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THE EFFECT OF TWO CRYOPROTECTANT MIXTURES ON FROZEN SURUBÍ SURIMI

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Abstract - "Surimi" itself is not a food; it is an intermediate phase of the production of "kamaboko"(a gel formed by the addition of salt to the surimi and direct heating to 80-90ºC) and a series of high-priced shellfish analogs. The protective effect that two cryoprotectant mixtures exerted during freezing and frozen storage of frozen surimi of surubí (*Pseudoplatystoma coruscans*) on the functional quality of the gels prepared was studied. The selected washing conditions selected to obtain an acceptable functional quality of gels prepared from frozen surimi (25% extracted proteins and of final moisture) using the response surface methodology were wash temperature, 18ºC; washing time for each of the three washing cycles, 4.62 min. and water-mince ratio, 3.5:1. Cryoprotectant mixtures used were sucrose/sorbitol (1:1) and maltodextrin/sorbitol (1:1) and they were added (8%) to the washed and drained minced fish before freezing. To evaluate the functionality of the frozen surimi during six months of storage, the penetration test to measure the gel strength was chosen; samples were assessed at 4, 45, 90 and 180 days of frozen storage. Results showed that even with the cryoprotectants freezing decreased gel strength, since it produced a decrease of almost 32% in the strength of the gel prepared with fresh surimi. However, the two cryoprotectant mixtures tested showed very good behaviour throughout frozen storage; specially at 45 and 90 days of storage the surimi gels with the sucrose/sorbitol mixture had a greater resistance than those with maltodextrin/sorbitol.
Keywords: gel strength, frozen storage of surimi, protein functionality, surubí surimi and cryoprotectant.

INTRODUCTION

Surimi is a wet, frozen concentrate of the myofibrillar proteins of fish muscle (Lanier 1986). The technology for obtaining frozen surimi derived from warm-water fish species can be an interesting alternative for better preservation and therefore for extending shelf-life during commercialization.

The washing procedure is of great importance for the final quality of surimi because it not only removes fat and undesirable material but, more importantly, increases the concentration of myofibrillar protein, thereby improving the gel-forming ability and decreasing the protein denaturation during frozen storage (Lee 1984, 1986). The gel texture or surimi functionality varies with the fish species used, the salt concentration needed for protein solubilization, the temperature and time at which the surimi is blended with salt, the frozen surimi moisture and the heat treatment (Suzuki 1981; Lee and Toledo 1976; Lee 1984; Lanier 1986).

The quality of the surimi is a function of its rheological properties, in particular the force and strain at failure of the gels obtained by thermal processing (Lanier 1986). The higher the rheological parameters, the better the quality of the surimi (Montejano et al. 1994; Hernández et al. 1995).

It was also found that the textural properties and water-holding capacity of cooked fish gels varied greatly between the different species used (Cheng et al. 1979a). The fact that many types of gel structures and textures may be described in terms of two basic

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rheological parameters, rigidity and strain at breaking (that is, the stress and strain at breaking, which are actually directly measured), yields not only a convenient system for measuring gel texture, but also a means of specifying the functional properties of surimi (Lanier 1986).

The objective of this work was to determine the protective effect that two cryoprotectant mixtures exerted during freezing and frozen storage of surubí surimi on the functional quality of the gels prepared.

MATERIALS AND METHODS

Response surface methodology (RSM), was used for the experimental design (Montgomery, 1991), and the model proposed by Box and Behnken (1960) was selected to study the washing stage. The experimental design adopted for this work, together with its independent variables, its codified variables and their three levels, is shown in Table 1, and the 15 experiments were carried out at random.

Version 7.1 of the Statgraphic Statistical Graphics System Plus program was used for data analysis and efficiency of the model was verified by analysis of variance (ANOVA).

The raw material used in the experiments was surubí (Pseudoplatystoma coruscans) due to its low fat content (2-3%).

In order to characterize the product obtained (surimi) chemically and functionally, total protein (AOAC 1984), total ash -A- (AOAC 1984) and moisture -M-(Lanier et al. 1985) in both the fresh muscle and the surimi were determined, and the punction test was also performed to measure deformation strength in the surimi gel (Lanier et al. 1985). Apart from this, total soluble protein (total soluble protein nitrogen) in the fresh muscle (Cheng et al. 1979b) and total fat in edible sections were also analyzed (AOAC 1984).

The average composition of edible sections of surubí fresh muscle was the following:

Moisture: 80.02 ± 0.72; total protein: 17.31± 0.80; total fat: 1.50 ± 0.54; ash: 1.17 ± 0.24; (n=10; $p<0.05$).

Preparation of Frozen Surimi

The surubí was obtained from the fish region of Santa Fe (Argentina). The muscle was separated from skin, bone and dark muscle by hand with a knife.

surubí mince was prepared with a food processor to obtain 5 mm-diameter particles. The washing system employed was designed and constructed by the working group (Medina 2000) and it consists of a 30-mesh stainless steel cylindrical basket (60 mm diameter x 300 mm height). The empty stainless steel basket was weighed and then filled with 200 gr of surubí mince conditioned at the washing temperature set by the model.

