AN ABSTRACT OF THE THESIS OF

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Title: Frozen Stabilized Mince, its Production, and Thermophysical Properties

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The potential to produce good quality surimi from stabilized/unstabilized frozen mince and headed and gutted (H & G) fish after storage was investigated. The investigation was divided in two parts, firstly to determine the feasibility of the process and secondly to optimize processing conditions. Several samples of stabilized/unstabilized mince and H & G were prepared and kept in frozen storage to evaluate their potential to produce good quality surimi. Surimi was produced from fresh mince as a control and stored at -34.4°C. Stabilized mince (12% w/w sucrose and 0.2% w/w polyphosphates) demonstrated that it can be used for the manufacture of good quality surimi. After six months, stabilized mince kept at -20°C as well as -50°C retained good protein functionality and gel forming capabilities when compared to the surimi control.

A second phase considered practical aspects to implement this stabilized mince alternative including: different cryoprotectant mixtures, expected yield, and freezing rate effects. Seven samples of frozen mince which had been mixed

with different cryoprotectant mixtures from 12-6% w/w sucrose with/without polyphosphates were tested. Surimi made from stabilized mince with 12 and 6% w/w sucrose and 0.2% w/w polyphosphates were produced for determination of yield. Four different freezing rates were also investigated. Results showed that sucrose levels approaching 6% were adequate for production of good quality surimi from stabilized mince that has been stored -20°C for up to 6 mo. All seven samples obtained an acceptable value for whiteness (>75). Surimi yields from stabilized mince were shown to be comparable to those found with normal surimi production. Freezing rates were shown to have minimal or no effect in gel forming capability of surimi made from stabilized mince.

To complement the results found in this study a new approach for the estimation of thermophysical properties of foods at freezing temperatures in the range from -22°C to initial freezing point was analyzed and discussed. The accuracy of this new methodology was validated using surimi as a food model. Although the set of determined parameters appeared to characterize the heat transfer process, parameters were not necessarily the true values. The proposed procedure could be successfully applied for the determination of thermal conductivity in the freezing range and would involve the determination of one parameter.

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
General considerations	1
Minced Fish	3
Cryoprotection	5
Stabilized fish mince and its potential	9
Parameter estimation	11
Research goals and objectives	13
References	15
II. THE FEASIBILITY OF PRODUCING SURIMI FROM PARTIALLY PROCESSED AND FROZEN PACIFIC WHITING (*MERLUCCIUS PRODUCTUS*)	20
Abstract	21
Introduction	22
Materials and Methods	25
Fish	25
Freshness	25
Sample preparation	26
Surimi processing	27
Non surimi samples	28
Gel preparation and rheological testing	28
Dimethylamine (DMA)	30
Statistical analysis	30
Results and Discussion	30
K-value	30
Rheological properties	30
Dimethylamine (DMA)	33
Practical considerations	34
Conclusions	34
References	42
III. PROCESS VARIABLES AFFECTING SURIMI MADE FROM FROZEN STABILIZED MINCE OF PACIFIC WHITING (*MERLUCCIUS PRODUCTUS*)	45
Abstract	46
Introduction	47
Materials and Methods	49
Fish	49
Freshness	50
Mince preparation	50
Surimi processing	51
Surimi from stabilized mince	51
Gel preparation and rheological testing	51
Dimethylamine (DMA)	52
Color measurements	52
Yield experiments	52
Freezing rate experiments	53

Statistical analysis 54
Results and Discussion 54
K-value 54
Cryoprotectant mixtures 55
Yield experiments 57
Freezing rate experiments 58
Conclusions 59
References 68

IV. AN EXPLORATORY ANALYSIS OF A NEW APPROACH TO ESTIMATE THERMOPHYSICAL PROPERTIES OF FOODS AT FREEZING TEMPERATURES 71

Abstract 72
Introduction 74
Materials and Methods 76
Problem description 76
Materials 77
Apparatus and operating conditions 78
Measurement of initial freezing point (T_{sh}) 78
Measurement of heat transfer coefficient (h) 79
Heat transfer model 79
Thermophysical properties 81
Identifiability 84
Search procedure 85
Statistical analysis 86
Results and Discussion 88
Heat transfer coefficient (h) and initial freezing point (T_{sh}) 88
Identifiability 90
Thermophysical properties determination 92
Statistical analysis 94
Validation experiment 94
Conclusions 96
Nomenclature 111
References 114

BIBLIOGRAPHY 117

APPENDICES 126
Appendix I: Identifiability 127
Appendix II: Computer Program 131

LIST OF FIGURES

Figure		Page
II.1	Experimental design	36
II.2	Stabilized mince process	37
II.3	Surimi Process	38
II.4	True strain at failure versus storage time and temperature	39
II.5	Shear stress at failure versus storage time and temperature	40
II.6	Dimethylamine levels versus time of frozen storage	41
III.1	Dimethylamine levels in treatments during frozen storage	65
III.2	Change in true strain at failure during storage	66
III.3	Change in shear stress at failure during storage	67
IV.1	Experimental set up for thermophysical property determination	103
IV.2	A general diagram of the bootstrap method	104
IV.3	a. Sensitivity coefficients for S_k and k_r b. Sensitivity coefficients for C_{11}, C_{12}, and C_{13}	105
IV.4	Thermophysical properties determination	106
IV.5	Apparent specific heat of surimi sample	107
IV.6	Thermal conductivity of surimi sample	108
IV.7	Predicted and experimental temperatures for validation #1	109
IV.8	Predicted and experimental temperatures for validation #2	110
AI.1	Sensitivity coefficients for a and b, Equation AI.9	130

LIST OF TABLES

Table		Page
III.1	Sample specification for different cryoprotectant mixtures added to samples (w/w)	61
III.2	Sample specification for freezing rate experiments	62
III.3	Change in true strain at failure during frozen storage for samples with decreasing levels of sucrose	63
III.4	Whiteness for surimi produced from stabilized mince samples and control	64
IV.1	Proximate composition of surimi sample (% w/w)	98
IV.2a	Correlation matrix for parameters in Equations IV.8 and IV.10 (1 thermocouple location)	99
IV.2b	Correlation matrix for parameters in Equations IV.8 and IV.10 (6 thermocouple locations)	99
IV.3a	Correlation matrix for parameters in Equations IV.10 and IV.11 (1 thermocouple location)	100
IV.3b	Correlation matrix for parameters in Equations IV.10 and IV.11 (3 thermocouple locations)	100
IV.3c	Correlation matrix for parameters in Equations IV.10 and IV.11 (6 thermocouple locations)	100
IV.4	Bootstrap estimators	101
IV.5	Parameters and properties estimated with proposed procedure and based in food composition	102

"Do not worry about your difficulties in mathematics; I can assure you that mine are still greater"

A. Einstein

Frozen Stabilized Mince, its Production, and Thermophysical Properties

I. INTRODUCTION

General considerations

Pacific whiting (*Merluccius productus*) is the largest stock of trawl fish off the west coast of the contiguous United States of America. Summer surveys by U.S. and U.S.S.R. researchers have provided biomass estimates ranging from 445,000 to 3,440,000 t. Commercial catches have ranged from about 68,000 to 237,000 t annually since 1967 (Dark, 1985). Whiting are most abundant from Spring through Fall when large feeding aggregations occur in depths of 55-550 m (Dark, 1985; Dark et al., 1980). In late September, Pacific whiting begin to move off the continental shelf into deeper water and, by December most adults have left the area (Fiscus, 1979).

The Fishery Conservation and Management Act of 1976 intensified the interest of the fishing industry in Pacific Whiting (Miller and Spinelli, 1982). Until 1984, the Pacific whiting fisheries were a combination of foreign fisheries and joint venture (JV) fisheries between coastal capture vessels and foreign processing ships (Radtke, 1991). From 1985-1990 the majority of the harvests were taken by JV operations. The fishery was considered underutilized because only a small proportion of the harvest was processed by U.S industry (Morrissey et al., 1992). In 1991, because of the increased interest by U.S. processors in Pacific whiting the joint

venture operations with foreign processing vessels were excluded from the quota (Morrissey et al., 1992).

Domestic utilization of Pacific whiting has been restricted, in spite of their abundance, because of the soft texture associated with proteolysis of muscle proteins (Patashnik et al., 1982). The tissue softening makes it imperative that the fish be handled differently than other species (Patashnik et al., 1982; Chang-Lee et al., 1989). The effectiveness of Pacific whiting handling is affected by several factors, such as, biological and physicochemical factors including infestation of Myxosporidian parasites, the presence of a fat layer associated with rancidity, and the high levels of protease that rapidly break down the tissue (Morrissey et al., 1992).

Production of surimi was found to be an important potential for Pacific whiting utilization. The texture degradation problem can be prevented with the addition of protease inhibitors (egg white, beef plasma protein) (Morrissey et al., 1992; Chang-Lee et al., 1990). According to Pacheco-Aguilar et al. (1989) investigations have indicated that Pacific whiting could serve as a resource for the production of surimi.

Shore-based production of Pacific whiting surimi allows, for example, the adaptation of new and evolving processes for recovering proteins from wash water. Less expensive labor and

utilities, and surimi plants could be located immediately adjacent to analog plants.

One drawback to shore-based surimi production is the seasonal availability of whiting which would limit a plant's operating schedule to approximately six months a year. A potential solution would be to first freeze the fish, then later process it into surimi in a shore-based plant operating year-round. If the fish were minced prior to freezing, refrigeration energy would not be wasted on that portion of the fish which is typically discarded. Recovery of the mince from headed and gutted product would be about 50% (Crapo et al., 1988).

Minced fish

Special processing procedures have been invented and implemented to augment and improve the utilization of fish as a human food (Regenstein and Regenstein, 1991). The methods often achieve complete utilization of a given fish. One of the most studied and implemented procedures is mincing fish. Minced fish is a product processed by mechanically grinding the edible flesh. As discussed by Regenstein and Regenstein (1991), there are several issues that favor the idea of mincing fish for human food: "(1) filleting fish leaves a lot of edible fish on the skeleton; (2) too many species of fish are not accepted in the market place, particularly if they are boney, and are therefore underutilized; and (3) too many small

fish are thrown back into the water, often dead". Also, it can be added that the stock of seafood is limited and that increased utilization of harvested fish is desirable.

Minced fish is a precursor of surimi and can be utilized as is, as an ingredient in prepared foods (fish sticks, chowders) or as a main ingredient in surimi production. Minced fish has several advantages because of its versatility. It can be colored, flavored, molded, stabilized, blended, for making a greater variety of products. Minced fish has the intrinsic nutritional quality of seafoods, but with less fat and calories than minced red meat products (Regenstein, 1986).

Storage stability is one of the critical factors in minced fish industrialization. The storage stability varies considerably with species (Babbitt et al., 1972). According to Crawford et al. (1979) textural deterioration of minced blocks is the major sensory factor affected by storage time. Decomposition of trimethylamine oxide (TMAO) appeared to be responsible for the physical alteration (Crawford et al., 1979). As reported by Regenstein (1986), frozen minced fish cannot preserve quality as well as frozen fish because of the changes induced by grinding, such as, tissue disruption and the incorporation of air. Gadoid fish, such as Pacific whiting, are of particular concern due to the presence of TMAO. Fish of the order Gadiformes produce larger quantities of dimethylamine (DMA) and formaldehyde (FA) than other groups of fish (Rehbein, 1988). TMAO can be broken down to DMA and

FA, possibly by the action of the enzyme trimethylamine N-oxide demethylase. Blood and kidney tissue of gadoids appear to have high activity of TMAOase (Haard, 1990). Gadoid fish have positive correlation between texture toughening and DMA formation during frozen storage (Haard, 1990). Formaldehyde is a reactive compound that can denature proteins, thus leading to textural changes (Regenstein, 1986). Apparently, minced particles become crosslinked and the water retained by the product can be expelled and then reabsorbed (Regenstein, 1986). One way to partially overcome deterioration is to store the fish at cold temperatures (below -30 °C) where the enzymatic activity is severely reduced (Mackie, et al., 1986; Regenstein, 1986). Unfortunately, this is not a common practice in U.S. fish processing plants. Another alternative is washing the mince to reduce or eliminate TMAO. This process, although effective, removes several compounds of nutritional value. This kind of process removes approximately 25% of the total protein, some fish fat and most of the water soluble vitamins and minerals (Regenstein, 1986).

Cryoprotection

Frozen storage has been practiced for centuries, however, it was not until the end of last century that a massive application, with industrial potential, was developed. The last decade has provided the most important storage methods for muscle foods that prevent bacterial growth over an almost

unlimited length of storage (Park, 1993). As discussed by Park (1993), the food product is subjected to an inevitable deteriorative effect of protein functionality and several other quality problems. Quality losses are attributed to a loss of succulence, an increase in toughness, and loss of functional properties due to the aggregation of myofibrillar proteins (MacDonald, 1992).

According to Levine and Slade (1988) cryostabilization (also referred to as cryoprotection) is a concept introduced to describe a new industrial technology for the storage stabilization of frozen (freezer-stored, and freeze-dried) foods. Cryostabilization or cryoprotection is a way to protect products when they are stored for long periods of time at normal freezer temperatures (-18°C). The protection is normally referred to as an inhibition of detrimental changes of foods in texture, structure, and chemical composition, such as, enzymatic activity, oxidative reactions, flavor/color degradation (Levine and Slade, 1988).

In the development of surimi technology, the major discovery was the prevention of denaturation of muscle proteins of Alaska pollock during frozen storage with the addition of cryoprotectants (Matsumoto and Noguchi, 1992). Cryoprotection of surimi blocks allowed surimi to be kept in frozen storage up to 18 months without loss of quality. The utilization of cryoprotectants allowed processors to generate a more uniform raw material flow, augment investment in

production facilities, and produce high quality products for the market on a continuous basis (MacDonald, 1992). Cryoprotection is only possible when protein molecules and cryoprotectant agents are in intimate contact. Thus, muscle protein functionality will be optimally maximized in a minced or comminuted muscle system (MacDonald and Lanier, 1991).

According to Matsumoto and Noguchi (1992) cryostabilization of fish muscle proteins in surimi is affected by two factors: "(1) physicochemical factors (of which the effect of leaching the fish mince is most important), and (2) chemical factors, which include the effects of cryoprotectant compounds such as sucrose, sorbitol, and phosphates".

Cryoprotectant agents have been studied in different fields. Examples of utilization of cryoprotectants, other than in food materials, are the applications in materials such as enzymes, vaccines, blood, and organs (Meryman, 1966). A wide variety of chemical compounds have been studied for their cryoprotective potential. Carbohydrate compounds (low and high molecular weight), amino acids, carboxylic acids, quaternary amines have a cryostable effect on various proteins and enzymes (Jiang et al., 1987; Loomis et al., 1988,1989). Cryoprotectants like sugars and polyalcohols or polyols have been found to protect foods and living cells. The native conformation of many proteins and enzymes is well protected with the incorporation of carbohydrates and polyalcohols

(Park, 1993). The chemical attributes that are characteristic of cryoprotective compounds according to Noguchi (1974) are as follows:

"1. The molecule has to posses one essential group, either -COOH or -OH, and more than one of the following supplementary groups: -COOH, -OH, -SH, $-NH_2$, $-SO_3H$, $-OPO_3H_2$.

2. The functional groups (both essential and supplementary ones) must be suitable spaced and oriented relative to each other.

3. The molecule must be comparatively small".

According to a study carried out by Park et al. (1988) the latter requirement seems to be contradicted due to the positive cryoprotective effect of some high molecular weight carbohydrates like Polydextrose® (Matsumoto and Noguchi, 1992).

Different theories have been proposed and studied to understand the mechanism of cryoprotection. Some theories propose that the presence of cryoprotectants change the water/ice structure; others emphasize the contribution of the surface functional groups of protein molecules in the process of freezing (Matsumoto and Noguchi, 1992). According to Arakawa and Timasheff (1982) the denatured structure of proteins is thermodynamically less favorable in sugar solution than in water. Based on their results, they proposed that stabilizing solute molecules (sugars, low-MW polyols) were

excluded from the surface of the protein molecule, thus "preferentially hydrating" the protein (MacDonald and Lanier, 1991).

As previously mentioned, the intimate contact of cryoprotectants and food materials appear to be a strict requirement. This is probably the main reason why preservation of intact muscles has not been successful (Krueger and Fennema, 1989). Several chemical additives have been tested to inhibit toughening of frozen fish fillets with no significant improvement (Racicot et al., 1984, Regenstein et al., 1981).

