assumed to contribute to the undesired herring taste and sauce consistency of the product to be improved. Databases such as Scopus and Web of Science as well as the library catalogues of Swedish University of Agricultural Sciences and Umeå University were employed for literature research. Data on raw material treatment was provided by the purchase department of the refining company.

3.3 Raw material

The fish used for sample production was North Sea Herring (*Clupea Harengus*) caught in the Northeast Atlantic in December 2015. The fresh fish was kept on ice until gutting, where head and guts were removed. The herring was then filleted and cut into 24 mm pieces. The fillet pieces were put into barrels of salt and acidic brine for maturation and storage. This took place three days after capture. The herring was stored in brine at approximately 0°C for one month at the supplier and then for further three months at approximately 2°C until usage.

3.4 Sauce production

Xanthan gum was pre-dispersed in rapeseed oil and then mixed with water for one minute in a Stephan vacuum mixer at 3000 rpm with the pressure -650 mbar. Preservatives were pre-dispersed in water and then added to the mixing bowl together with water, sugar solution, the remaining rapeseed oil and water, egg yolk powder, seasonings and acidification agents. The mixture was run for three minutes at 3000 rpm. Then dried herbs were added and the sauce was mixed for another 30 seconds at 2000 rpm with the same pressure as before. All sauces had pH values within the span 4.5 to 4.8 which is desirable from safety and preservation perspective. The sample sauces were kept at 4°C for 48 hours before put together with herring. Herring pieces and sauce were assembled in glass jars of 250 g. Each jar was filled with approximately 120 g of herring and 130 g of sauce. The pickled herring were then kept at 4°C and the jar content was reversed with three to four day intervals. After three weeks of storage the samples were evaluated instrumentally and sensorially.

3.5 Recipes

All recipes within the sample series are reformulations of Sample 1, the small scale version of the Original sauce. All samples (except for Competitor X that is produced by a competing company) contain the same ingredients but in different amounts. The only parameters altered are sugar, water, oil and Xanthan gum (Table 1). The flavoring is the same for all sauces within the series and it is identical to the original sample. In all recipes, egg yolk powder for emulsification was kept at a constant ratio in relation to oil.

 Table 1. Modifications of samples in the test series

Sample no.	2	3	4	5	6	7	8	9	10
Sugar	-14.82	-8.07	-14.82	±0.00	±0.00	-14.82	-10.66	-10.66	-10.66

Water	+14.82	+18.79	+23.7	+10.72	+0.24	+6.25	+5.48	+8.69	+2.09
Oil	±0.00	-10.25	-8.49	-10.25	±0.00	+8.21	+4.96	+1.89	+8.21
Xanthan gum	±0.00	±0.00	±0.00	±0.00	-0.24	±0.00	±0.00	±0.00	±0.00
(Egg yolk)	±0.00	-0.47	-0.39	-0.47	±0.00	+0.36	+0.22	+0.08	+0.36

The table shows how the parameters sugar, water, oil and xanthan gum have been altered among the samples within the test series. Egg yolk powder was always kept at the same ratio in relation to oil. The values are in percentage and the changes are given in relation to Sample 1 which is the small scale version of the original sample.

3.6 Rheology measurements

Rheological measurements were conducted on the samples within the sample series with the Original sample and Competitor X as references. Flow properties of the herring sauce were studied over the shear rate 0-100 s⁻¹ at 20°C using a C-VOR Bohlin Rheometer. All samples were analysed in randomly selected triplicates. The sauces were sieved through a tea sieve to reduce any solid material before conducting the measurements. Approximately 2 ml of sample was applied to the rheometer for each measurement. A parallel plate system (20 mm diameter, 1 mm gap) was employed for the measurements. The viscosity at shear rate 21.45 s⁻¹ was selected for further analysis in order to mimic the shear rate of mastication.

3.7 Salt and acid measurements

Salt and acid measurements were conducted on Sample 1, 4, 8, 9 and 10. Sample 8 and Sample 9 were selected in order to establish whether a small variation in water and oil content affects the diffusion process. Sample 4 and Sample 10 were included in case a larger variation would be necessary to observe differences. Sample 1 was selected as a reference as the formula is identical to the original sample. Herring pieces were removed from the cover sauce and minced to even consistency prior to the measurements of salt and acid.

3.7.1 Salt content

Three replicates from each sample of minced herring (0.5-1.0 g) were placed in individual beakers and dissolved in 125 ml of de-ionized water containing 0.3 % of 4N nitric acid. The salt contents of the herring pieces from each sample were measured using a Metrohm 730 sample changer. The measurements were conducted according to the instructions from the device manufacturer.