The basket with mince was placed within a 65.5 mm diameter x 500 mm height stainless steel tube, which contained the water for each washing cycle (three washing cycles). This stainless steel tube was then placed in a bath thermostatted at the temperature required for each experiment.

Meanwhile, by means of a metallic arm, the basket was connected to a reducing motor with a speed selector. The up-down velocity of the basket in the washing water was set at 60 ups per min for all the experiment.

After the third washing was completed, the basket with the mince was placed at a 24º slope and dewatered by gravity drainage for 15 min. The following step was pressing. The basket was now placed in a vertical position and a 2 kg load, with a 58 mm external diameter was placed inside on top of the mince and was left for 10 minutes.

Immediately after the mince recovered was weighed and the yield (Y= dewatered mince weight/fresh mince weight) was determined. Cryoprotectants at a 1:1 ratio of sucrose to sorbitol were later added at a level of 7,4 % a the final block basis, and the mix was then kneaded for about 4-5 min. After that, this mass was chopped in to blocks (3 cm diameter x 12 cm height), and the blocks were frozen by immersion in liquid nitrogen for 5 min and then stored at –21 ºC until the total protein, moisture (M), ash (A) and gel strength (GS) were analyzed.

Gel Preparation and Éffectiveness of Two Cryoprotectant Mixtures

Following the technique proposed by Lanier et al. (1985), frozen surimi (stored at – 21°C for six months) was tempered until it reached –3°C and blocks were cut in regular width slices. The sequence adopted was described by Medina and Garrote (1999).

Gel strength (GS) was obtained as the product of stress (first peak on the graph) and strain deformation (distance from the first peak). This determination was performed at least four times.

The protective effect of two cryoprotectant mixtures during freezing and frozen storage of surubí surimi was studied and the same working methodology was used for studying this effect. The same working conditions as those of the independent variables were selected for verification of the regression models developed.

The two cryoprotectant mixtures were as follows: mixture Nº1: sucrose-sorbitol and mixture Nº 2: maltodextrin-sorbitol (Maltrin® – M100; DE 10). The total frozen storage time was six months and frozen surimi gel strength was evaluated at 4, 45, 90 and 180 days of storage. Preparation of the surimi samples was changed only by incorporation of the cryoprotectants, which were added at a 1:1 ratio and at 8% on a dewatered mince basis.

RESULTS AND DISCUSSION

The average composition of the three nitrogen fractions making up the total nitrogen content of the surubí muscle was the following (means ± standard deviations): Myofibrillar protein nitrogen: 198 ± 0.16%; Sarcoplasmic protein nitrogen: 0.53 ± 0.08%; Nonprotein nitrogen: 0.31 ± 0.04%; Soluble nitrogen fraction: 0.83 ± 0.08%; Total nitrogen: 2.81 ± 0.16%.

It can also be seen that about 19% of the total nitrogen corresponds to sarcoplasmic proteins, whose removal by water washing benefits preservation of the muscle in the frozen state, and that about 33% of the total nitrogen is soluble in water or salt solution of low ionic strength *(I*=0.05).

The response values obtained from each experiment (Table 2) and the analysis of variance (Table 3) indicate that the models adopted were appropriate for the extracted proteins, moisture and ash of the surimi and for the gel strength obtained from it, with lack of fit not being significant. The predictive models developed to evaluate surimi gel strength (GS), variation in protein extraction (EP= [total protein nitrogen –surimi protein nitrogen] / total protein nitrogen) and moisture (M) were the most adequate and had the best fit and were thus chosen to determine the most acceptable working areas by using the superimposition of the corresponding contour graphs.

Series of contour graphs were developed for each of the three responses versus R and t, and T was adopted as a constant factor since its effect was the least significant. Conditions taken into account were that % M should be below 79% and % EP below 25%, so as to produce surimi of acceptable functional quality.

A point selected to verify these three regression models is the following: R = 3.5:1; T = 18 ºC and t = 4 min 37 sec/cycle.

Frozen surimi gel strength was evaluated after six months of storage, in accordance with the data from which the regression model was adopted. The models developed were clearly verified, and there are no significant differences between experimental and predicted values at $p<0.05$.

Variation in Gel Strength with Time of Frozen Storage

Conditions the same as those of the independent variables were selected for verification of the regression models developed for % EP, % M and GS, and the same working methodology was used for studying this variation.

The efficiency of the two cryoprotectant mixtures during frozen storage, while maintaining the functional quality of proteins, was evaluated in surimi samples specially prepared for this purpose.

Table 4 shows mean values for gel strength from at least four replicates using sucrose-sorbitol and maltodextrin-sorbitol, both at 7,4 % based upon the final block weight.