Stabilized fish mince and its potential

It is generally recognized that frozen fish mince does not hold up as well as frozen fish, mainly due to the changes induced by mincing, such as, tissue disruption and the incorporation of air (Regenstein, 1986; Babbitt, 1986). As reported by Babbitt (1986) there were significant changes in texture, flavor, and color of minced fish blocks during frozen storage. Minced fish is recognized for its unique texture-forming properties, making it an excellent base for manufacturing a great variety of seafood products (Lanier, 1981). Normally minced fish has been considered a source of low-cost protein. In minced fish stabilization, it is necessary to consider the expected chemical, physicochemical, biochemical and microbiological changes, and also the cost involved in stabilization.

Successful mince stabilization has been always done by washing out TMAO (Grantham, 1981; Regenstein, 1986). Recently Aguilera and Figueroa (1992) applied combined methods technology (or hurdle technology) in the preservation of the pelagic washed fish mince. They used a combination of preservation techniques such as, reduced pH; potasium sorbate as a preservative; mild heat processing; depression of a_w by sodium chloride; and packaging. Another alternative to stabilize fish mince is to add cryoprotectant agents such as, sugars and sugar-like compounds (e.g., sorbitol). Cryoprotectant compounds like Polydextrose® have the advantage of not contributing to the product's sweetness. As reported by Grantham (1981), other ingredients used in mince stabilization include alginates, carrageenan, xanthan gum or pectin. MacDonald et al. (1990) carried out an investigation on stabilized mince. Their approach was to combine low temperature storage (-20 °C and -50 °C) with cryoprotectant addition (12% w/w sucrose and 0.2% w/w polyphosphates) in stabilizing mince fish (Hoki, *Macruronus novaezelandiae* Hector). Results indicated that stabilized mince can be stored for up to six months and still be used to produce good quality surimi.

Although the research study carried out by Macdonald and co-workers was intended to stabilize fish mince to later produce surimi, stabilized fish mince could provide other alternatives to produce a variety of seafood products. If

cryoprotectants, less sweet than sucrose, are employed stabilized mince could serve as a base product for a variety of prepared seafoods. Stabilized mince, with improved textural and organoleptic properties, can provide seafood processors with new options for increased utilization of the harvest. Mince stabilization could achieve a better quality in terms of protein functionality than frozen stored fish and also have the advantage of being a more efficient process in terms of refrigeration energy requirements.

Parameter estimation

Thermophysical properties of frozen foods are of interest for modeling freezing and frozen storage process and in designing equipment. Since the composition of agricultural and marine products vary with variety and species respectively, the work involved in thermophysical properties determination would be enormous without an efficient way to predict these properties. One way to overcome this difficulty is to solve the problem based on parameter estimation techniques.

Parameter is defined by *Webster's New World Dictionary* as "a quantity or constant whose value varies with the circumstances of its application". The same dictionary defines property as "any of the principal characteristics of a substance". In the field of food science and technology the substance is a food material. The present research work has

restricted the parameter definition to quantities or constants associated with a mathematical model.

One of the priorities of engineering and science is to obtain information from data. Parameter estimation is a discipline that provides tools for the efficient use of data in the estimation of constants appearing in mathematical models and also for aiding in modeling of phenomena (Beck and Arnold, 1977).

As expressed by Clark, (1978) modeling is of practical and philosophical value, but its prime motivation is philosophical. The practical application of mathematical modeling needs the knowledge of parameters and properties.

Parameter estimation problems appear in both curve fitting and model estimations. In principle, model fitting is not much different from curve fitting, except that we can no longer guide the selection of a functional form by considerations of computational convenience (Bard, 1974). In model fitting it is meaningful to ask for the true value of the property or parameter.

Food science and technology is just beginning to investigate and utilize mathematical modeling for research and practical applications; whereas, other sciences have been using and receiving the benefits of this approach for several decades. Due to the nature of foods, mathematical models used are often complex and most of the time require extensive computer work for their evaluations. In the last ten years,

the use of mathematical modeling has increased substantially in the field of food science. One interest in this area is the increased need to quantify properties and parameters. In some cases, direct determinations or measurements of food properties can be hard, extensive and expensive work.

Parameter estimation can also be visualized as a study of inverse problems (Beck and Arnold, 1977). Parameter estimation from transient temperature measurements is considered an attractive technique both from the experimental and methodological point of view (Milano et al., 1991). The apparatus needed is simple and experimental procedures are typically short. Moreover, during the test, the specimen is subjected to a thermal transient that reflects the working condition in most applications (Milano et al., 1991). A successful application of this technique in the determination of thermophysical properties of foods in the freezing range temperatures will represent a powerful tool.

Research goals and objectives

The goal of our research efforts has been to produce a stable fish/fish product under low-temperature storage (-20 °C through -50 °C). The species of interest is Pacific whiting (*Merluccius productus*). This goal was achieved by identifying the following objectives:

1. To evaluate the potential of producing good quality surimi from stabilized frozen mince (12% w/w sucrose

and 0.2% polyphosphates), unstabilized frozen mince, and headed and gutted fish.

2. To evaluate the potential of producing good quality surimi using decreased levels of sucrose, from 12 to 6% (w/w). Samples were prepared with/without the addition of polyphosphate. Samples were analyzed for yield production and tested under different freezing rates.
3. To explore and analyze a new methodology for the simultaneous determination of thermophysical properties in the freezing range temperatures.

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II. The Feasibility of Producing Surimi from Partially Processed and Frozen Pacific Whiting (*Merluccius productus*)

ABSTRACT

The potential of producing surimi from partially processed and frozen Pacific whiting (*Merluccius productus*) was evaluated. Stabilized mince (12% w/w sucrose and 0.2% w/w polyphosphates) made from fresh mince stored at -20 °C for up to 6 mo can be used for the manufacture of good quality surimi. Surimi was produced as a control and stored at -34.4°C. Surimi gels were evaluated by the torsion test measuring deformation to failure and reported as shear stress and true strain. After 6 mo, there was no significant difference ($p>0.05$) between surimi samples prepared from stabilized mince (stored at -20°C and -50°C) and surimi stored as a control. Additionally, DMA formation was significantly reduced by storing at low temperatures and adding sugar. The addition of cryoprotectants to mince before freezing can be viewed as a useful method for stabilizing fish muscle protein during frozen storage.

INTRODUCTION

The fishery for Pacific whiting (*Merluccius productus*) has been the object of considerable interest and research for nearly 20 years (Nelson et al., 1985). Summer surveys by U.S. and U.S.S.R. researchers have provided biomass estimates ranging from 445,000 to 3,440,000 t. Commercial catches have ranged from about 68,000 to 237,000 t annually since 1967 (Dark, 1985), the largest trawl fishery off the west coast of the United States. The majority of Pacific whiting landed have an inherent myxosporidian parasite linked to rapid and severe enzymatic softening when stored and cooked (Nelson et al., 1985). A primary value is considered to be its potential for making surimi, in which suitable enzyme inhibitors can be well-distributed and effective (Chang-Lee et al., 1990).

There has been considerable interest in developing shore based processing plants for Pacific whiting in the Pacific Northwest. Shore-based production of Pacific whiting surimi allows adaptation of new and evolving processes for recovering proteins from wash water. The surimi plant could be located immediately adjacent to an analog plant resulting in cheaper labor and utilities.

One drawback to shore-based surimi production is the seasonal availability of whiting which limits a plant's operating schedule to approximately 6 mo a year. A possible solution would be to first freeze the fish, then later process

it into surimi in a shore-based plant operating year-round. Although two problems arise from this potential solution. First, muscle proteins loose gel-forming ability during frozen storage (MacDonald, 1992). Second, if the fish were minced, prior to freezing, refrigeration energy would not be wasted on that portion of the fish which is typically discarded. Recovery of the mince from headed and gutted product would be about 50% (Crapo et al., 1988).

One problem with the mince is that severed tissue walls release compounds which support deterioration. For example, the enzymatic conversion of trimethylamine oxide (TMAO) to dimethylamine (DMA) plus formaldehyde promotes protein denaturation and decreases water holding capacity; a greater contact of lipids with oxygen promotes oxidative rancidity. Textural changes and decreased gel-forming abilities are recognized as results of severe denaturation of muscle proteins (Jiang et al., 1985; Sikorski et al., 1976; Sikorski, 1980; Matsumoto, 1979, 1980; Acton et al., 1983). These biochemical changes can be controlled through a combination of lower temperatures, use of stabilizing agents (e.g., sucrose), and controlling storage atmospheres (e.g., packaging). Physical changes occurring in foods, during freezing and frozen storage, are caused directly or indirectly by water to ice transformation (Mittal and Barbut, 1991). Therefore, the rate of these physical changes can be reduced by the initial formation of small ice crystals, preventing the growth of

these ice crystals and minimizing temperature fluctuations during storage (Mittal and Barbut, 1991). As reported by Matsumoto (1979), the cryostabilization of muscle proteins of surimi is affected by two elements; physicochemical factors and chemical factors. Considering the mince-stabilization problem to be parallel to that of surimi stabilization, it is necessary to take into account both aspects for mince stabilization. Some of the physicochemical factors are pH, freezing/frozen storage/thawing procedures, and temperature tolerance of the myofibrillar proteins. Chemical factors include the effects of cryoprotectant compounds such as sucrose, sorbitol, and phosphates.

As discussed by MacDonald (1992), polyphosphates can play an important role in maintaining water holding capacity of myofibrillar proteins. Okada (1986) indicated that phosphate increased the textural strength and moisture retention of surimi-based products through increased water binding. However, the presence of polyphosphates in mince-stabilization could increase dewatering time during surimi production and this would be a disadvantage in processing mince that later will be used in surimi production.

Arakawa and Timasheff (1982) determined that denaturation of proteins is thermodynamically less favorable in sugar solution than in water (MacDonald and Lanier, 1991). Arakawa and Timasheff (1982) showed that the stabilizing solute molecules were excluded from the surface of the protein

molecule, thus preferentially hydrating the protein (MacDonald and Lanier, 1991).

While intimate addition of cryoprotectants to the intact fish muscle is not practically possible, production of mince enables a more thorough contact of tissue with the appropriate stabilizers (MacDonald et al., 1990).

The aim of this study is to evaluate the potential of producing good quality surimi from stabilized frozen mince, unstabilized frozen mince, and headed and gutted fish, stored for various time periods and at different temperatures. The species of interest is Pacific whiting (*Merluccius productus*).

MATERIALS AND METHODS

Fish

Fish were commercially caught, chilled onboard, then preprocessed onshore into fillets and headed and gutted product forms. After transporting in ice to our laboratory, they were frozen and processed as described below. Maximum time from harvest to final processing was 18 hr.

Freshness

Fish freshness was assessed by K-value analysis following the method of Ryder (1985). K value, calculated as the ratio of the sum of hypoxanthine and inosine to the total amount of

adenosine 5′-triphosphate related compounds, was determined in triplicate on minced fish samples.

Sample preparation

The experimental design is described in Figure II.1. The samples to be tested were headed and gutted (H & G), unstabilized mince (UM), stabilized mince (SM) and surimi as the control. The samples of H & G fish (60 kg) were frozen (blast freezer at -30°C), and stored at -20°C and -50°C to evaluate the potential of short-term (6 mo) storage at these two temperatures to produce good quality surimi.

To prepare stabilized mince, unstabilized mince and surimi samples, 160 kg of fillets were minced in a meat grinder Model 601 Hp (Autio Co. Astoria, OR). This mince produced 41 kg of unstabilized mince, 86 kg of stabilized mince, and 15 kg of surimi. Figure II.2 shows a schematic diagram of the stabilized mince process. To stabilize the mince, 12% w/w sucrose (C. & H. Pure Cane Sugar, Concord, CA) and 0.2% w/w Brifisol S-1 (tetrasodium pyrophosphate and sodium tripolyphosphate--B.K. Ladenburg Corp., Cresskill, NJ) were used as cryoprotectants. The mixture was prepared in a Hobart mixer Model S-301 (The Hobart Co., Troy, OH). All samples were packed in 600 g containers and frozen overnight in a blast freezer at -30°C. Stabilized and unstabilized mince samples were then stored at -20°C (Kenmore chest freezer with a temperature controller, Independent Energy Inc.) and -50°C

(chest freezer, Puffer Hubbard, Ashville, NC); surimi was stored at -34.4°C (SO-LOW freezer Model PR40-17, Environmental Equip. Co., Cincinnati, OH). To quantify freezing time, temperatures were recorded at the mid-point of three containers. Freezing time was approximately 3.5 hr. Temperature fluctuations during frozen storage were minimized by packaging container-samples in styrofoam boxes.

Surimi processing

Minced samples were washed/dewatered three times with a ratio of 3:1 (water:mince). Each wash consisted of stirring the mince-water slurry in a 30 gal plastic barrel using a Lightnin Mixer (Mixing Equipment Co. Inc., Rochester, NY) for 5 min followed by holding for 5 min. In each wash, the temperature was maintained under 5°C by adding ice. Washed mince was dewatered in a screw press dehydrator, Model SD-8 (Ikeuchi Tekkosho/Sano, Ltd., Japan) (hole size .001 m). The last wash included 0.25% NaCl to facilitate dewatering. The resultant washed mince was refined to separate white meat from connective tissue with an Akashi strainer Model S-1 (Akashi Tekkosho Co., Japan). Surimi was prepared by mixing the washed and refined mince with cryoprotectants. The cryoprotectant mixture consisted of 4% w/w sucrose, 4% w/w sorbitol (GBC Corp. Chester, PA), 0.2% w/w Brifisol S-1 including 1% w/w enzyme inhibitor beef plasma protein (BPP) (American Meat Protein Corp. Ames, IA). A schematic diagram of the surimi

process is shown in Figure II.3. The mixing of cryoprotectants and BPP was accomplished in a Stephan Vertical-Cutter/Mixer Model UM-5 (Stephan Machinery Co., Columbus, OH) for 2 min. The temperature was maintained below 5°C during the mixing process. Samples of 600 g were vacuum packed and frozen in a blast freezer at -30°C (freezing time approximately 3.5 hr). Control samples were stored at -34.4°C in a SO-LOW freezer Model PR40-17 (Environmental Equip. Co., Cincinnati, OH). To minimize temperature fluctuations, samples were stored in styrofoam boxes.

Non surimi samples

Frozen mince (stabilized and unstabilized) and H & G were made into surimi which was then compared to the surimi control. Stabilized and unstabilized mince were thawed in a cold room (2-4°C) for 4-6 hr and then sliced into small pieces prior to washing. H & G samples were thawed for 3-4 hr in cold running water, then filleted and minced for surimi preparation. The resulting surimi test samples were then frozen overnight at -30°C (blast freezer) prior to gel preparation the following day.

Gel preparation and rheological testing

All surimi samples were removed from frozen storage and tempered overnight at 2-4°C. The blocks were sliced into pieces and chopped in a Stephan Vertical-Cutter/Mixer Model

UM-5 (Stephan Machinery Co., Columbus, OH). During the first minute, salt and ice/water were added to adjust for 2% w/w and 78% w/w, respectively. The last 3 min of mixing was carried out under vacuum conditions (Lanier et al., 1991). The resulting paste was stuffed into stainless steel tubes (0.175 m length and 0.0187 m internal diameter) using a sausage stuffer Model 14208 (Sausage Maker, Buffalo, N.Y.) . The tubes were sprayed with a lecithin-base release agent (PAM) to facilitate removal of the cooked gel from the tubes. The tubes were placed in a water bath and cooked at 90°C for 15 min and then removed and cooled in ice/water. Gels were removed from stainless steel tubes, packed in plastic bags and stored at 2-4°C before testing. Tests were run within 24 hr after gels were heat-set. Before testing gels were removed from the cold room and warmed to room temperature for at least 1 hr. Samples were shaped into an hourglass geometry by grinding the cylindrical cooked gels on a lathe-type apparatus (Gel Consultants, Inc., Raleigh NC). The texture of gels was measured by deformation to failure in the torsion mode as described by Kim et al. (1986). Eight subsamples were used for each determination. The hourglass-shaped samples were twisted at 2.5 rpm until structural failure on a Torsion Gelometer apparatus (Gel Consultants, Inc., Raleigh NC). The maximum recorded torque and angular displacement indicate shear stress and true strain (Hamann, 1991).

Dimethylamine (DMA)

All samples were tested for dimethylamine content. Dimethylamine content was determined by a modified copper dimethyldithiocarbamate colorimetric procedure (Mackie and Thomson, 1974; Dowden, 1930).

Statistical analyses

Statistical analysis of data were carried out by using one way analysis of variance. Differences among mean values were established using the Least Significant Difference (LSD) multiple range test (Steel and Torrie, 1980). Values were considered significant when $p<0.05$.

RESULTS & DISCUSSION

K-value

K-value was found to be 8% ±.12% indicating that the samples were very fresh and had been properly handled (Ehira and Uchiyama, 1974).