3.7.2 Titratable acidity

For each sample, 6.0 g of minced herring was weight out in a 4*4 cm bed of aluminium foil. The minced herring was then put into an E-flask of 200 ml de-ionized water together with the aluminium foil. The fish was brought to boil and after cooling, three replicates of 20 ml each were taken from every sample. Each replicate was then titrated with 0.1 M sodium hydroxide.

3.8 Sensory analysis

Sample 1, 8, 9 and 10 were tested sensorially in order to state whether the taste intensity of salt and acid within the herring pieces would correlate to the actual salt and acid content (Appendix 1-2). A two-tailed paired comparison test was performed according to the ISO 5495:2007 procedure (International Organization for Standardization, 2007). The test consisted of two sessions and in each session the assessors were instructed to indicate which of two samples having the sharpest taste. Sharpness was defined as intensity of remaining salt and acid flavour from the brining procedure. The assessors were recruited from the Agriculture and Food Science Programme at the Swedish University of Agricultural Sciences. The test was conducted with two different groups of students at two separate occasions. The first test occasion included 12 participants while eight students took part at the second occasion. The samples were presented in a reversed order at the second test occasion compared to the first one. The samples were brought from cold storage at 4°C to room temperature about one hour prior to serving. Sample preparation and test setup was arranged before the assessors entered the room. The herring pieces were pulled against the jar edge to reduce the accompanying sauce and two fillet pieces were then placed in each sample container. Each assessor evaluated four samples in total divided in two sessions with two samples in each session.

3.9 Data analysis

Mean values and standard deviations based on triplicate measurements from rheology, salt and acid data were calculated and analysed using a one-way ANOVA procedure. Tukey's HSD (Honestly Significance Different) test was adopted to identify the salt and viscosity differences. Results from the paired comparison test were compared to the critical number for significant difference obtained from a binomial table for two-sided paired comparison tests

4 Results

4.1 Rheology measurements

Measurements with a rheometer were conducted in order to compare the rheological properties of the different sauces.

Three measurements were conducted for each sauce and all samples showed a linear decrease of viscosity with an increasing shear rate similar to that of Sample 9 in Figure 1. Competitor X showed a significantly higher viscosity compared to all other samples at a shear rate of 21.45 s^{-1} (Table 2). The factory-made original sauce was not significantly different from Sample 1 which is the small scale version of the original sauce. As illustrated by Table 2, there are five samples (2, 7, 8, 9 and 10) with viscosities higher than Sample 1 and four samples (3, 4, 5 and 6) with lower viscosities. Sample 1 and Sample 6 have similar formulas except for a difference in Xanthan gum (0.47% and 0.26% respectively) and the measurement result showed a significantly higher viscosity for sample 1 compared to Sample 6 (Figure 2). When comparing 3 samples only differing in oil and water content the viscosity increased with the amount of oil (Figure 3).

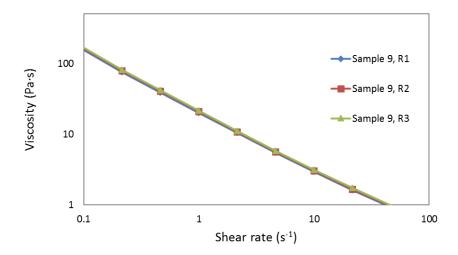


Figure 1. Viscosity as a function of shear rate. Measurements of three replicates (R1, R2 and R3) of Sample 9 show a decreasing viscosity with an increasing shear rate.

Sample	Viscosity (Pa·s)
Competitor X	2.265 ± 0.102^{a}
Sample 10	1.982 ± 0.060^{b}
Sample 7	1.965 ± 0.022^{b}
Sample 2	$1.785 \pm 0.082^{ m bc}$
Sample 9	$1.678 \pm 0.065^{\circ}$
Sample 8	$1.660 \pm 0.085^{\text{dc}}$
Sample 1	1.461 ± 0.106^{d}
Original	$1.456 \pm 0.067^{ m d}$
Sample 5	0.999 ± 0.014^{e}
Sample 3	$0.925 \pm 0.068^{\text{fe}}$
Sample 4	$0.855 \pm 0.054^{\text{fe}}$
Sample 6	$0.733 \pm 0.029^{ m f}$

Table 2. Average viscosity and standard deviation of the different samples

The results are based on three measurements per sample at $21.45s^{-1}$ and the samples are presented in decreasing viscosity order. Significant difference (P <0.05) between samples is symbolized by letters. Samples marked by dissimilar letters are significantly different.