Student´s t-test and the null hypothesis test were used for comparison of means with the same treatment. No significant differences appear, for either mixture Nº 1 or Nº 2, between any of the gel strength mean values in Table 4 ($p> 0.05$).

Using a similar procedure, means between columns, correlated for each time of frozen storage, were compared in Table 4. Significant differences were observed for 45 and 90 days between the gel strengths corresponding to each mixture ($p<0.01$), with sucrose-sorbitol appearing to be the most appropriate.

Table 5 shows the average values for gel strength at several frozen storage times for sucrose-sorbitol mixture at 0, 4 and 20 days.

The first line value indicated as 0 day of frozen storage corresponds to just-made surimi added to the mentioned cryoprotectants but without freezing, i. e., the gel of “fresh” surimi. According to these results, freezing itself is observed to severely affect gel strength of “fresh” surimi, reducing it by 32%.

Table 1: Independent variables and their levels

Independent variables	Symbol		Levels	
	Coded	Real	Coded	Real
Water-to-mince ratio (gr./gr.)	X_1	R	-1 0 +1	2:1 5:1 8:1
Wash temperature (ºC)	X_2	T	-1 0 +1	2 10 18
Wash cycle time (min./cycle)	X_3	t	-1 0 +1	1 4 7

Table 2: Experimental data

Exp.	R (gr/gr)	T (ºC)	t (Min)	Y (%)	EP (%)	M (%)	A (%)	GS (grcm)
1	8:1	18	4	101.7	35.7	80.8	0.2	171.0
2	2:1	18	4	99.3	13.7	76.0	0.6	280.6
3	8:1	2	4	91.4	33.5	80.2	0.2	161.8
4	2:1	2	4	105.6	20.0	78.1	0.4	207.8
5	5:1	18	7	111.6	31.6	80.4	0.2	193.3
6	5:1	18	1	98.7	18.1	77.5	0.4	215.2
7	5:1	2	7	112.4	41.6	80.9	0.1	92.24
8	5:1	2	1	100.3	15.5	77.0	0.5	232.3
9	8:1	10	7	105.0	39.7	81.2	0.1	117.6
10	8:1	10	1	99.6	18.0	77.5	0.4	180.1
11	2:1	10	7	110.3	27.7	78.8	0.3	179.5
12	2:1	10	1	99.7	12.7	76.5	0.6	249.6
13	5:1	10	4	110.7	34.2	80.8	0.22	192.0
14	5:1	10	4	106.3	32.2	80.6	0.24	200.7
15	5:1	10	4	106.8	37.9	81.1	0.27	212.8

Table 3: Analysis of variance for response variables

Source	df	Sum of squares				
		Y	GS	EP	M	A
Model	9	462.2	30822.3	1372.1	47.9	0.339
Linear	3	246.3	24577.0	1093.1	34.4	0.307
Quadratic	3	139.5	1723.9	209.5	11.1	0.024
Cross product	3	76.3	4521.4	69.4	2.5	0.008
Residual	5	31.6	398.1	60.9	2.0	0.016
Lack of fit	3	20.2	180.8	44.0	1.9	0.015
Pure Error	2	11.4	217.3	17.0	0.1	0.001
r^2 (%)		93.6	98.7	95.8	96.0	95.6

Table 4: Mean values of surimi gel strength (g.cm) during frozen storage

Time (days)	Mixture Nº 1 (Sucrose/Sorbitol)	Mixture Nº 2 (Maltodextrin/ Sorbitol)
4	264.60^{a}_{c}	235.53^{b}_{c}
45	256.58^{a}_{d}	198.81^{b}_{e}
90	247.33^{a}_{f}	195.92^{b}_{g}
180	245.00^{a}_{h}	190.52^{b}_{h}

Means in the same column followed by equal superscripts are not significantly different ($p>0.05$).
Means in the same row followed by different subindexes are significantly different ($p<0.01$)

Table 5: Mean values of gel strength (g.cm) at several frozen storage

Time (days)	Mixture Nº 1 (Sucrose/Sorbitol)
0*	416.1 [a]
0	282.6 [b]
4	264.6 [b]
20	259.5 [b]

* Without freezing
Values with different superscripts are significantly different ($p<0.05$)

CONCLUSIONS

Surubí flesh proved to be a suitable raw material for surimi production, as shown by gel strength values for unfrozen "fresh" surimi.

Nineteen percent of total nitrogen was found to come from soluble sarcoplasmic proteins. The second-order mathematical-statistical models with the best fit were those related to GS responses of surimi gel, % M and % EP; no significant differences were found between experimental and predicted values.

Even with the addition of cryoprotectants, freezing decreases gel strength since it produced a decrease of about 32% in fresh surimi gel strength. The sucrose-sorbitol mixture was more suitable than maltodextrin-sorbitol, as shown by the higher strength of frozen gels stored for 45 and 90 days.

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