Rheological properties

Good quality surimi, in terms of texture characteristics has been shown to have a true strain value with a range of 2.0 to 3.0 (Lanier et al., 1991). After 6 mo storage, stabilized mince samples stored at -20°C and -50°C produced surimi (true strain ~ 2.3) superior to that made from other treatments (less than 1.9) (Figure II.4). There was no significant

difference ($p>0.05$) between surimi samples prepared from stabilized mince -20°C and -50°C and surimi stored as a control. The cryoprotectant was effective in the freezing and frozen storage steps.

H & G and unstabilized mince stored at -50°C produced surimi having a significantly lower but constant true strain value when compared with the control ($p<0.05$). Thus, for these samples it appeared that the major decrease in gel-forming ability resulted from the freezing (versus storage) process.

Surimi made from H & G and unstabilized mince stored at -20°C showed a sharp decrease with time. For these two samples the true strain gave a poor value (less than 1.5) within 1 mo storage. As with the other samples without cryoprotectant (H & G and UM -50°) the true strain was significantly reduced at day 0 as compared with the control.

Surimi produced from stabilized mince at 1 mo and 2 mo (SMS-1 mo and SMS-2 mo) was subsequently stored at -34.4°C and tested at various intervals over a 9 mo period. No significant differences ($p>0.05$) for true strain values were found when SMS-1 and SMS-2 samples were compared with surimi control.

As discussed by Okada et al. (1973) water-soluble proteins reduce the elasticity of the "Kamaboko" by interrupting the continuum of the cross-linking process itself. They have also proposed that proteolytic activity of the water-soluble protein fraction may adversely affect the ability of the myofibrillar protein to form cross-linkages.

1973). Both theories address the possibility that the deleterious effect of soluble-proteins occurs during gel formation and not necessarily during storage. Apparently the combination of cryoprotection/low temperature storage and washing mince prior to surimi production were sufficient to produce good quality surimi.

Figure II.5 shows the results of shear stress against time for several treatments. All indicate a fairly low value for shear stress (< 20kPa) (Lanier et al., 1991). Shear stress demonstrated high variability and cannot be associated with any particular pattern. Several authors have found high coefficients of variation for shear stress relative to that of true strain (Hamann, 1983; MacDonald, 1992; Montejano et al., 1984). According to Montejano et al. (1984) the length of cooking process determines that once an elastic protein matrix is formed, further thermal processing has a smaller effect on elasticity (related to true strain), and a larger effect on the rigidity (stress/strain) of the structure. A different explanation could be based on the fact that loss of cohesiveness (related to true strain) of frozen stored fish is less temperature dependent than toughening (related to shear stress) (Kim and Heldman, 1985).

The data analyses for true strain suggest that the addition of the cryoprotectant mixture (12% w/w sucrose and 0.2% w/w polyphosphates) was able to prevent denaturation of fish muscle proteins during the freezing process and the

period of frozen storage. Significant differences were found when samples with and without cryoprotectant mixture were compared with gel forming ability at day 0 indicating "damage" during freezing. Low temperature storage could prevent further protein denaturation but it cannot repair the damage produced during the freezing process.

Dimethylamine (DMA)

Low temperatures significantly reduced the rates of DMA formation (Figure II.6). Due to experimental difficulties the DMA content of sample SM -20°C and H & G -50°C were not determined at day 180. The combination of cryoprotectant mixture and low temperature storage (-20°C) enables the production of good quality surimi from stabilized mince after a 6 mo period. Treatments at -50°C were very effective in reducing the activity of the enzyme in unstabilized mince samples, given that DMA levels were much less than in treatments stored at -20°C (UM -50°C compared with UM -20°C, $P<0.05$). The addition of cryoprotectants also significantly lowered DMA formation rate (UM -50°C compared with SM -50°C, $P<0.05$). Possibly, the addition of 12% sucrose to the mince reduced water activity sufficiently to inhibit TMAOase activity (MacDonald et al, 1990). As reported by Hinton et al. (1969), the addition of sucrose decreased the activity of some enzymes.

Practical considerations

Several aspects of practical importance were observed during the course of the investigation. In an early state of the project, the addition of cryoprotectants to the mince was done in a silent cutter. During subsequent surimi preparation from the stabilized mince, most of the mince was washed out in the dewatering step. This unexpected finding was attributed to the use of the Hobart cutter mixer Model VCM-40 (Hobart Manufacturing Co., Troy, OH) for cryoprotectant mixing. The silent cutter-mixer was replaced by a Hobart mixer Model S-301 (The Hobart Co., Troy, OH) and the dewatering step for stabilized mince was then almost equivalent to that for fresh mince. Longer dewatering time was necessary for stabilized mince samples compared with other treatments and fresh mince. This could be related to the fact that stabilized mince sample had polyphosphates as a part of the cryoprotectant mixture. Polyphosphates are known to improve water holding capacity (MacDonald, 1992; Okada, 1986).

CONCLUSIONS

This study suggests that stabilized mince (12% w/w sucrose and 0.2% w/w polyphosphates) prepared from fresh Pacific whiting (*Merluccius productus*) can be stored up to 6 mo at -20°C and -50°C and still be used to commercially produce good quality surimi.

This is of practical significance because typical surimi plants generally have storage facilities capable of maintaining a -20°C temperature level.

DMA formation was kept at low levels due to both storage temperature and addition of cryoprotectants.

A comparison between strain values showed no significant difference ($p>0.05$) in the ability of the two stabilized mince samples (SM at -20°C and -50°C) to produce cohesive gels. Also, no statistical difference ($p>0.05$) was detected between the surimi control and surimi produced from stabilized mince stored at -20°C and -50°C.

The type of mixer used to blend stabilizers with mince, and perhaps other mixing parameters, were found to influence the dewatering process during surimi production. Additionally, a slightly longer dewatering time could be expected when producing surimi from stabilized mince.

Although this study has indicated the potential to produce good quality surimi from frozen stabilized mince, results may not be directly extrapolated to a large scale operation. It is first necessary to carry out further experiments to investigate expected production yield, test influence of freezing rates, and find minimum cryoprotectant levels and costs.