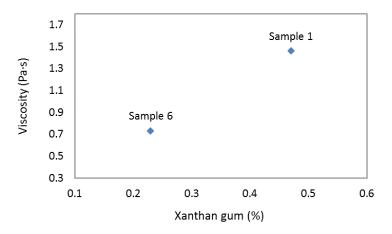


Figure 2. Viscosity as a function of Xanthan gum amount. Sample 6 and Sample 1.

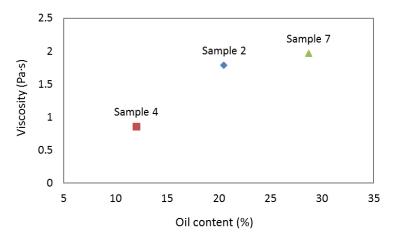


Figure 3. Viscosity as a function of oil content. Sample 4, Sample 2 and Sample 7. The sugar and xanthan gum content were identical in all of the three samples.

4.2 Salt and acid measurements

Salt and acid content of the herring pieces were measured to investigate the efficiency of the diffusion process between fillet pieces and sauce.

The only sample to stand out in terms of salt content was Sample 10 that showed a significantly higher content of salt compared to the other samples on a 5 % level (Table 3). The results were also tested for difference at a P level of 0.01 but no significant results could be seen. No statistical significance (P=0.05) could be observed from the acid results (Table 3).

Table 3. Average salt and acid content with standard deviations

Sample	Salt content (%)	Titratable acidity (g/l)
Sample 1	4.46 ± 0.02^a	1.2 ± 0^{a}
Sample 4	4.44 ± 0.20^{a}	1.4 ± 0^a
Sample 8	4.56 ± 0.06^{a}	1.3 ± 0^a
Sample 9	4.58 ± 0.03^{a}	1.3 ± 0^a
Sample 10	4.86 ± 0.05^{b}	1.4 ± 0^a

The results are based on three measurements per sample. Significant difference (P <0.05) between samples is symbolized by letters. Samples marked by dis-similar letters are significantly different.

4.3 Sensory analysis

The salt and acid intensity of the herring pieces were evaluated sensorially (Figure 4) to be compared to the actual salt and acid content (Table 3).

Results from session one show that 14 out of 20 assessor thought Sample 9 had a sharper taste than Sample 10 which is significant on a 20 % level. In several test sheets there were comments dropping words synonymic to sharp, such as pungent (the Swedish word frän). Some assessor described Sample 9 as unpleasant and more "fishy" compared to Sample 10. There were also some comments stressing that the acidity differed between the samples.

In session two there was one assessor that did not feel any difference between Sample 1 and Sample 8, that is why the number of assessors is 19 instead of 20. Of 19 assessors 15 thought that Sample 8 had a sharper taste than Sample 1 which is significant on a 5 % level. There were several comments regarding high acidity of Sample 8. One opinion stated that Sample 1 was too sweet and another that the sweetness was well balanced. Synonyms to sharp was used by the assessors to comment Sample 8.

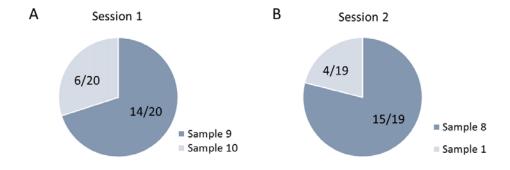


Figure 4. (A-B) Paired comparison test indicating sharpness performed by students at the Agriculture and Food Science Programme in April 2016. Comparison between Sample 9 and Sample 10 in session one and between Sample 8 and 1 in session two.

5 Discussion

5.1 Altering one parameter changes the whole formula

The development of a food recipe for industry is a complex process influenced by many aspects such as economy, customer demands and operative factors. In food recipes employed within the present food company, the amount of each ingredient is specified in percentage. This means changes in the amount of a single constituent will change the percentage amount of each and every ingredient in the recipe. The percentage content of some ingredients might be fixed from the beginning of the process due to product safety or customer demands. This could be seen as the recipe contains a limited space. Therefor the development of a new recipe often implies a number of compromises.

5.2 Choice of method for evaluation of consistency

Measurements with a rheometer were conducted in purpose of obtaining results that could be used for evaluation of the consistency improvement part of the project. The possibility of using a Texture analyzer for evaluation of the specific parameter stickiness was considered but rejected when the type of sauce to be analyzed turned out to be too thin for measurements with the Texture Analyzer available. A Rheometer was instead used to analyze the overall rheological properties.

5.3 Procedure of rheology measurements

Each sample was evaluated in triplicates. The results showed that all samples, including the factory-made ones, displayed viscoelastic properties which was expected due to the content of Xanthan gum (Figure 2). The viscosity at shear rate

21.45s⁻¹ was selected for analysis in order to mimic the shear rate occurring in mouth during mastication (Chung *et al.*, 2012).

5.4 Use of references

Sample 1 has a formula identical to the original sauce which is to be improved and Competitor X is the sample to be emulated. Significant differences between Competitor X and Sample 1 enable using these samples as references when evaluating whether samples from the test series have rheological properties better or worse than Sample 1. To begin with, it is clear that at least some of the alternated parameters sugar content, water content, oil content and Xanthan gum have an impact on the sauce viscosity since the viscosity turned out to differ between the samples. However, it is difficult to predict which parameter affecting the viscosity to what extent when it is not possible to change one parameter without changing the percentage of the remaining parameters as well.

5.5 Outcome of rheology measurements

5.5.1 Increase of both water and oil gives higher viscosity

All samples in which the sugar content was decreased and replaced by an increased content of oil and water have higher viscosity than Sample 1, regardless of the ratio between oil and water in the sample. An increased fraction of water has been reported to increase the viscosity of a surfactant stabilized water-in-oil (w/o) emulsions (Al-Yaari et al., 2014). In contrast, the viscosity of o/w emulsions has been shown to decrease with an increasing fraction of water. Stronger interaction between oil droplets due to shorter inter-droplet distances was presented as a possible explanation (Thakur et al., 2007). Perhaps this is also true for the water droplets in w/o emulsions. If so, the fraction of dispersed phase, regardless of whether it is water or oil, could be an important parameter for viscosity of an emulsion. To investigate this hypothesis further it is necessary to know the character of the emulsions within the sample series. Besides fraction size of oil and water, type and amount of emulsifier employed play a great role for whether an o/wor a w/o emulsion is formed (Zhang et al., 2015). According to the Bancroft rule, egg yolk can serve to emulsify all types of emulsions since it has both a hydrophilic and hydrophobic part (Ruckenstein, 1996). Even concentration of salt influence the phase distribution at some occasions (Zhang et al., 2012). Since changes in conductivity and fluorescent intensity typically take place when a phase inversion occurs (Ozhovan, 1993) these parameters could be measured in order to state whether the mixture is an o/w or w/o emulsion. Another option would be to use

microscopy for the determination of emulsion type (Zhang *et al.*, 2015). In addition to emulsion composition, droplet size is suggested to affect the viscosity of emulsions. Finer emulsions with small droplets generally exhibit higher viscosity than coarser emulsions (Pal, 1996). Also the microstructure could be investigated further by employing microscopic techniques (Fieber *et al.*, 2011).

5.5.2 Decrease of oil lower the viscosity

As opposite to the samples containing an increased amount of both oil and water (Sample 7, 8, 9 and 10), samples with an increased amount of water but a decreased amount of oil (Sample 3, 4 and 5) displayed lower viscosities than Sample 1. This indicates that oil influences the viscosity. This is further encouraged by the results from a comparison between three samples only differing by water and oil content which showed an increasing viscosity with increasing oil content and decreasing water content (Figure 3).

5.5.3 Xanthan gum affects viscosity

Significantly different viscosities for two samples with different Xanthan gum concentrations (Figure 2) proves that Xanthan gum influence the viscosity. However, this thickening agent has in literature been pictured as a contributor of slimy, and when overdosed, even rubbery texture (McKenna, 2003). Taking this knowledge into account, xanthan gum would probably have to be exchanged for another thickening agent in order to get rid of the slimy appearance entirely.

Starch is described to provide thickness while keeping a "short" structure. Unfortunately, most starch types are dependent on a rise of temperature in order to swell. This questions whether starch would be a suitable thickening agent for pickled herring products since the production process does not include any heat treatment. Furthermore, the low pH would in combination with heat cause native starch to hydrolyze (Olsson *et al.*, 2013). A modified cold-swelling starch that tolerates acidic conditions may be an alternative.

5.6 Salt and acid content by measurements and sensory analysis

5.6.1 Titratable acidity as measure of acid content

Acid-base-titration was selected for analysis of residual acetic acid in herring after being stored in thick sauce for three weeks. Titratable acidity gives a measure of the total amount of hydrogen ions present in the sample. Both associated and dissociated ions contribute to sour taste why titratable acidity was employed instead of pH which only measures disassociated hydrogen ions. Titration includes a moment of color estimation that could be considered rather subjective but when the aim is to compare acid content among a group of samples this method is suitable.