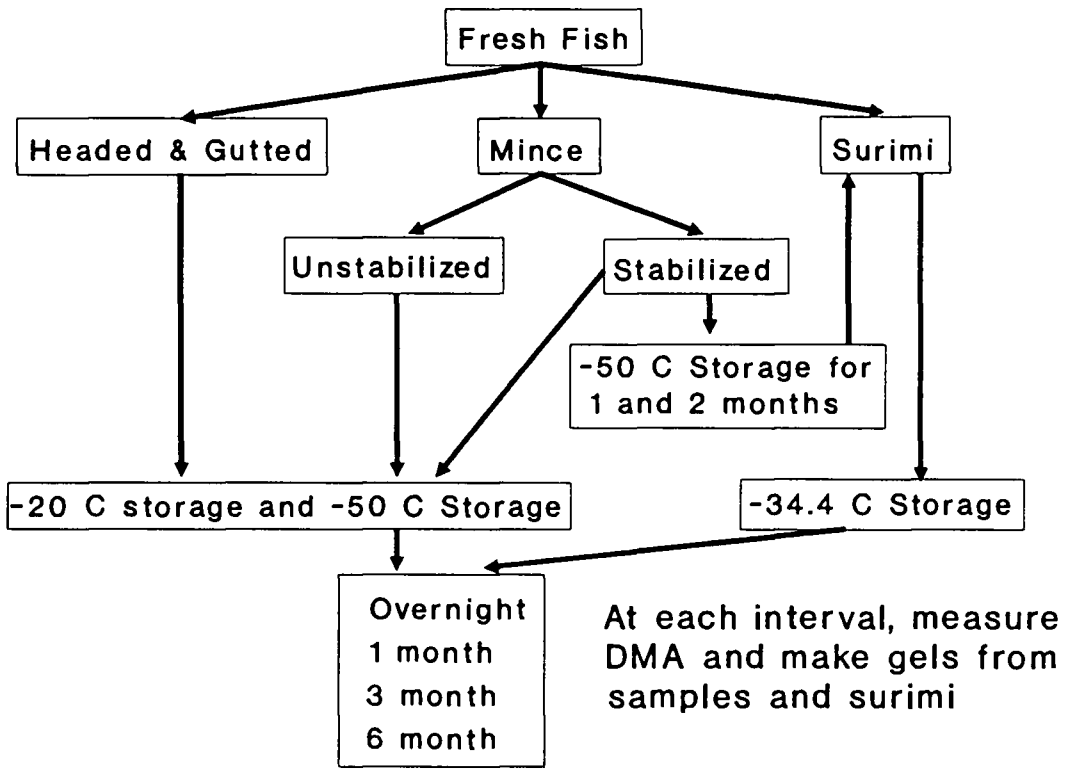

Figure II.1 Experimental design

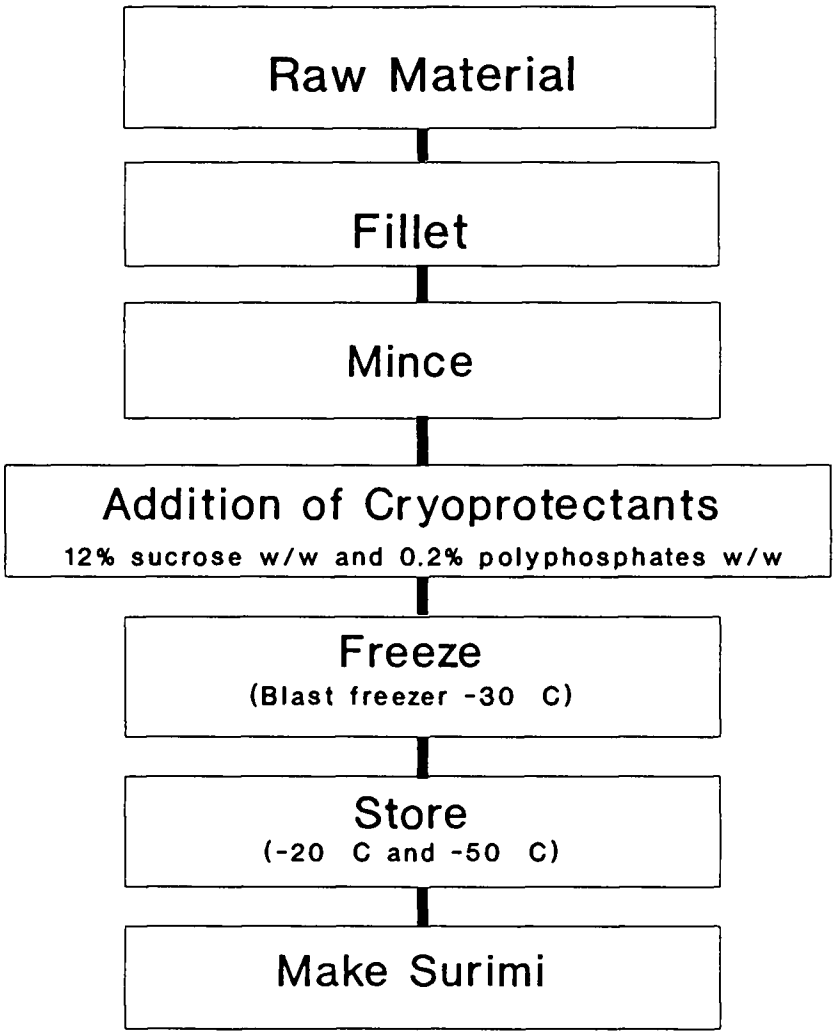

Figure II.2 Stabilized mince process

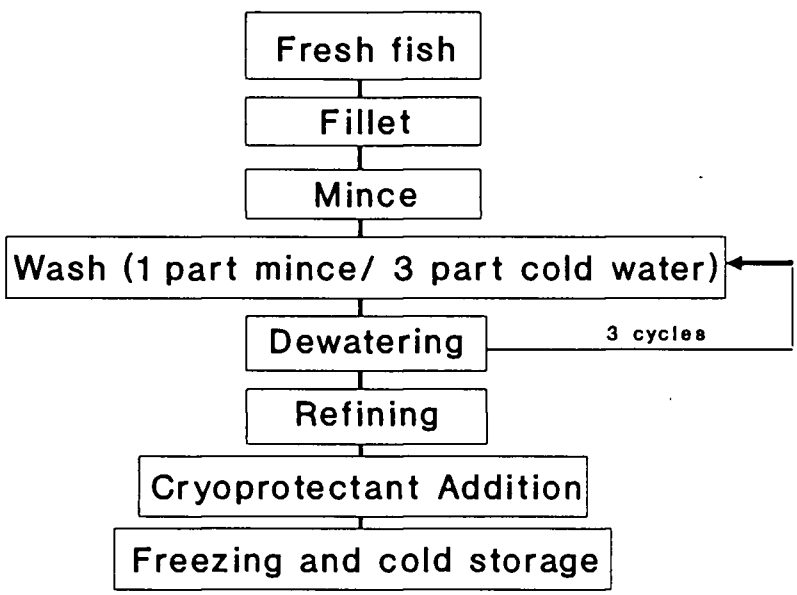

Figure II.3 Surimi process

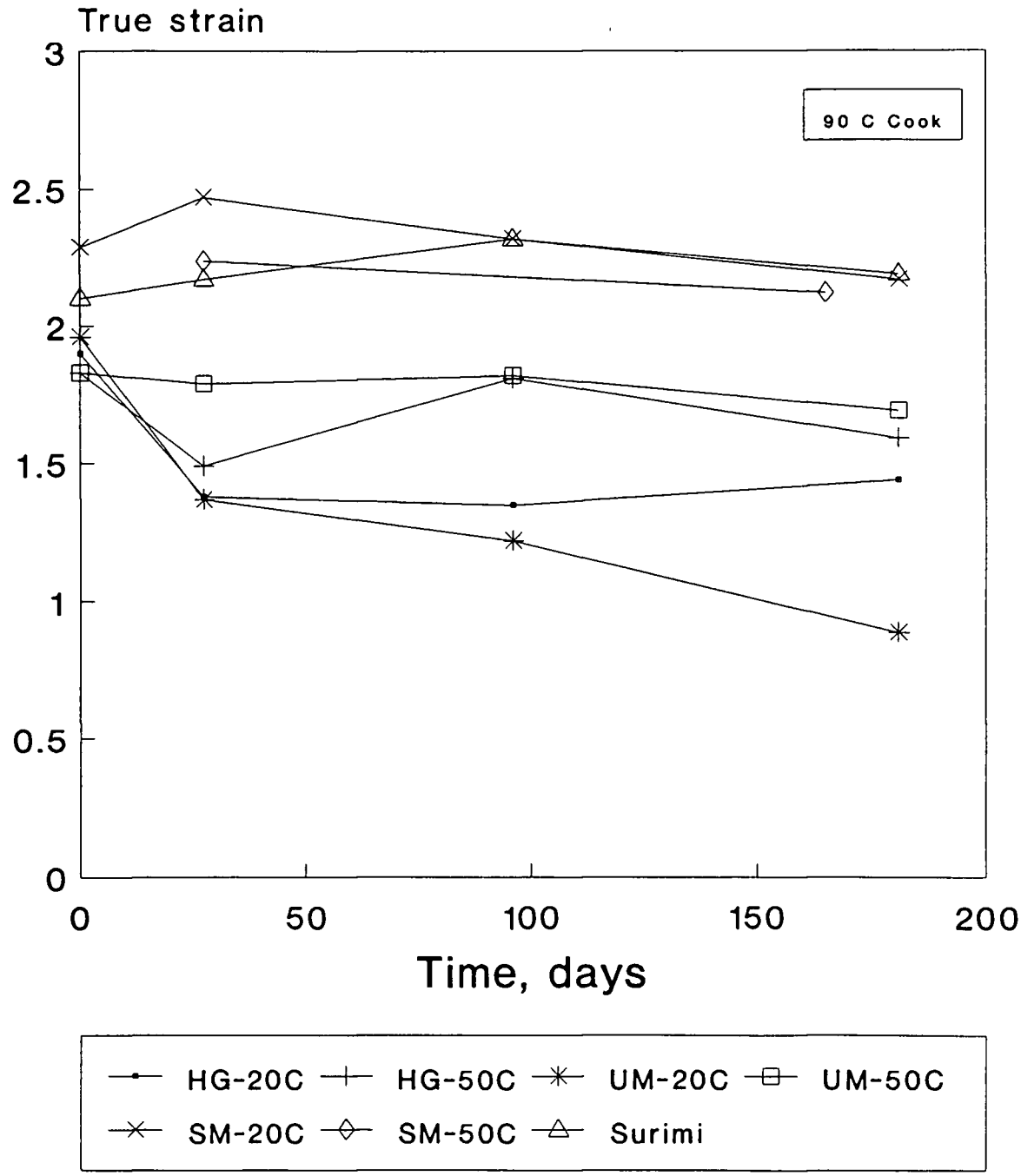

Figure II.4 True strain at failure versus storage time and temperature

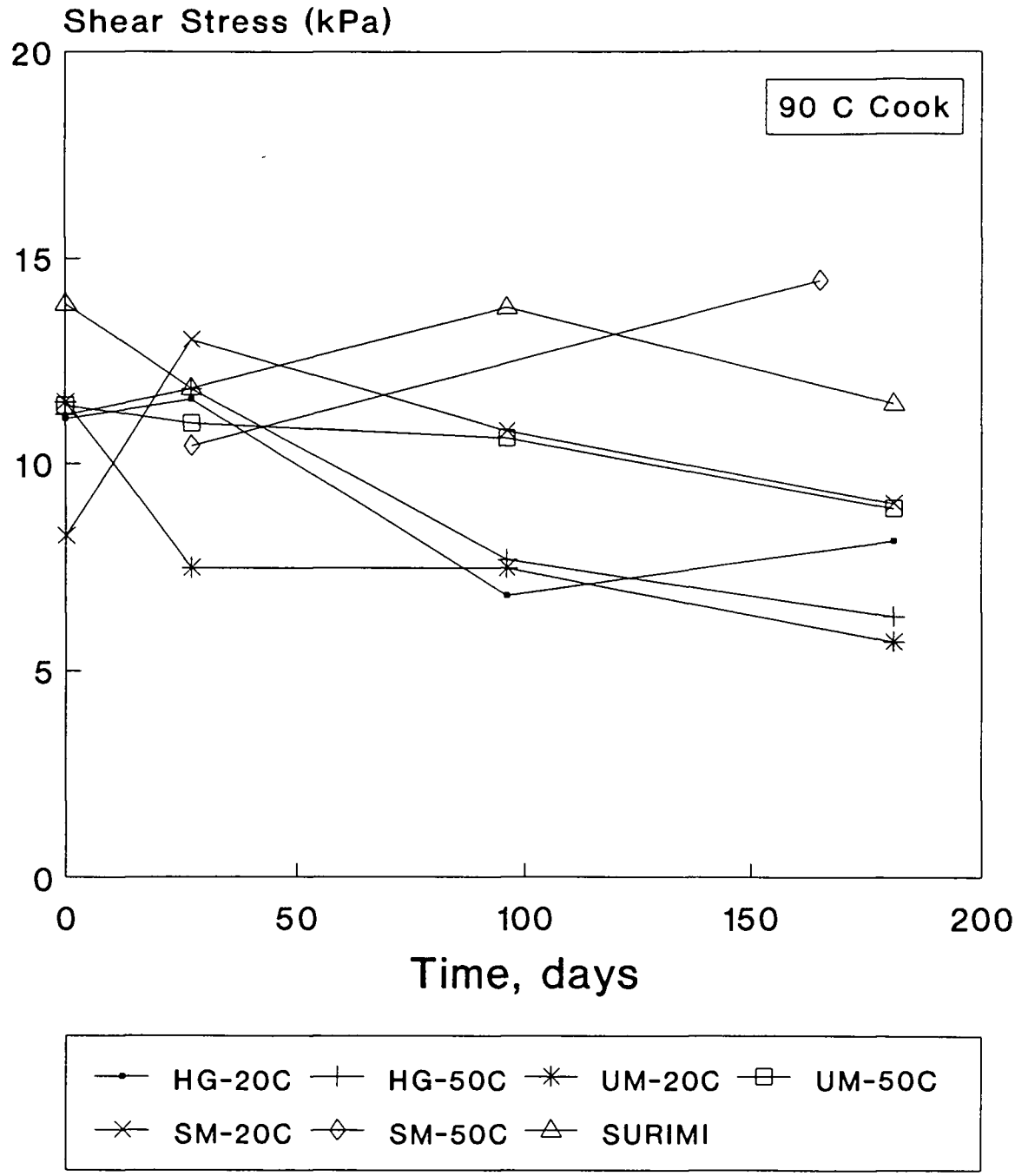

Figure II.5 Shear stress at failure versus storage time and temperature

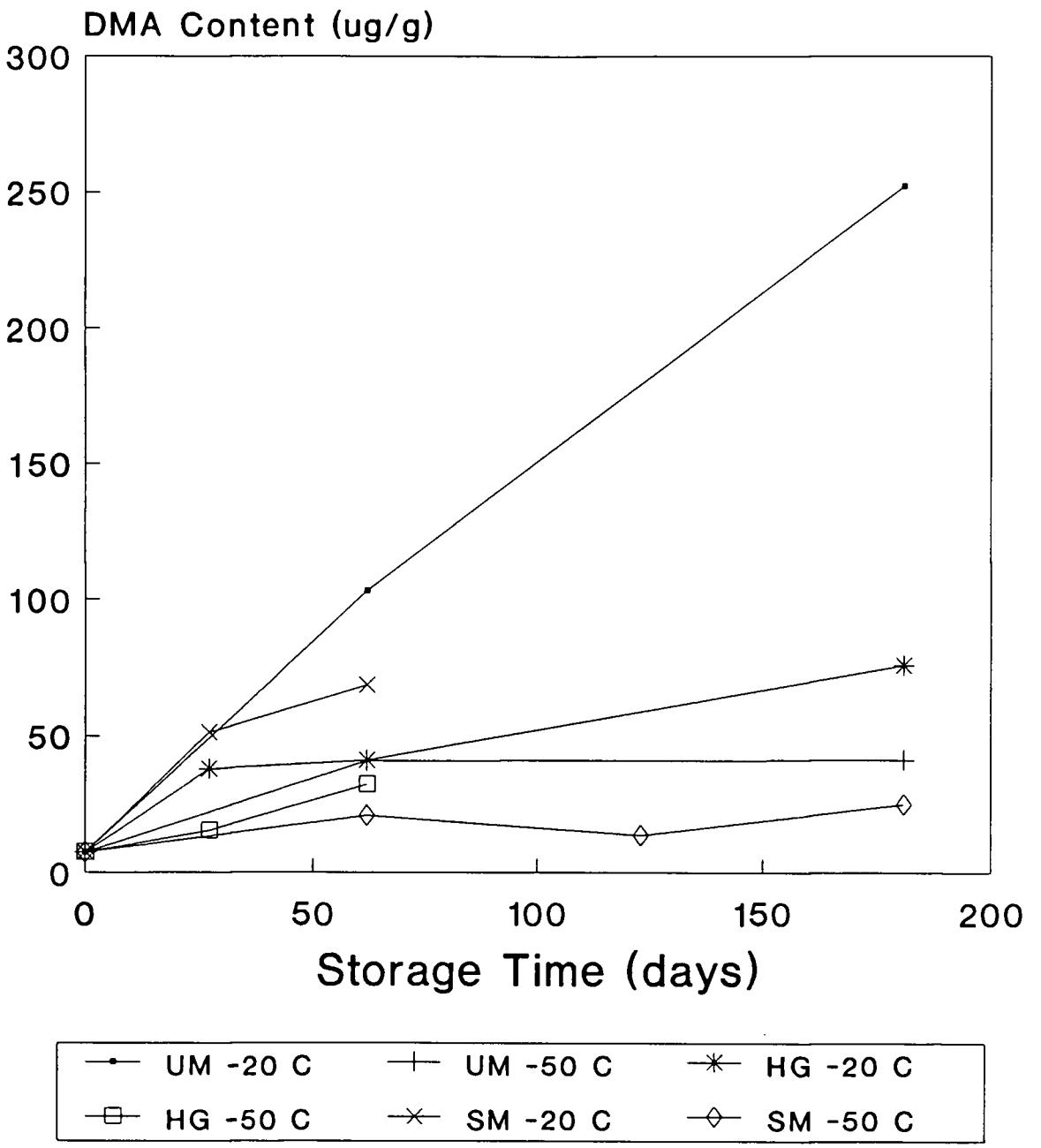

Figure II.6 Dimethylamine levels versus time of frozen storage

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III. Process variables affecting surimi made from frozen stabilized mince of Pacific whiting (*Merluccius productus*)

ABSTRACT

Mince, made from Pacific whiting fillets, was mixed with varying levels of sucrose (6 to 12% w/w) including 0.2% w/w polyphosphates. The stabilized mince samples were stored in frozen storage and used at different time intervals for surimi production. Samples were compared to surimi made from fresh mince and analyzed for texture (strain and stress), color and yield. The effect of different freezing rates on stabilized mince was also investigated. Results showed that good quality surimi could be produced from stabilized mince stored at -20°C with cryoprotectant levels at 6% w/w sucrose and 0.2% w/w polyphosphates. Although there was a slight decrease in whiteness in surimi made from the stabilized mince samples when compared to the control, whiteness values were acceptable. Surimi yields made from stabilized mince were comparable to yields of surimi made from fresh mince.

Different freezing rates were shown to have minimal or no detrimental effect in the gel-forming ability of surimi made from stabilized mince.

INTRODUCTION

Pacific whiting (*Merluccius productus*) is an important commercial species on the West coast of the contiguous United States. This fish can be processed into a good quality surimi, having the ability to produce strong and cohesive gels with the use of protease inhibitors (Chang-Lee, et al., 1990). Surimi is made from a wet concentrate of proteins of fish muscle produced by water washing of minced flesh, then adding cryoprotectants (normally 4% w/w sucrose, 4% w/w sorbitol, and 0.15-0.3% w/w polyphosphates). Surimi can be stored frozen for a year or more and still be used to produce high quality gels (MacDonald, 1992; Iwata et al., 1968; 1971).

It is well known that good quality surimi can only be made from fish whose myofibrillar proteins have not been denatured (Matsumoto, 1979.; Suzuki, 1981.; MacDonald et al., 1990a). Additionally, in making surimi the myofibrillar proteins have been separated from the water-soluble fraction where certain components are known to have a stabilizing effect during frozen storage (Jiang et al., 1987a,b; Loomis et al., 1989). Although undesirable changes such as microbial growth and other chemical alterations are controlled by frozen storage, changes in functional properties can occur (Shenouda, 1980). Adverse effects of freezing and frozen storage on muscle proteins include ice crystallization, proteins denaturation, and intermolecular aggregation or changes in

intramolecular conformation (Park, 1993a). Causative factors influencing protein denaturation during freezing and frozen storage include changes in salt concentration, pH, ionic strength, surface tension, mechanical effects of ice, and dehydration effect (Park, 1993a). The myofibrillar proteins of most fish, are known to be more labile to denaturation than the contractile proteins of homeotherms commonly converted to meat for food, including beef, pork, and poultry (MacDonald, 1992; Connell, 1961). For this reason, surimi requires the addition of cryoprotectants prior to freezing to ensure a long term stability of the proteins in frozen storage.

A major drawback for surimi production on the U.S. West Coast is the seasonal availability of Pacific whiting which limits a plant's operating schedule to approximately 6 mo per year. A potential solution to this problem was studied by Simpson et al. (1993). In that study, good quality surimi was produced from stabilized mince (12% w/w sucrose and 0.2% w/w polyphosphates) that had been stored at -20°C for a period of 6 mo. Although this finding suggests major opportunities for shore-based plants, there still remain several questions concerning stabilized mince. The cryoprotectant mixture used to stabilize mince in the previous study contained a high percentage of sucrose (12% w/w). Decreased concentrations of sucrose need to be investigated.

Another question of practical significance is the expected surimi yield when using stabilized mince. From an

economical point of view it is important to obtain surimi yields that are comparable to yields obtained during normal commercial production. These are on the order of 21-24% (Lee, 1984).

The freezing rate of stabilized mince may also have an effect on protein denaturation and on quality of surimi made from mince. There are a variety of freezing methods and freezing conditions in U.S. fish processing plants. How different freezing rates affect quality characteristics of stabilized mince is an important consideration.

The objectives of this study were to evaluate the potential of producing good quality surimi from frozen stabilized mince prepared with cryoprotectant mixtures with decreasing levels of sucrose, from 12 to 6% (w/w). In order to determine yields obtained from surimi made with stabilized mince, test samples and surimi made from fresh mince were analyzed and compared. Finally, the effect of freezing rates on the ability of stabilized mince samples to produce good quality surimi were also investigated.

MATERIALS AND METHODS

Fish

Pacific whiting fillets, made from fish harvested less than 18 hr previously, were obtained from Ilwaco Fish Co. in Ilwaco, WA, and transported in ice to Oregon State University

Seafood Laboratory in Astoria, OR. The fillets were processed into mince within 2 hr after their arrival at the laboratory.

Freshness

Fish freshness was assessed by K-value analysis following the method of Ryder (1985).

Mince preparation

Fillets were minced in a meat grinder Model 601 Hp (Autio Co. Astoria, OR). Stabilized mince was prepared by mixing different levels of sucrose (C.H. Pure Cane Sugar, Concord, CA) and Brifisol S-1 (Tetrasodium pyrophosphate and Sodium Tripolyphosphate) (BK Ladeburg Co., Cresskill, NJ) with the freshly ground mince in a Hobart mixer Model S-301 (The Hobart MFG Co., Troy, OH). The mixing step was accomplished in 5 min and measured temperatures did not exceeded 8°C. Five stabilized mince samples were prepared by adding different cryoprotectant mixtures as defined in Table III.1. All samples (approximately 600 g) were vacuum packed and frozen overnight in a blast freezer at -30°C (freezing time approximately 3.5 hr). Then samples 1 through 6 were stored at -20°C (Kenmore chest freezer with a temperature controller, Independent Energy Inc.) and sample 7 and the surimi were stored at -34.4°C (SO-LOW freezer Model PR-40-17, Environmental Equip. Co., Cincinnati, OH).

Surimi processing

The surimi process was following a standard process (Chang-Lee, 1990; Simpson et al., 1993). The sample as a mince was washed/dewatered three times with a ratio of 3:1 (water:mince). Each washed consisted of stirring the mince with the water for 5 min. In each wash the temperature was maintained under 5°C by the addition of ice. The last wash included 0.25% Nacl to facilitate dewatering. The resultant washed mince was refined to separate connective tissue. Cryoprotectants consisted in a mixture of 4% sucrose, 4% sorbitol, 0.2% polyphosphates including enzyme inhibitor, beef plasma protein (BPP).

Surimi from stabilized mince

Stabilized mince samples were thawed at each testing time and made into surimi as previously described. Stabilized mince samples were thawed in a cold room (2-4°C) for 4-6 hr and then sliced into small pieces prior to washing. Surimi test samples were then frozen overnight at -30°C (blast freezer) prior to gel preparation (the following day).

Gel preparation and rheological testing

Samples were removed from storage and tempered overnight at 2-4°C. The blocks were sliced into pieces and chopped in a cutter mixer (Stephan Machinery Co., Columbus, OH). During the first minute salt and ice were added to adjust for 2% and 78%

w/w respectively. The last 3 min of mixing was carried out under vacuum. The resulting paste was cooked at 90°C per 15 min. Samples were stored at 2-4°C before texture testing (Simpson et al., 1993).

Dimethylamine (DMA)

All five mince samples described in Table III.1 were tested for dimethylamine content (at times 0, 1, 3, and 6 mo). Dimethylamine content was determined by a modified copper dimethyldithiocarbamate colorimetric procedure (Mackie and Thomson, 1974; Dowden, 1938).

Color measurements

The color of all the surimi gels was measured using Minolta Chroma Meter CR-300 (Minolta Camera Co. Ltd., Osaka, Japan) which reports L^*, a^*, and b^* color coordinates as an output. The instrument was calibrated by using a Minolta white plate and a standard hitching tile recommended by Surimi Technical Committee of National Fisheries Institute (Lanier et al., 1991) (perfect diffuse reflector; $L^*=82.13$; $a^*=-5.24$; $b^*=-0.55$). Samples were compared for whiteness calculated as $100-((100-L^*)^2+a^{*2}+b^{*2})^{1/2}$ (Lanier et al., 1988).

Yield experiments

Surimi made from fresh mince was used as the control. The two samples selected for yield analysis were: stabilized mince

with 12 and 6% w/w sucrose w/w and 0.2% w/w polyphosphates w/w. Samples of 15 kg each were made into surimi after different storage periods (0, 1, and 3 mo).

To evaluate and compare the yield obtained from mince samples and the control, yield was defined in the following terms:

$$\%Yield = \frac{M_{WR} - H_2O}{M - H_2O - Cryoprotectants} * 100 \qquad \text{Eq.III.1}$$

M : $Mince(kg)$; M_{WR} : $Washed,\ refined\ mince(kg)$

Mince and washed and refined mince were directly weighed. Moisture content was determined by heat desiccation of samples (triplicate) until constant weight in a microwave heater (Almonacid, 1991). The weight of cryoprotectants was calculated by considering its specific % in the mince sample. This formula has the assumption that the original cryoprotectant mixture will be washed out during the production of the washed, refined mince.