5.6.2 Oil influence the diffusion of salt

Sample 10 had a significantly higher in salt content compared to the other samples. This could be a result of the high oil-to-water ratio. Studies have shown that diffusion of salt and acid from brine into the herring is inhibited by a high content of fat in the fish (Rodger *et al.*, 1984). Perhaps there is a similar correlation appearing in the reversed diffusion process, when salt and acid migrates from the fish to the surrounding sauce. There have been studies on how diffusion of solutes and migration of water molecules takes place during the brining process of herring but there is no detailed literature available on how the diffusion processes proceeds when the fish is placed in the final, thicker sauce. It is clear that diffusion of solutes and migration of water molecules in a two-phase food system are dependent on many parameters. It would be interesting to further investigate how thermodynamic properties such as water activity affects the exchange of molecules. Nuclear Magnetic Resonance is reported as a technique capable for investigation of molecular migration and could be worth trying (Carini *et al.*, 2013).

5.6.3 Oil contributes to a milder taste experience

When Sample 10 was compared to Sample 9 in terms of sharp taste, a majority of the assessors picked Sample 9 as sharpest (Figure 4), in contrast to the actual salt content (Table 3). These numbers do not present proof of detectable difference between the samples but may still show a tendency of detectability (Weisbjerg *et al.*, 2013). This indicates that perception of salt is influenced by other parameters than just the actual salt content, as suggested by W-Y Kuo and Y Lee (Kuo & Lee, 2014). Oil and water are the only parameters differing between Sample 9 and Sample 10 why at least one of these ingredients could be assumed to influence the oral perception of salt. There are different theories on how salt perception is affected by oil concentration. Lynch et al. suggest that salt perception is suppressed by oil because the fat is creating a mouth-coating film that coats the taste buds and blocks the taste receptors (Lynch *et al.*, 1993). This could be a reason why Sample 9 was considered more sharp in taste than Sample 10. The mouth coating theory is supported by other sources as well but Valentová and Pokorný argue that salt and acid ions are small enough to penetrate such a layer (Valentová & Pokorný, 1998).

5.6.4 Sugar decrease the sharp taste

In the second session where Sample 8 was presented along with Sample 1, 15 assessors out of 20 thought that Sample 8 had the sharpest taste (Figure 4). These numbers are significant at a 5 % level and indicates a detectable difference in salt perception between the samples. Sample 1 and Sample 8 do not only differ in water and oil content; they also contain diverse concentrations of sugar. As already been mentioned in the theory part, sugar is known to neutralize sour taste. This makes sense when analyzing the results from session two since the sample with higher sugar concentration was considered less sharp in taste, even though the sharper sample contained more oil. Further analysis of single factors would be necessary to define to what extent specific parameters affect the perception of salt and acid.

5.6.5 Choice of assessors and vocabulary

The Paired comparison test is described as a method that can be used to detect differences between two samples based on intensity of specified attributes. No panel training is required as long as the assessors are familiar with the vocabulary adopted to define the attributes to be evaluated (Meilgaard et al., 1999). For the two test sessions conducted within this study, the term sharp was employed to describe the taste of residual acetic acid and salt from the marinating process. This word was selected because of its common occurrence within the industry. The assessors taking part in the test were all students at the Agriculture Programme directed towards Food Science at the Swedish University of Agricultural Sciences. The choice of participants was based on the belief that they all possess a general interest of food and some knowledge about the present product type. This probably enhanced the chance of the participants taking the task seriously. Prior to the test the term "sharpness" was presented and explained to the panelists. The comments given throughout both sessions mainly touched upon the acidity which gives reason to believe that the acid taste was easier to identify than the taste of salt. In the test sheets, many of the comments contained words being synonyms of the word sharp which confirms that the term sharp was appropriate to use.

6 Conclusion

Water and oil are important parameters for viscosity in context of thick sauces for pickled herring. A simultaneous increase of both oil and water resulted in sauces with increased viscosity while a decrease of oil resulted in lower viscosity. The mechanisms behind these actions need to be further investigated but might be connected to the higher viscosity of oil compared to water as well as the type of emulsion formed and the droplet size distribution.

Hydrocolloids also turned out to be an important matter for rheological properties of sauces. This study indicated a rise of viscosity when the concentration of Xanthan gum was increased from 0.24 % to 0.47 %. However, the literature claims that Xanthan gum contributes to the undesired slimy and "long" structure observed. Consequently, other hydrocolloids should be considered for employment in order to get rid of the unwanted texture completely. Nevertheless, more data on how Xanthan gum is influenced by other ingredients, such as sugar, could probably be used to improve sauce consistency to a certain degree without changing any ingredients. Future studies on the subject of sauce consistency would gain reliability if managing to measure and evaluate the particular parameters of interest (such as sliminess) more specifically than what has been possible in the present study.

It is well known that molecules of salt and acid penetrates the herring flesh when stored in brine for preservation. The molecule migration is to some extent obstructed by the fat in the fish. A similar mechanism seems to occur also when herring is placed within the final sauce. Herring covered by an oily sauce did not drop as much salt as when placed in sauce with lower oil content.

Eventually one could state that it is not only the actual salt content that sets the taste experience of the product. Both sugar and oil were ingredients shown to decrease the sharpness of remaining salt and acetic acid from the brining process.

References

- Al-Yaari, M., Al-Sarkhi, A., Hussein, I. A., Chang, F. & Abbad, M. (2014). Flow characteristics of surfactant stabilized water-in-oil emulsions. *Chemical Engineering Research and Design*, 92(3), pp 405–412.
- Carini, E., Curti, E., Littardi, P., Luzzini, M. & Vittadini, E. (2013). Water dynamics of ready to eat shelf stable pasta meals during storage. *Innovative Food Science & Emerging Technologies*, 17, pp 163–168.
- Chung, C., Degner, B. & McClements, D. J. (2012). Rheology and microstructure of bimodal particulate dispersions: Model for foods containing fat droplets and starch granules. *Food Research International*, 48(2), pp 641–649.
- Fieber, W., Hafner, V. & Normand, V. (2011). Oil droplet size determination in complex flavor delivery systems by diffusion NMR spectroscopy. *Journal of Colloid and Interface Science*, 356(2), pp 422–428.
- Garcia-Ochoa, F., Santos, V. E., Casas, J. A. & Gomez, E. (2000). Xanthan gum: production, recovery, and properties. *Biotechnology advances*, 18(7), pp 549–579.
- Hill, S. E., Ledward, D. A. & Mitchell, J. R. (1998). Functional Properties of Food Macromolecules. Springer Science & Business Media. ISBN 978-0-7514-0421-0.
- International Organization for Standardization (2007). ISO 5495:2007: Sensory analysis Methodology – Paired comparison test. Swedish Standard Institute.
- Kuo, W.-Y. & Lee, Y. (2014). Effect of Food Matrix on Saltiness Perception-Implications for Sodium Reduction. *Comprehensive Reviews in Food Science and Food Safety*, 13(5), pp 906–923.
- Laaman, T. R. (Ed) (2011). Hydrocolloids in food processing. Ames, Iowa: Wiley-Blackwell. (IFT Press series). ISBN 978-0-8138-2076-7.
- Li, J.-M. & Nie, S.-P. (2016). The functional and nutritional aspects of hydrocolloids in foods. *Food Hydrocolloids*, 53, pp 46–61.

- Lorenzo, G., Zaritzky, N. & Califano, A. (2008). Modeling rheological properties of low-in-fat o/w emulsions stabilized with xanthan/guar mixtures. *Food Research International*, 41(5), pp 487– 494.
- Lynch, J., Liu, Y.-H., Mela, D. J. & MacFie, H. J. H. (1993). A time—intensity study of the effect of oil mouthcoatings on taste perception. *Chemical Senses*, 18(2), pp 121–129.
- Mandala, I., Savvas, T. & Kostaropoulos, A. (2004). Xanthan and locust bean gum influence on the rheology and structure of a white model-sauce. *Journal of Food Engineering*, 64(3), pp 335–342.
- McKenna, B. M. (2003). Texture in Food, Volume 1 Semi-Solid Foods. 1. ed Woodhead Publishing. ISBN 978-1-85573-673-3.
- Meilgaard, M., Civille, G. V. & Carr, B. T. (1999). Sensory evaluation techniques. 3rd ed. Boca Raton, Fla: CRC Press. ISBN 978-0-8493-0276-3.
- Olsson, E., Menzel, C., Johansson, C., Andersson, R., Koch, K. & Järnström, L. (2013). The effect of pH on hydrolysis, cross-linking and barrier properties of starch barriers containing citric acid. *Carbohydrate Polymers*, 98(2), pp 1505–1513.
- Ozhovan, M. I. (1993). Dynamic uniform fractals in emulsions. *Journal of Experimental and Theoretical Physics*, 77(6), pp 939–943.
- Pal, R. (1996). Effect of droplet size on the rheology of emulsions. AIChE Journal, 42(11), pp 3181-3190.
- Phillips, G. O. & Williams, P. A. (2009). Handbook of Hydrocolloids. CRC Press. ISBN 978-1-84569-414-2.
- Rodger, G., Hastings, R., Cryne, C. & Bailey, J. (1984). Diffusion Properties of Salt and Acetic Acid into Herring and Their Subsequent Effect on the Muscle Tissue. *Journal of Food Science*, 49(3), pp 714–720.
- Ruckenstein, E. (1996). Microemulsions, macroemulsions, and the Bancroft rule. *Langmuir*, 12(26), pp 6351–6353.
- Saha, D. & Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: a critical review. *Journal of Food Science and Technology*, 47(6), pp 587–597.
- Sampels, S. (2015). The effects of processing technologies and preparation on the final quality of fish products. *Trends in Food Science & Technology*, 44(2), pp 131–146.
- Savant, L. (2001). Suppression of sourness in binary and tertiary model mixture solutions. [online], Available from: http://ir.library.oregonstate.edu/xmlui/handle/1957/25906. [Accessed 2016-03-15].