Freezing rate experiments

Four different freezing rates were established to study the effect of freezing on the ability to produce good quality surimi from stabilized mince (12% w/w sucrose and 0.2% w/w Brifisol S-1). Samples of 10 kg each were packed and frozen in a blast freezer at -30°C, stored at -20°C and tested as a surimi at 0, 1, and 3 mo for gel texture.

Based on the study carried out by Simpson (1993), the thermophysical properties of stabilized mince (apparent volumetric specific heat and thermal conductivity over and under the freezing range) were determined using an inverse procedure. The heat transfer coefficient (h) was reported in our previous study (Simpson, 1993).

To obtain different freezing rates, samples were designed with geometries and dimensions as specified in Table III.2. Freezing times for infinite slab geometries were calculated according to Simpson (1993).

Statistical analysis

Statistical analysis of data was carried out by using one way analysis of variance. Differences among mean values were established by using the Least Significant Difference (LSD) multiple range test (Steel and Torrie, 1980). Values were considered significant when $p<0.05$.

RESULTS & DISCUSSION

K-value

K-value was found to be 10% ±1.8% indicating that the samples were very fresh and had been properly handled (Ehira and Uchiyama, 1974).

Cryoprotectant mixtures

After 6 mo of storage at -20°C, all five samples of unwashed, stabilized mince (Table III.1) produced surimi of good quality as determined by true strain values (see Table III.3). There were no significant differences ($p>0.05$) between the stabilized mince samples having 6 and 10% w/w sucrose and the surimi control, when measured at 6 mo. One sample, stabilized mince with 12% w/w sucrose/0.2% w/w polyphosphate, had a statistically higher value for strain than the control at 6 mo ($p<0.05$). Even at the lowest cryoprotectant mixture (6% w/w sucrose and 0.2% w/w polyphosphates) stored at -20°C, cohesive gels were made from mince that had been stored for up to 6 mo (true strain >2). Good quality surimi, in terms of texture has been shown to have a true strain with a range of 2.0-3.0 (Lanier et al., 1991). Similar results were reported by MacDonald et al. (1990b) and Simpson et al. (1993) in the stabilization of mince produced from New Zealand hoki and Pacific whiting respectively. In their studies, mince stabilized with 12% w/w sucrose and 0.2% w/w polyphosphates, was used to produce good quality surimi after 6 mo of frozen storage. Our results demonstrated that there was sufficient protection against denaturation of the myofibrillar proteins in frozen mince at approximately half the cryoprotection concentrations used in previous studies.

DMA formation versus time for all five treatments are shown in Figure III.1. Previous experiments (Simpson et al.,

1993) showed DMA in unstabilized mince (stored at -20°C for 6 mo) reached a level of ~260 μg/g. Although significant differences were found among samples, all treatments kept DMA formation to a relatively low level (below 120 μg/g). Possibly the addition of sucrose as low as 6% w/w to the mince, combined with low temperature storage (-20°C) reduced water activity sufficiently to inhibit TMAOase activity. Similar results were found by MacDonald et al. (1990b) and Simpson et al. (1993) with 12% w/w sucrose. The ideal frozen storage temperature for fish is -30°C or lower (Regenstein and Regenstein, 1991). For stabilization of Pacific whiting mince, the combination of cryoprotectants and -20°C storage temperature was sufficient to protect muscle proteins against denaturation and maintain their gel forming capabilities.

Significant differences ($p<0.05$) were found in whiteness when all five samples and control were compared after 6 mo of storage. Although whiteness for all sample treatments was 77 or greater after 6 mo of storage, significant differences (lower) were found when compared with surimi (81.25) (see Table III.4).

A whiteness value greater than 75 is considered acceptable for good surimi (Park, 1993b). Lower values in whiteness could be explained by the denaturation of the heme pigments of the stabilized mince during frozen storage. Removal of color through the washing steps may be more

difficult in frozen mince than removal of color from fresh mince (Shimizu et al., 1992).

Yield experiments

No significant difference ($p>0.05$) in yield production (as defined in Equation III.1) was found when both stabilized mince samples (6 and 12% w/w sucrose/0.2% w/w polyphosphates) and surimi made from fresh mince were compared. The different yields obtained were: control 54.75 ±3.58%, stabilized mince (6%w/w sucrose/0.2% w/w polyphosphates) 57.28 ±2.54%, and stabilized mince (12% w/w sucrose/0.2% w/w polyphosphates) 55.28 ±3.59%. A surimi yield of 55% from Pacific whiting stabilized mince was similar to results from Chang-Lee et al. (1990). Also similar yields are normally obtained in our pilot plant productions (Richardson, 1993). This corresponds to a net surimi yield from round fish of approximately 21-24%, which is comparable to commercial production (Lee, 1984). Although the statistical analysis showed no significant yield differences among samples, several aspects need to be addressed. The yield from both stabilized mince samples was slightly higher than the yield from the control. Furthermore, the coefficient of variation for yield evaluated using Equation III.1 was in the range of 4-7%. The relatively high coefficient of variation could be explained by the fact that the tests were carried out in a pilot plant scale (size effect). The slightly higher yields for both stabilized mince

samples in comparison with the control could be related with the assumption in Equation III.1 that all sucrose added to the mince was leached out in making surimi. The addition of polyphosphates could be considered negligible.

Freezing rate experiments

Freezing rate experiments were designed to detect any detrimental effect in gel forming ability due to varying rates of freezing. Four freezing rates that were characterized in Table III.2 were investigated.

True strain values versus time for the four treatments were shown in Figure III. 2. Significant differences ($p<0.05$) were found when samples were compared after 3 mo of storage. A multicomparison test showed that true strain for the highest freezing rate was significantly different (lower) when compared to the other treatments. A possible explanation for this could be related to the experimental conditions established to obtain different freezing rates. To control the freezing rates, the thickness of the sample was considered the control-variable. The highest freezing rate (smallest thickness) had the highest area per unit volume. As shown in Table III.2 the area per unit volume of EHFR sample was 11 times higher than SFR sample. The high area per unit volume could be detrimental in terms of surface effects. For example, the rate of oxygen transfer was 11 times higher in sample EHFR when compared with sample SFR. A statistical comparison among

samples at time 0 showed no significant difference for true strain. This supports the idea that factors other than freezing rate caused the detrimental effect in the sample treated with the highest freezing rate.

Shear stress for the four treatments versus time are shown in Figure III. 3. No significant difference ($p>0.05$) among treatments were found in shear stress. As previously reported by MacDonald (1992); Hamann (1983); Montejano et al. (1984), shear stress tends to have a higher coefficient of variation when compared with true strain.

CONCLUSIONS

All five cryoprotectant levels showed that they are effective in stabilizing mince made from Pacific whiting. Surimi produced from frozen, stabilized mince had similar gel strength as surimi produced from fresh mince. Texture test results demonstrated that sucrose levels of 6% w/w could be used to stabilize whiting mince for as long as 6 mo frozen storage and still produce good quality surimi. There were minor losses in whiteness in surimi made from the stabilized mince. Cryoprotectant mixtures combined with low temperature storage were sufficient to stabilize the myofibrillar proteins in mince.

Yield experiment results showed that surimi made from stabilized mince with 6% w/w sucrose or 12% w/w sucrose and

0.2% w/w polyphosphates were not significantly different from a control surimi after 3 mo storage. Stabilized mince with 12% w/w sucrose and 0.2% w/w polyphosphates produced good quality surimi independent of the freezing rate after 3 mo of storage at -20°C. The study showed the potential of using stabilized mince as a source for surimi production in the Pacific whiting fisheries.

Table III.1. Sample specification for different cryoprotectant mixtures added to samples (w/w).

Sample	% Sucrose	% Polyphosphate[a]	Storage Temperature
Mince 1	12	0.2	-20°C
Mince 2	10	0.2	-20°C
Mince 3	8	0.2	-20°C
Mince 4	6	0.2	-20°C
Mince 5	6	0.2	-34.4°C
Surimi	Normal cryoprotectant[b]		-34.4°C

a: Brifisol S-1 (sodium tripolyphosphate and tetrasodium pyrophosphate).
b: 4% w/w sucrose, 4% w/w sorbitol, 1% w/w BPP, and 0.2% w/w polyphosphates[a]

Table III.2. Sample specification for freezing rate experiments.

Sample	Geometry	Dimension(s) (m)	Freezing Time[a] (hr) Surface-Bottom
SFR	Infinite Slab	0.11	25-45[b]
NFR	Infinite Slab	0.03	8.3-8.8[b]
HFR	Paralelepiped	0.13x0.10x0.05	3.5[c]
EHFR	Infinite Slab	0.01	1.5-1.7[b]

a: Time to reach -10°C
b: Estimated freezing time (Simpson, 1993)
c: Experimentally determined freezing time
SFR: Slow freezing rate; NFR: Normal freezing rate;
HFR: High freezing rate; EHFR: Extra high freezing rate

Table III.3. Change in true strain at failure during frozen storage for samples with decreasing levels of sucrose.

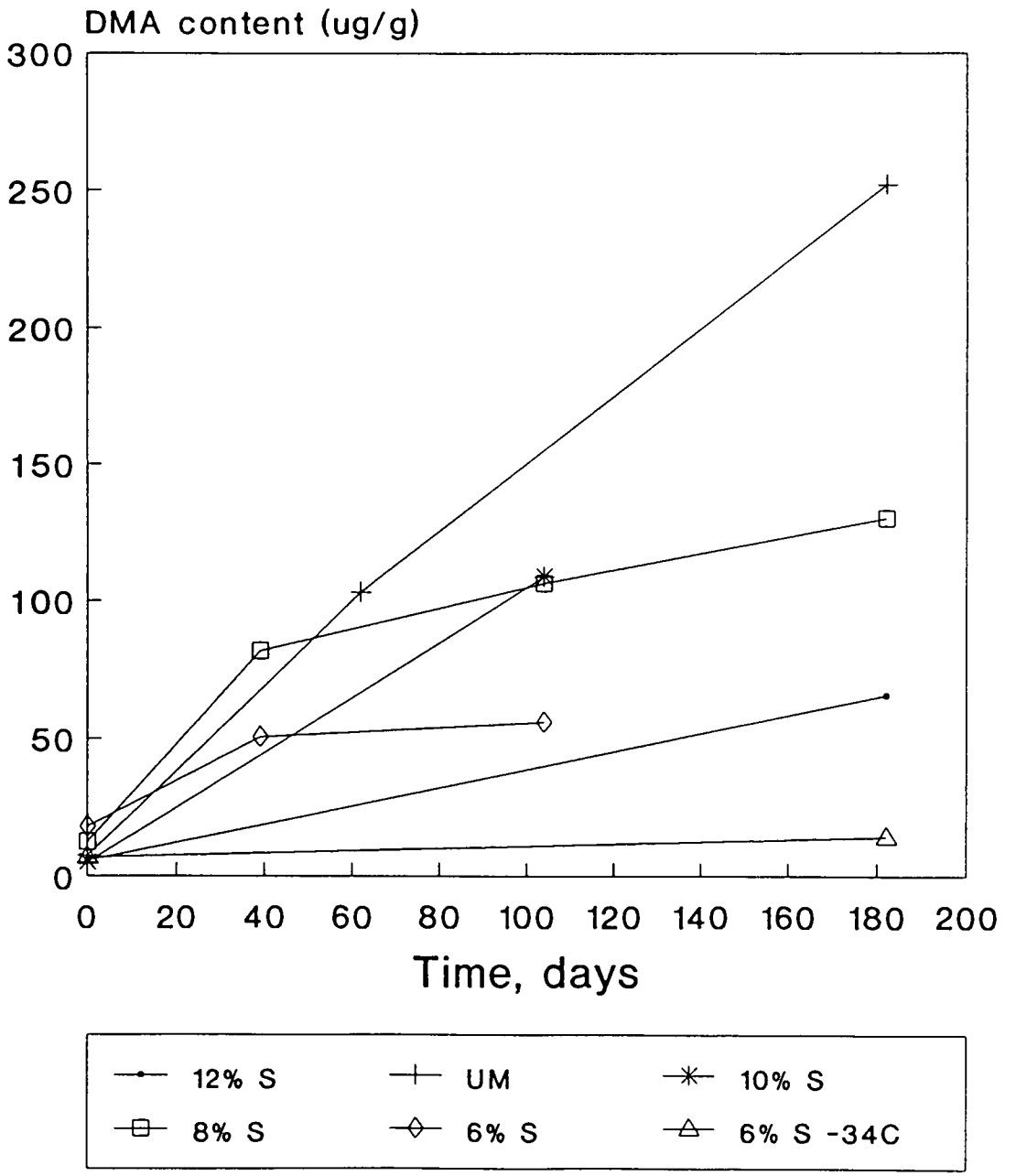
Time (days)	12% S	10% S	8% S	6% S	6% S[1]	Surimi
0	2.58	2.65	2.44	2.58	2.58	2.28
39	2.26	2.42	2.38	2.21	2.23	2.36
104	2.53	2.33	2.28			2.24
111					2.38	
182	2.45^{a}	$2.20^{b,c}$	2.18^{c}	$2.25^{b,c}$	$2.34^{a,b}$	$2.16^{b,c}$

1: Storage temperature was -34.4°C
-Letters are referred to homogeneous groups (LSD analysis)
-All samples included 0.2% w/w polyphosphates

Table III.4. Whiteness for surimi produced from stabilized mince samples and control.

Sample[a]	Whiteness[b]	Std. dev.
Mince 1	78.7	± 0.45
Mince 2	77.7	± 0.40
Mince 3	77.4	± 0.21
Mince 4	78.2	± 0.33
Mince 5	79.6	± 0.36
Surimi	81.3	± 0.45

a: Table III.1
b: Calculated according to Lanier et al. (1988).



UM reported in Simpson et al. (1993)