- Sikorski, Z. E. (1990). Seafood: Resources, Nutritional Composition, and Preservation. CRC Press. ISBN 978-0-8493-5985-9.
- Szymczak, M. & Kołakowski, E. (2012). Losses of nitrogen fractions from herring to brine during marinating. *Food Chemistry*, 132(1), pp 237–243.
- Szymczak, M., Szymczak, B., Koronkiewicz, A., Felisiak, K. & Bednarek, M. (2013). Effect of Cover Brine Type on the Quality of Meat from Herring Marinades: Effect of cover brine on marinades.... Journal of Food Science, 78(4), pp S619–S625.
- Thakur, R. K., Villette, C., Aubry, J. M. & Delaplace, G. (2007). Formulation–composition map of a lecithin-based emulsion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 310(1–3), pp 55–61.
- TT (Tidningarnas Telegrambyrå). (2015). *Krämig sill strömmar till*. Available from: http://www.gp.se/nyheter/sverige/1.2750917-kramig-sill-strommar-till. [Accessed 2016-03-10].
- Valentová, H. & Pokorný, J. (1998). Effect of edible oils and oil emulsions on the perception of basic tastes. *Food / Nahrung*, 42(6), pp 406–408.
- Weisbjerg, M. R., Larsen, M. K., Hymøller, L., Thorhauge, M., Kidmose, U., Nielsen, J. H. & Andersen, J. B. (2013). Milk production and composition in Danish Holstein, Danish Red, and Danish Jersey cows supplemented with saturated or unsaturated fat. *Livestock Science*, 155(1), pp 60– 70.
- Zhang, J., Li, L., Wang, J., Sun, H., Xu, J. & Sun, D. (2012). Double Inversion of Emulsions Induced by Salt Concentration. *Langmuir*, 28(17), pp 6769–6775.
- Zhang, T., Xu, Z., Cai, Z. & Guo, Q. (2015). Phase inversion of ionomer-stabilized emulsions to form high internal phase emulsions (HIPEs). *Phys. Chem. Chem. Phys.*, 17(24), pp 16033–16039.

Acknowledgements

This project was conducted in cooperation with a seafood company who requests to be anonymous. I would like to thank my supervisor at the company for all support and encouragement. Warmest thanks also to the rest of the crew at the company for all help and for hosting me during these four months. Moreover, I want to thank my supervisor Jana Pickova at SLU for valuable guidance through the process. I am also very grateful to all students who took part in the sensory test. Eventually I want to express my deepest gratitude to Patricia Lopez Sanchez for helping me out with the rheology measurements and for providing me with precious advice for the report. Appendix 1 Paired Comparison test, Test sheet A

Sensoriskt test av inlagd sill Paired Comparison Test

Del 1 - Smaktest

Bedömning av skarphet hos sillbitarna

Smaka först på proverna <u>från vänster till höger</u> innan du eventuellt går tillbaka och smakar igen. Gör sedan din bedömning och ange ett av svarsalternativen. Om du inte upplever någon skillnad mellan proverna (eller att proverna inte är jämförbara) skall ett alternativ ändå anges och en kommentar lämnas i kommentarsfältet.

Smaka först på de två prover som ligger på provplattorna närmast dig (vänster först) och besvara fråga 1. Provet kan spottas ut efter provsmakningen. Skölj munnen med vatten efter provomgången och provsmaka sedan de två proverna på plattorna längre bort (vänster först) och besvara fråga 2.