Figure III.1 Dimethylamine levels in treatments during frozen storage

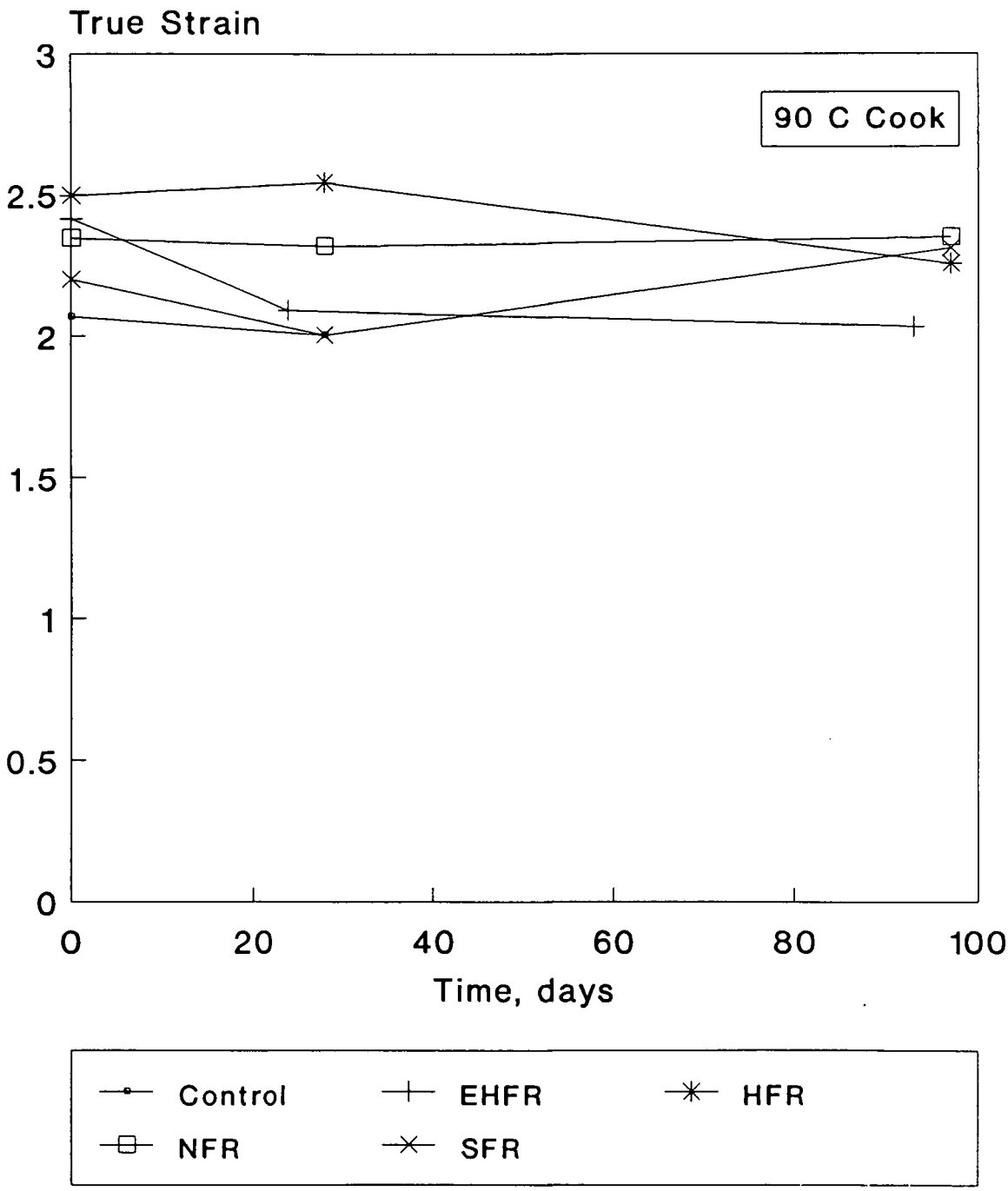


Figure III.2 Change in true strain at failure during storage

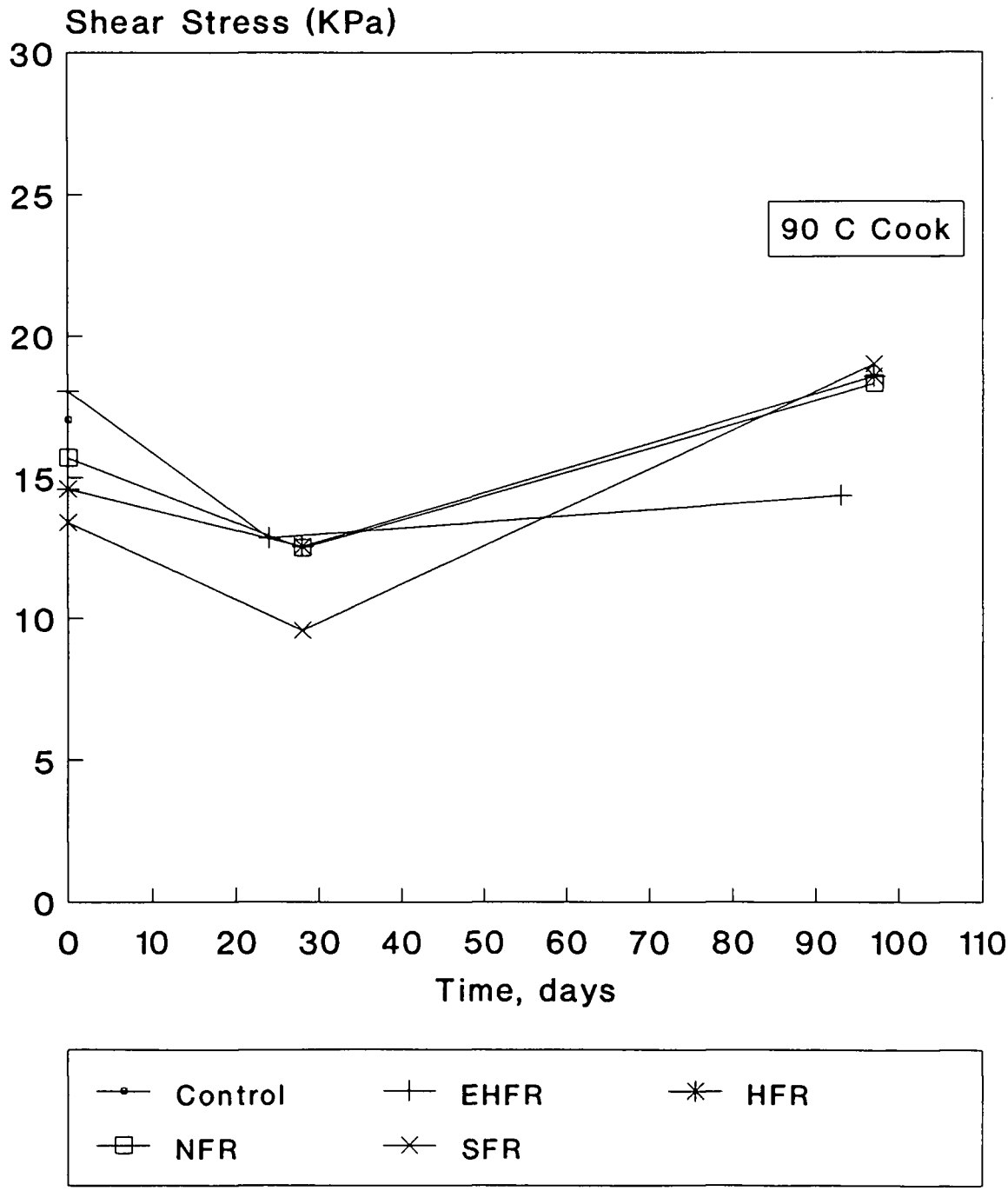


Figure III.3 Change in shear stress at failure during storage

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IV. AN EXPLORATORY ANALYSIS OF A NEW APPROACH TO ESTIMATE THERMOPHYSICAL PROPERTIES OF FOODS AT FREEZING TEMPERATURES

ABSTRACT

An inverse procedure for the estimation of thermophysical properties of foods at freezing temperatures in the range from -22 °C to initial freezing point was explored, analyzed and discussed. The selected thermophysical properties were apparent volumetric specific heat (ρC) and thermal conductivity (k). Empirical and semi-empirical formulas were considered for predicting thermophysical properties.

The accuracy of this new methodology was validated using surimi as a food model. Although the set of determined parameters (C_1, C_2, C_3, k_f, k_1, C) seems to well characterize the heat transfer process, parameters were not necessarily the true values. This evidence was confirmed when parameters were compared with published data and with parameters based on food composition.

INTRODUCTION

In a highly dynamic food industry a considerable number of new products are regularly introduced to the market. Since the composition of agricultural and marine products vary with variety and species respectively, the work involved in thermophysical properties determination would be enormous without an efficient way to predict these properties.

The thermophysical properties of frozen foods are of interest to food engineers in modeling freezing and frozen storage processes and in designing equipment. Simulation of freezing and frozen storage is no longer the problem it once was. With the advent of modern computers and numerical methods, nonlinear heat conduction equations can accurately be solved (Wang and Kolbe, 1990). However, reliability of these predictions is directly related to the accuracy with which the researcher is able to predict thermophysical property values of the food system in the frozen temperature range (Hayakawa, 1977). Thermophysical properties required for these predictions include enthalpy or apparent specific heat, density, and thermal conductivity. The effect of density change on thermal properties is often included by using volume-based specific heat capacity $C(T)$ rather than mass-based $c(T)$ (Cleland, 1990). The effect of density change on object size and shape is normally ignored in prediction of freezing times.

The accuracy of experimental data for thermophysical properties of frozen food could be questioned due to the procedures used to measure such values (Heldman, 1974). This concern is more evident than the case of thermal conductivity due to the need to establish a heat flux in the product during measurement (Heldman, 1974). Another concern is that thermal conductivity obtained from steady state data in freezing calculations implies an assumption that the shapes of these curves are independent of rate (Cleland and Earle, 1984). This is not necessarily true (Cleland and Earle, 1984). A study by Wang and Kolbe, (1990) was conducted to determine sample history effects on thermal conductivity measurements. Results of this test on the effect of sample history indicated no significant difference for measured k values at 30 °C and -30 °C; the same conclusion was found for the effects of refrigerated storage time postmortem and of freezing rates during experiments.

No experimental procedure has been developed to accurately determine thermophysical properties at temperatures slightly below the initial freezing point. As suggested by Wang and Kolbe, (1990) thermal conductivity in this temperature range could be more accurately determined by predicting it using an accurate model rather than measuring it. Although it is possible to accurately measure thermophysical properties of foods below some specific temperature (i.e., -10 °C), the existing approach not only has

the disadvantage of failing to obtain values slightly below the freezing point, but also involves extensive and expensive experimental work. Several researchers have developed theoretical formulas for predicting the temperature dependent thermophysical properties by using information on moisture content and initial freezing point. Heldman 1974, Heldman and Gorby 1975, and Schwartzberg 1983, have developed theoretical formulas for estimating thermal conductivity and apparent specific heat. These formulas could be very useful since one may predict the property values by using readily measurable chemical and physical data. However, there are significant differences between experimental and predicted values when one uses theoretical equations based on greatly simplified assumptions concerning the composition of the food system (Succar and Hayakawa, 1983).

The determination of thermophysical properties from transient temperature measurements is an attractive technique both from the experimental and methodological point of view. The apparatus needed is simple and experimental procedures are typically short. Moreover, during the test, the specimen is subjected to a thermal transient that reflects the working condition in most applications (Milano et al., 1991).

Literally hundreds of papers have been published on the subjects of determining thermal conductivity, specific heat, and density. The main difference between the methodology to be examined in this paper and the traditional approach is in the

experimental simplicity and the simultaneous determination of all parameters of interest. A successful validation of this new procedure would represent a powerful tool for thermophysical property estimation in the freezing temperature range.

The objective of this paper is to explore and analyze a new methodology for the simultaneous determination of thermal conductivity and apparent volumetric specific heat in the range between -22 °C and the initial freezing point. Each thermophysical property will be described by an empirical equation.

MATERIALS & METHODS

Problem description

Assuming known functions for thermophysical properties (apparent volumetric specific heat and thermal conductivity) of a specific food in the freezing temperature range, a heat transfer experiment was designed to estimate the unknown parameters. Because the food material was exposed to temperatures above the freezing range, apparent volumetric specific heat (C) and thermal conductivity (k_1) in this temperature range were also considered as unknowns. Temperature versus time was recorded for different locations in the food model undergoing freezing by one-dimension. The partial differential equation was solved using

time-temperature histories as an input and parameters for thermophysical property functions as unknowns. Solving the partial differential equation with a finite difference method coupled with an optimization technique, parameters were selected to provide the least square fit between the experimental and predicted time-temperature curves.

Several mathematical formulations for apparent volumetric specific heat and thermal conductivity were used in the optimization over the freezing range temperatures. The search of mathematical models was constrained to find the best formulations for the non linear regression procedure and with an appropriate fitness with experimental data.

Materials

Surimi samples were made from Pacific whiting (*Merluccius productus*). Surimi manufacture followed the standard process and the cryoprotectant mixture used was 4% w/w sucrose, 4% w/w sorbitol, 0.2% w/w polyphosphates, and 1% enzyme inhibitor (beef plasma protein, bpp) (Simpson et al., 1993). Surimi is a Japanese term for mechanically deboned fish flesh that has been washed with water and mixed with cryoprotectants for a good frozen shelf life (Lee, 1984). Samples were frozen at -30 °C (blast freezer) and stored at -34.4 °C for four months. Prior to the freezing experiment, samples were tempered overnight at 2-4 °C and then adjusted for moisture content to

78%. The proximate composition of the surimi sample before moisture adjustment is given in Table IV.1.

Apparatus and operating conditions

Figure IV.1 shows the experimental set up for the heat transfer experiments. Before placement in the experimental box, the surimi samples were tempered for 4-6 hours. Special care was used to avoid air bubbles when depositing the surimi sample in the experimental box. In each experiment three thermocouples (copper-constantan) were placed in the sample, one at the bottom, one at the top, and the other in an intermediate position. Thermocouples were calibrated at 0 °C by an NBS-certified thermometer. Ambient temperatures were recorded at one minute intervals with three thermocouples. The experimental box was stored in a cold room (approximately 3 °C) until temperature equilibration was experimentally verified. Due to the uncertainties in placing thermocouples in the sample (mainly the intermediate location), their locations were verified by taking X-ray photographs after the completion of experiments. Temperature measurements were programmed and recorded by a Campbell Scientific 21X Datalogger (Campbell Scientific, Inc., Logan, UT).

Measurement of initial freezing point (T_{sh})

Initial freezing point was measured by placing a thermocouple (copper-constantan)) in a surimi sample deposited

in the experimental box described in Figure IV.1. The freezing point was calculated (4 replicates) from the long temperature plateau which follows supercooling on a graph of time versus temperature (Fennema et al., 1973).

Measurement of heat transfer coefficient (h)

The heat transfer coefficient (h) was estimated using an aluminum block. An experimental box similar to the one shown in Figure IV.1 was used to simulate an infinite slab. The dimensions of the aluminum block were 0.1m x 0.1 m x 0.0254 m. As with the surimi sample, the aluminum block was insulated on all faces except that in contact with the air. Three thermocouples were placed in different locations to experimentally confirm the assumption of uniform temperature at all times within the block (Welty et al., 1984). Because of the slightly but constantly changing ambient temperature the energy balance was solved numerically (integrated with trapezoidal rule).

The heat transfer coefficient (h) was determined using the procedure of Bonacina and Comini, (1973) for heat transfer experiments designed to validate the proposed procedure for parameter estimation.

Heat Transfer Model

One-dimensional transient heat conduction for an infinite slab and for a homogeneous product with temperature dependent

properties, and a boundary condition that takes into account convective heat transfer (third kind), can be described by the following equations.

$$C(T)\frac{\partial T}{\partial \theta}=\frac{\partial}{\partial X}\left(k(T)\frac{\partial T}{\partial X}\right) \qquad 0<X\leq L;\ \theta>0 \qquad \text{IV.1}$$

$$\textit{Initial condition} \quad T(X,0) = T_i \qquad 0\leq X\leq L\ ;\ \theta=0 \qquad \text{IV.2}$$

$$\textit{Boundary condition} \quad h(T_a-T) = -k(T)\left.\frac{\partial T}{\partial X}\right|_{X=0}\ ;\ \theta>0 \qquad \text{IV.3}$$

Due to the characteristics of the mathematical problem (one-dimension and homogeneous material), finite differences are preferred over finite element method for the solution of these partial differential equations (Cleland, 1990). A fully explicit scheme was selected, mainly because of its computer efficiency. Using this numerical scheme, Equation IV.1 can be described in the following terms:

$$C_n^i\frac{T_n^{i+1}-T_n^i}{\Delta\theta}=\frac{1}{(\Delta X)^2}\left[k_{n+1/2}^i(T_{n+1}^i-T_n^i)\ -\ k_{n-1/2}^i(T_n^i-T_{n-1}^i)\right] \qquad \text{IV.4}$$

The boundary condition was derived from a heat balance over the surface space increment (Cleland and Earle, 1977).

$$\frac{k_{+1/2}}{\Delta x}(T_1-T_0)-h(T_0-T_a) = C(T_0)\frac{\partial T_0}{\partial t} \qquad \text{IV.5}$$

Using the fully explicit scheme, Equation IV.5 can be expressed as follows:

$$\frac{k^i_{1/2}}{\Delta X}(T^i_1-T^i_0)-h(T^i_0-T_a) = \frac{1}{2}C^i_0\,\Delta X\,\frac{(T^{i+1}_0-T^i_0)}{\Delta\theta} \qquad \text{IV.6}$$

Thermophysical Properties

As mentioned earlier, several mathematical models for thermophysical property estimations were tested. The criterion to select the appropriate model was based on its ability to fit experimental data and on its reliability for the simultaneous nonlinear parameter estimation (uncorrelated parameters).

Several authors have derived equations to predict thermophysical properties in the frozen temperature range (e.g., Hsieh et al., 1977; Heldman 1974; Heldman and Gorby 1975; Schwartzberg 1976 and 1983). Due to simplifications of the composition of the food and the assumption of dilute solution, these equations are not always in agreement with experimental data. Succar and Hayakawa (1983) developed empirical equations to fit experimental data describing apparent specific heat, density, and thermal conductivity in

the frozen temperature range. Empirical equations are simple to use and have been shown to fit well with experimental data. The following are Succar-Hayakawa empirical equations:

$$C_{pa} = C_e + \frac{D}{(T_{sw}-T)^{n_c}}; \quad T \leq T_{sh} \qquad \text{IV.7}$$

$$k = k_r + S_k(T_{sh}-T) + (k_l-k_r)\left[\frac{(T_{sw}-T_{sh})}{(T_{sw}-T)}\right]; \quad T \leq T_{sh} \qquad \text{IV.8}$$

$$\rho = \rho_r + S_d(T_{sh}-T) + (\rho_l-\rho_r)\left[\frac{(T_{sw}-T_{sh})}{(T_{sw}-T)}\right]; \quad T \leq T_{sh} \qquad \text{IV.9}$$

The use of these expressions in our computer search strategy would require the estimation of 7 parameters ($C_e, D, n_c, k_r, S_k, \rho_r,$ and S_d). Thermal conductivity and density above the freezing range (k_l and ρ_l respectively) could be estimated in a separate experiment. To simplify the search procedure, the possibility of using one equation for apparent volumetric specific heat (ρC_{pa}) was investigated. The proposed equation for ρC_{pa} was:

$$\rho * C_{pa} = C = C_1 + \frac{C_2}{(T_{sw}-T)^{C_3}}; \quad T \leq T_{sh} \qquad \text{IV.10}$$

Using published data (Cleland and Earle, 1984), it was found that the correlation coefficient for the above equation (Equation IV.10) was always 0.98 or higher, showing that

Equation IV.10 will accurately represent the temperature dependency of apparent volumetric specific heat (ρC_{pa}).