1. Vilket prov upplever du som skarpast i smaken?

□ 573 □ 378

2.	Vilket prov upplever du som skarpast i smaken?
	□ 862
	□ 371

Appendix 2 Paired Comparison test, Test sheet B

Sensoriskt test av inlagd sill Paired Comparison Test

Del 1 - Smaktest

Bedömning av skarphet hos sillbitarna

Smaka först på proverna <u>från vänster till höger</u> innan du eventuellt går tillbaka och smakar igen. Gör sedan din bedömning och ange ett av svarsalternativen. Om du inte upplever någon skillnad mellan proverna (eller att proverna inte är jämförbara) skall ett alternativ ändå anges och en kommentar lämnas i kommentarsfältet.

Smaka först på de två prover som ligger på provplattorna närmast dig (vänster först) och besvara fråga 1. Provet kan spottas ut efter provsmakningen. Skölj munnen med vatten efter provomgången och provsmaka sedan de två proverna på plattorna längre bort (vänster först) och besvara fråga 2.

- 1. Vilket prov upplever du som skarpast i smaken?
 - □ 573 □ 378

2.	Vilket prov upplever du som skarpast i smaken?
	□ 862
	□ 371

Recipe alterations for improvements of sauce consistency and herring piece taste in a product containing pickled herring in thick sauce

Pickling is an ancient way of preparing herring that remains popular especially in the Nordic countries. The fish is first marinated in a brine containing salt and acetic acid. This procedure helps to preserve the fish by changing its physical properties so that no hazardous bacteria or molds can grow. It also promotes tenderizing and flavor development of the flesh. Even though salt and acid is favorable during the marinating process, a strong taste of salt and acid within the fish pieces are not desirable within the final product. The fish pieces are presented to the consumer in a cover sauce containing sugar and other seasoning such as onions or mustard in order to make the herring more appealing. The cover sauce consists of either a clear brine or a thicker sauce. Consistency is an important property of a thick sauce since it adheres to the herring piece and thus belongs to the edible portion of the product in contrast to a clear brine which drips off. The aim of this project was to improve sauce consistency and taste of the herring pieces in a product containing pickled herring in thick sauce.

The product subjected to improvements was a "private label" product which means it is produced by one manufacturing company but sold under another company's brand name. In this case, a brand owner had made specific inquiries regarding one of their products containing pickled herring in thick sauce. The brand owner wanted the sauce to be less slimy and rubbery in consistency and they want the herring pieces to taste less of salt and acid. A lot of scientific articles about herring, sauce consistency and chemical processes that takes place in pickled herring, were read in order to investigate which parameters that could be contributing to the undesired properties of the product. Four of the sauce ingredients; water, oil, sugar and thickening agent were suspected to be involved in sauce consistency and herring taste of the product.

A series of samples similar to the original product but with varying amounts of water, oil, sugar and thickening agent were prepared and evaluated in order to establish whether alteration of these ingredients would improve the product according to the brand owner's demands. Different methods were employed for evaluation of the samples.

The consistency was evaluated by testing the samples with an instrument called a Rheometer. A Rheometer measures the thickness (even called the viscosity) of a fluid. By measuring the viscosity of the samples within the sample series and then compare these values to the values of the original sauce and a competing product with good consistency, one can conclude which alterations have had positive and negative effects on sauce consistency. I.e., samples with a viscosity similar to the competing product are considered good. One of the conclusions drawn from the measuring results was that an increase of oil and water rises the viscosity which means the consistency gets more similar to the competing product and thus better fulfills the brand owner's demands. In addition, the thickening agent turned out to be crucial for the viscosity. The thickener used in this recipe could perhaps be changed for another type of thickening agent but it should not be excluded without replacement.

While storing the herring pieces in marinade, salt and acid migrates into the herring flesh. When assembling the herring together with cover sauce, one conversely wants salt and acid to migrate from herring pieces to cover sauce and instead bring sugar and species to enter the herring pieces. These events occur by a process called diffusion and is known to happen more or less effectively depending on the ingredients. The only parameter indicated to affect the diffusion process was the oil. A higher content of oil within the sauce inhibited the migration of salt from herring to cover sauce. This was established by measuring the salt content within the herring pieces in the series samples and then comparing them to each other.

Eventually, the taste of some of the test samples were evaluated by a taste panel in order to state whether the true salt content could be detected when tasting the samples. This was done by letting the taste panel try the samples in pairs and then indicate which of the two samples having the sharpest taste. Most of the panel participants did not recognize the herring pieces with higher salt content as sharper in taste. This suggests that there are more parameters than just actual salt content that influences the taste experience. By the results from this test, sugar and oil were identified as ingredients having an ability to tone down the sharpness.