To further reduce the number of parameters in the computer implemented search, the original expression for thermal conductivity derived by Schwartzberg, (1983) was considered.

$$k = k_f + (k_1 - k_f)\left[\frac{(T_{sw} - T_{sh})}{(T_{sw} - T)}\right]; \quad T \leq T_{sh} \qquad \text{IV.11}$$

Using published data (Cleland and Earle, 1984), it was found that Equation IV.11 fit well the data in the range of temperatures considered in the present study, -22 °C to initial freezing point.

Considering Equations IV.10 and IV.11, the computer search can be used in this case to determine 4 parameters in the freezing range, C_1, C_2, and C_3 associated with apparent volumetric specific heat and k_f related with thermal conductivity. Using equations IV.10 and IV.11 the search will consider the estimation of 6 parameters (4 in the freezing range and 2 above the freezing range). Although Equations IV.7, IV.8, and IV.9 have a slightly better advantage over Equations IV.10 and IV.11 in fitting experimental data, the latter two equations facilitate the simultaneous determination of the unknown parameters. Formulations with fewer parameters could be better suited for non linear regression (Beck and Arnold, 1977).

Identifiability

As discussed by Beck and Arnold, (1977), "a convenient means of anticipating slow convergence or even non-convergence in estimating parameters can save unnecessary time and expense".

The following identifiability criterion was derived by Beck and Arnold, (1977). The derived criterion applies for linear and non-linear estimation. The derivation was based on a weighted sum of squares function which includes least squares, weighted least squares, and ML (Maximum Likelihood) estimation with normal errors, in each case with no constraints on the parameters.

$$\lambda_1 \frac{\partial T_{x,\theta}}{\partial C_1} + \lambda_2 \frac{\partial T_{x,\theta}}{\partial C_2} + \lambda_3 \frac{\partial T_{x,\theta}}{\partial C_3} + \lambda_4 \frac{\partial T_{x,\theta}}{\partial k_f} + \lambda_5 \frac{\partial T_{x,\theta}}{\partial k_1} + \lambda_6 \frac{\partial T_{x,\theta}}{\partial C} = 0 \qquad \text{IV.12}$$

Linear dependence occurs when there exist 6 parameters λ_i not all 0, so Equation IV.12 is true for all observations (further details in Appendix I).

A finite difference approximation of the sensitivity coefficient could be expressed by the following equation, taking parameter C_1 as an example:

$$\frac{\partial T}{\partial C_1} \cong \frac{T(C_1+\Delta C_1, C_2, C_3, k_f, k_1, C) - T(C_1, C_2, C_3, k_f, k_1, C)}{\Delta C_1} \qquad \text{IV.13}$$

As stated by Bard, (1974) a criterion to choose ΔP (where P is any parameter) is given by the following expression:

$$10^{-5} P < \Delta P < 10^{-2} P \qquad \text{IV.14}$$

For the problem described earlier, the number of thermocouple locations and thermophysical properties functions were chosen to fulfill the identifiability condition. Examples of the use of the identifiability condition are presented and discussed in Appendix I.

Search Procedure

Several mathematical optimization methods are available in the food engineering literature. An approach that has received increased attention is the Complex Optimization Method which is one of the available direct search techniques (Box, 1965; Beveridge and Schechter, 1970).

We considered a problem in which experimental values of temperature, T, were measured during a transient experiment by 3 thermocouples at 33 discrete times.

$$\tau_i^j = \tau(x_i, \theta_j) \quad \begin{matrix} i=1,2,3 \\ j=1,\ldots 33 \end{matrix} \qquad \text{IV.15}$$

The purpose of the experiment was to determine the magnitude of the parameters C_1, C_2, C_3, and k_f that are associated with apparent volumetric specific heat and thermal conductivity in the freezing temperature range. The search also included the estimation of thermal conductivity (k_l), and apparent

volumetric specific heat (C) above the initial freezing point of the food material. The model that describes the heat transfer experiments was presented in Equations IV.1 through IV.3. The solution to this model may be expressed as:

$$T_i^j = T(x_i, \theta_j, C_1, C_2, C_3, k_f, k_1, C) \qquad \text{IV.16}$$
$$i=1,2,3; \quad j=1,\ldots,33$$

Nonlinear least-squares determines the set of parameters which minimizes, in the least-squares sense, the difference between experimental and predicted temperatures.
Mathematically it is desired to minimize:

$$F = \sum_{i=1}^{3}\sum_{j=1}^{33} \left(\tau_i^j - T_i^j(C_1, C_2, C_3, k_f, k_1, C) \right)^2 \qquad \text{IV.17}$$

Statistical Analysis

The bootstrap technique (Efron, 1979) is a simple and straight-forward method for calculating approximated biases, standard deviations, confidence intervals, in almost any non-parametric estimation problem. In general terms bootstrap is described in Figure IV.2.

The following procedure was used to apply the bootstrap technique in our transient heat transfer experiment. The parameters obtained from the search procedure ($C_1^*, C_2^*, C_3^*, k_f^*, k_1^*$, and C^*) are the best estimates in a least square sense. The temperature error can be expressed as:

$$e_i^j = \tau_i^j - T_i^j(C_1^*, C_2^*, C_3^*, k_f^*, k_1^*, C^*) \qquad i=1,2,3; \quad j=1,\ldots,33 \qquad \text{IV.18}$$

With the set of 3x33 (99) independent errors it is possible to generate a new set of 99 errors using a random number generator to draw 99 new errors (e_i^{j*}) independently and with replacement from the original set. These new errors (which are the bootstrap sample) are a subset of the original ones. The new temperatures for the bootstrap sample are calculated as follows:

$$T_i^{j*} = T_i^j(C_1^*, C_2^*, C_3^*, k_f^*, k_1^*, C^*) + e_i^{j*} \qquad i=1,2,3; \quad j=1,\ldots,33 \qquad \text{IV.19}$$

The bootstrap estimates ($C_1^B, C_2^B, C_3^B, k_f^B, k_1^B, C^B$) are calculated exactly as was shown in Equation IV.17, but now using the bootstrap temperatures T_i^{j*}.

$$Min.\left[F^*(C_1, C_2, C_3, k_f, k_1, C) = \sum_{i=1}^{3}\sum_{j=1}^{33}(\tau_i^j - T_i^{j*})^2\right] \qquad \text{IV.20}$$

This whole process must be repeated at least 25 times (Efron, 1979) to accurately estimate the standard errors for each parameter.

The estimated variability of the parameters can be calculated as follows:

Bootstrap Sample	Bootstrap Estimators
1	$C_{1,1}$, $C_{2,1}$, $C_{3,1}$, $k_{f,1}$, . . . , C_1, $k_{1,1}$
2	$C_{1,2}$, $C_{2,2}$, $C_{3,2}$, $k_{f,2}$, . . . , C_2, $k_{1,2}$
3	$C_{1,3}$, $C_{2,3}$, $C_{3,3}$, $k_{f,3}$, . . . , C_3, $k_{1,3}$
.	. . . .
.	. . . .
25	$C_{1,25}$, $C_{2,25}$, $C_{3,25}$, $k_{f,25}$, . . , C_{25}, $k_{1,25}$

For a parameter P the mean P_m and the standard error σ_p are calculated as follow:

$$P_m = \frac{\left[\sum_{i=1}^{25} P_i\right]}{25} \qquad \text{IV.22}$$

$$\sigma_p = \left[\frac{\sum_{i=1}^{25} (P_i - P_m)^2}{24}\right]^{1/2} \qquad \text{IV.23}$$

RESULTS & DISCUSSION

Heat transfer coefficient (h) and initial freezing point (T_{sh})

The heat transfer model presented in Equations IV.1 through IV.3 coupled with the thermophysical properties functions has eight parameters (C_1, C_2, C_3, k_f, C, k_1, h, and T_{sh}). The initial freezing point (T_{sh}) and heat transfer

coefficient (h) were determined in separate experiments. The initial freezing point was -1.159 ±.027 °C, a value that compared well with the value reported by Wang and Kolbe, (1990) (-1.16 ±.09 °C).

The heat transfer coefficient was determined with an aluminum block in the blast freezer used for surimi experiments. Experimental conditions were established to match the ones used for the thermophysical properties estimation. Six experiments were carried out giving an average value for h of 15.4 w/m^2 °C (std. dev. ± 0.7). Temperatures were recorded once per minute both in the aluminum block and in the ambient air. Due to the slight but constantly changing ambient temperature, the energy balance was numerically integrated using the trapezoidal rule with a one minute interval. The assumption of constant heat transfer coefficient during the experiment was tested solving the energy balance for different time-periods. The time for the experiment (approximately 25 min per test) was divided in to two periods over which the heat transfer coefficient was averaged. In each experiment the heat transfer coefficient in the second period was slightly lower than in the first period. A statistical analysis showed no significant difference ($p>0.05$) between a constant h and the h estimated per each time period.

Identifiability

As previously discussed, the Succar-Hayakawa empirical formulas for thermophysical properties fit extremely well with the experimental data. In this study it was important to find formulas with good fitting characteristics and which are also well suited for non linear regression (assuming uncorrelated parameters). Due to the need to simultaneously determine the parameters involved in the thermophysical property functions, it was necessary to apply the identifiability condition in order to select the appropriate mathematical models and number of thermocouple locations.

Linear independence was verified using Mat Lab software evaluating the rank of the matrix generated by Equation IV.12. Figures IV.3a and IV.3b show the sensitivity coefficients for the parameters involved in the Succar-Hayakawa formula for thermal conductivity (Equation IV.8) and for the apparent volumetric specific heat formula (Equation IV.10). High correlations exist between parameters S_k and k_r (Figure IV.3a). Also, high correlations were found between parameters C_2 and C_3 in the apparent volumetric specific heat function (Figure IV.3b). Table IV.2a shows the correlation matrix for sensitivity coefficients when using one thermocouple in heat transfer experiments. As pointed out, high correlations exist among parameters in each model but also high correlations were found among parameters of thermal conductivity function and apparent volumetric specific heat. One possible solution for

this problem was to calculate the correlations among parameters in an experiment with a larger number of thermocouples. When the number of thermocouples was increased from 1 to 6 the correlation between the aforementioned parameters was just slightly reduced. Tables IV.2a and IV.2b shows the correlation matrix for experiments considering 1 and 6 thermocouples.

Besides increasing the number of temperature readings, another way to overcome this problem was to find a mathematical model for thermal conductivity that had fewer parameters (Equations IV.7 and IV.9 that include 6 parameters for apparent specific heat and density were already reduced to a 3 parameters model, Equation IV.10). Equation IV.11 was found to have a good fit with data in the range of -22 °C through the initial freezing point and had fewer parameters than the Succar and Hayakawa formula. Tables IV.3a, IV.3b, and IV.3c show the correlation matrices for parameters C_1, C_2, C_3, and k_f. When adding more thermocouples, the correlation between parameters was reduced, but no significant changes were realized when comparing 3 with 6 thermocouple locations. Although an experiment with 6 thermocouples could have a slight advantage over an experiment with 3 thermocouples in terms of correlation between parameters, it becomes experimentally more complex, thus increasing the experimental error.

The latter models for thermal conductivity and apparent

volumetric specific heat (Equations IV.10 and IV.11) showed less correlation when compared with the Succar-Hayakawa expression for thermal conductivity (Equation IV.8), but high correlation between parameters still remains. Specially between C_2 and C_3. According to Beck and Arnold, (1977) high correlation exists whenever an off-diagonal element(s) exceed 0.9 in magnitude and estimate(s) tend to be inaccurate.

Thermophysical properties determination

The proposed approach was analyzed for the case for which six parameters were treated as unknowns (C_1, C_2, C_3, k_f, C, and k_l). Due to the conception of the methodology under study, the experimental apparatus is simple but must be carefully designed. The mathematical model described in Equations IV.1 through IV.3 has some strict assumptions (homogeneous and isotropic material, infinite slab, constant thickness, etc.) that were considered in constructing the experimental box and during the experiment itself (see Figure IV.1). Dimensions of the experimental box (0.1 m x 0.1 m x .031 m) and experimental conditions to be considered were: expansion of the material during the freezing process, volume of thermocouple wires, Biot number, assumption of infinite slab, and the expected time for freezing experiments. The volume of the three thermocouple wires was approximately 0.03% of the total volume (considered negligible). Although the Biot number is not constant during the experiment, the experiment was designed to

obtain a Biot number in the range of 0.2-4 (Cleland and Earle, 1984). Another aspect of crucial relevance was the insulation of the experimental box (infinite slab assumption).

The freezing experiment was carried out in a blast freezer at approximately -26 °C. Temperatures were recorded once each minute at three locations in the surimi sample. Three thermocouples also recorded ambient temperatures. Due to the slight but constantly changing ambient temperature, experimental ambient temperatures were used in the boundary condition when solving the mathematical model. To accurately identify the position of each thermocouple, an X-ray photograph was taken immediately after the experiment.

Figure IV.4 shows the temperatures recorded in each location and also the best time-temperature curve estimated by the mathematical model (Equations IV.1 to IV.3 coupled with Equations IV.10 and IV.11). Thermophysical properties were treated as unknowns for the mathematical model. The predicted temperatures in Figure IV.4 correspond to the best fit in the least square sense between the experimental temperatures and the ones given by the mathematical model. Parameters (C_1, C_2, C_3, and k_f) and thermophysical properties (C and k_1) were considered the best estimates in the least square sense. Figures IV.5 and IV.6 show the predicted thermophysical properties for the surimi sample including the best estimates for the parameters in the freezing range. Apparent specific

heat and thermal conductivity above the freezing range were 4.24×10^6 J/m^{3}kg°C and .748 W/m°C respectively.

Statistical analysis

The errors (33 for each curve) were obtained from time-temperature curves presented in Figure IV.4. Errors represent the difference between the experimental temperatures and the ones predicted by the model. According to the Bootstrap procedure 25 sets of time-temperature curves (3 curves per set corresponding to 3 thermocouple locations) were generated. For each set the best Bootstrap estimates for parameters and thermophysical properties were obtained. Table IV.4, present the means, standard errors, and the best estimates for each Bootstrap sample.

Validation experiment

The experimental box (Figure IV.1) was decreased in thickness to 0.024 m and used to carry out a set of different experiments to test the accuracy of the determined parameters. The heat transfer coefficient (h) was obtained with the best fit between the predicted surface temperature and the experimentally recorded temperature for each validation experiment . An average value of 15.3 W/m°C was obtained in four experiments. A statistical comparison between the heat transfer obtained with the aluminum block experiments and the

one predicted with the estimated thermophysical properties showed no significant difference ($p>0.05$).

Figures IV.7 and IV.8 show two of the several validation experiments. In each figure the experimental and predicted temperatures for the bottom and surface locations on the sample are shown. Good agreement was found in every experiment. The freezing times were predicted with an error margin no more than 2.5%. It is important to note that the validation experiments differed from the original one but were in the same range of Biot number.

Although the estimated parameters (C_1, C_2, C_3, k_f, k_l, and C) showed high accuracy when tested in heat transfer experiments, their accuracy does not strictly mean that they are the true parameters. Because of the high correlation among parameters (previously discussed under identifiability), the whole set of parameters seems to characterize the system but not necessarily each parameter individually. Table IV.5 shows some of the parameters estimated with the proposed procedure and parameters based on sample composition (Table IV.1). Although properties based on food composition are not necessarily the true values, parameters estimated with the proposed procedure tend to overestimate the true values. For example, given that specific heat of ice is approximately half of that liquid water, we expected to find that $C_{-20°C} \sim C/2$. These parameters estimated with food composition tended to agree with this fact but not the ones estimated with

the proposed procedure. Thermal conductivity above the initial freezing point (k_1) was compared with data found in the literature. Wang and Kolbe, (1990) reported a thermal conductivity for pollock surimi of 0.492 W/m°C that compared well with the value estimated using food composition (.485 W/m°C), but again the thermal property based in the new procedure was higher (.748 W/m°C).

Interesting was to find that thermal difussivity (α) at temperatures in the range of -20 °C ($\alpha_{-20°C}=k_{-20°C}/C_{-20°C}$) was similar for both estimation procedures. This finding helps to explain in some degree (at temperatures below -20 °C) why with different parameters it is possible to obtain the same rate of heat transmission.

CONCLUSIONS

In an attempt to simultaneously determine apparent volumetric specific heat and thermal conductivity in the freezing range temperatures, a transient heat transfer experiment was designed. Because of the possible correlation between parameters, several models for apparent volumetric specific heat and thermal conductivity were studied. Using published mathematical models for these two thermophysical properties, high correlations between parameters were found when properties were calculated with the transient experiment. A new expression for apparent volumetric specific heat was

proposed in an attempt to reduce correlation between parameters. Although correlations between parameters were reduced as the number of parameters was reduced, high correlations between parameters C_2 and C_3 in the apparent volumetric specific heat function still remained, meaning that the determined parameters are not necessarily the true values.

Using parameters determined with the proposed procedure we were able to predict with high accuracy temperatures recorded in a different experiment. A preliminary analysis comparing the estimated parameters with parameters based on food composition confirmed that the individual parameters were not the true values. Further comparison with literature data showed the same pattern.

The proposed procedure could be more successfully applied to determination of thermal conductivity in the freezing range temperatures (only 1 parameter). If thermal conductivity above the initial freezing point were experimentally evaluated and also apparent volumetric specific heat above and below the freezing point, the proposed procedure will involve the estimation of 1 parameter (k_f in Equation IV.11). Several papers in the literature have shown the successful application of one parameter estimation (Bonacina and Comini, 1972; Uno and Hayakawa, 1980; Singh, 1982; Chavarria and Heldman, 1983).

Table IV.1. Proximate composition of surimi sample[a] (% w/w)

Parameter	Mean ±Std. Dev.	No. of Observations
Moisture	75.83 ±.19	3
Lipid	1.64 ±.10	3
Protein	13.39 ±.26	3
Ash	0.72 ±.01	3

a: The cryoprotectant mixture included 4% w/w sucrose, 4% w/w sorbitol, 1% beef plasma protein (bpp), and 0.2% w/w polyphosphates

Table IV.2a. Correlation matrix for parameters in Equations IV.8 and IV.10 (1 thermocouple location).

	C_1	C_2	C_3	k_r	S_k
C_1	1.0000	.9475	-.9595	-.9206	-.9544
C_2	.9475	1.0000	-.9984	-.9831	-.9982
C_3	-.9595	-.9984	1.0000	.9855	.9970
k_r	-.9206	-.9831	.9855	1.0000	.9775
S_k	-.9544	-.9982	.9970	.9775	1.0000

Table IV.2b. Correlation matrix for parameters in Equations IV.8 and IV.10 (6 thermocouple locations).

	C_1	C_2	C_3	k_r	S_k
C_1	1.000	.9398	-.9559	-.8765	-.8787
C_2	.9398	1.0000	-.9969	-.9002	-.9508
C_3	-.9559	-.9969	1.0000	.9123	.9468
k_r	-.8765	-.9002	.9123	1.0000	.9369
S_k	-.8787	-.9508	.9468	.9369	1.0000

Table IV.3a. Correlation matrix for parameters in Equations IV.10 and IV.11 (1 thermocouple location).

	C_1	C_2	C_3	k_f
C_1	1.0000	.9229	-.9354	-.9497
C_2	.9229	1.0000	-.9990	-.9965
C_3	-.9354	-.9990	1.0000	.9990
k_f	-.9497	-.9965	.9990	1.0000

Table IV.3b. Correlation matrix for parameters in Equations IV.10 and IV.11 (3 thermocouple locations).

	C_1	C_2	C_3	k_f
C_1	1.0000	.9270	-.9360	-.8900
C_2	.9270	1.0000	-.9982	-.9491
C_3	-.9360	-.9982	1.0000	.9519
k_f	-.8900	-.9491	.9519	1.0000

Table IV.3c. Correlation matrix for parameters in Equations IV.10 and IV.11 (6 thermocouple locations).

	C_1	C_2	C_3	k_f
C_1	1.0000	.9291	-.9357	-.8985
C_2	.9291	1.0000	-.9974	-.9533
C_3	-.9357	-.9974	1.0000	.9562
k_f	-.8985	-.9533	.9562	1.0000

Table IV.4 Bootstrap estimators

Sample number	k_f (W/m°C)	C_1 (J/m³°C)	C_2 (J-°K^{n-1}/m³)	C_3	C (J/m³°C)	k_1 (W/m°C)
1	2.36	3.09 E6	5.33 E8	2.63	3.15 E6	.49
2	2.50	3.16 E6	4.19 E8	2.55	4.22 E6	.73
3	2.56	3.03 E6	4.86 E8	2.50	3.56 E6	.65
4	2.96	2.94 E6	4.39 E8	2.37	4.23 E6	.58
5	2.64	3.19 E6	5.29 E8	2.63	4.10 E6	.67
6	2.40	3.06 E6	4.49 E8	2.42	4.20 E6	.74
7	2.60	3.22 E6	5.01 E8	2.56	3.96 E6	.73
8	2.88	2.83 E6	4.58 E8	2.40	3.53 E6	.44
9	1.88	2.98 E6	4.17 E8	2.37	3.71 E6	.60
10	2.56	3.03 E6	4.55 E8	2.43	4.35 E6	.67
11	2.72	3.31 E6	4.90 E8	2.54	4.36 E6	.62
12	2.75	3.00 E6	4.75 E8	2.47	4.23 E6	.58
13	2.45	3.12 E6	5.20 E8	2.63	4.70 E6	.76
14	2.76	3.00 E6	4.88 E8	2.51	4.05 E6	.59
15	2.51	3.03 E6	4.73 E8	2.48	4.03 E6	.68
16	2.83	3.24 E6	5.24 E8	2.59	2.86 E6	.55
17	2.31	3.04 E6	5.14 E8	2.59	3.41 E6	.68
18	2.46	3.17 E6	4.95 E8	2.54	3.89 E6	.71
19	2.28	3.20 E6	5.56 E8	2.69	3.34 E6	.67
20	2.58	3.41 E6	5.24 E8	2.64	3.89 E6	.69
21	2.42	3.34 E6	5.68 E8	2.75	3.67 E6	.70
22	2.64	3.10 E6	5.04 E8	2.54	3.22 E6	.56
23	2.58	3.09 E6	5.01 E8	2.54	3.43 E6	.69
24	2.50	3.46 E6	5.89 E8	2.79	3.43 E6	.56
25	2.42	3.13 E6	4.90 E8	2.53	3.83 E6	.71
Mean	2.54	3.13 E6	4.96 E8	2.55	3.81 E6	.64
Std. Dev.	.22	1.48 E5	4.30 E7	.11	4.48 E5	.08
C.V.(%)[a]	8.77	4.73	8.67	3.92	11.76	12.5

a: C.V. represents the coefficient of variation

Table IV.5 Parameters and properties estimated with proposed procedure and based in food composition.

Parameter/ Property	Present study[a]	Food composition[b,c]
C	4.24×10^6	3.81×10^6
$C_{-20°C}$	3.09×10^6	1.93×10^6
k_1	0.748	0.485
$k_{-20°C}$	2.445	1.900

a: units are ($J/m^3kg°C$) for C, $C_{-20°C}$ and ($W/m°C$) for k_1 and $k_{-20°C}$

b: C and $C_{-20°C}$ estimated using Schwartzberg's data (1983).

c: k_1 and $k_{-20°C}$ estimated using Murakami and Okos Equations (1989).

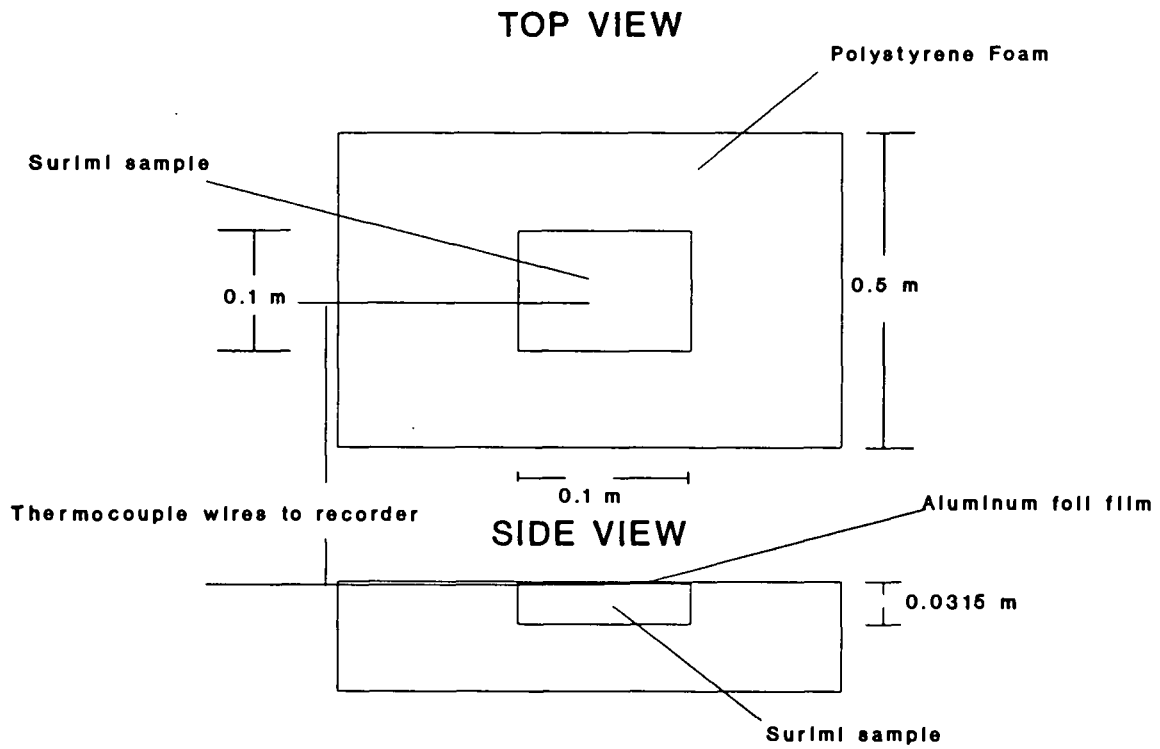


Figure IV.1 Experimental setup for thermophysical property determination

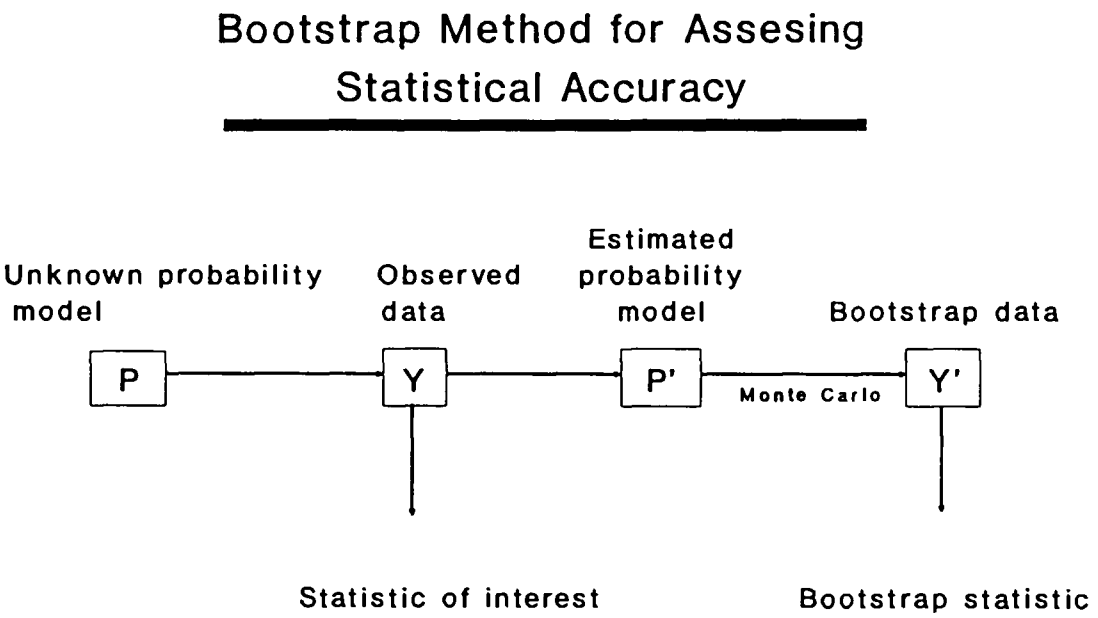
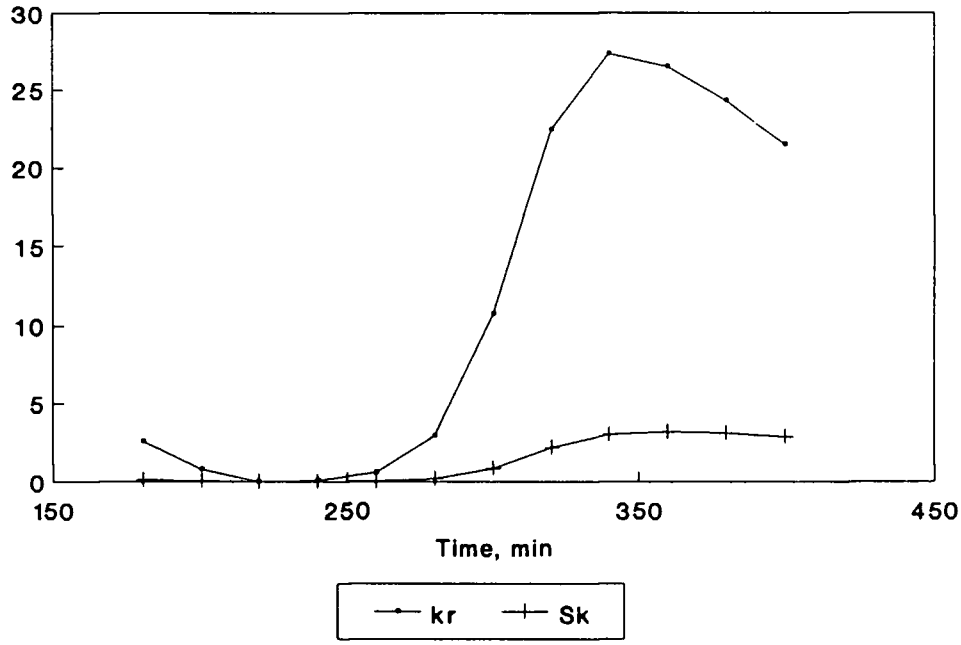
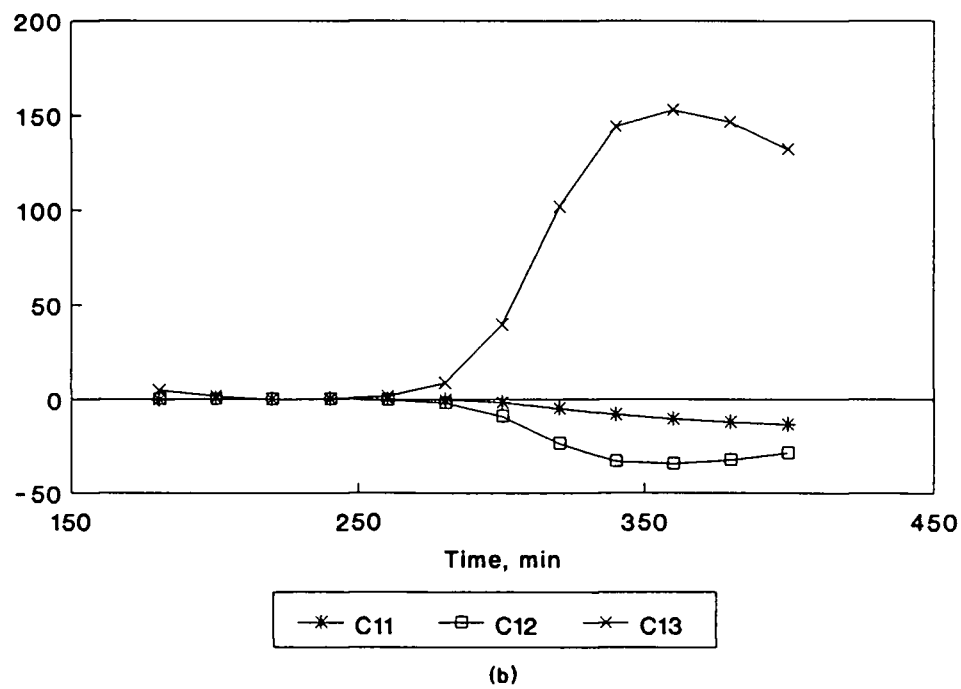


Figure IV.2 A general diagram of the bootstrap method



(a)



(b)

Figure IV.3 a. Sensitivity coefficients for S_k and k_r
b. Sensitivity coefficients for C_{11}, C_{12}, and C_{13}

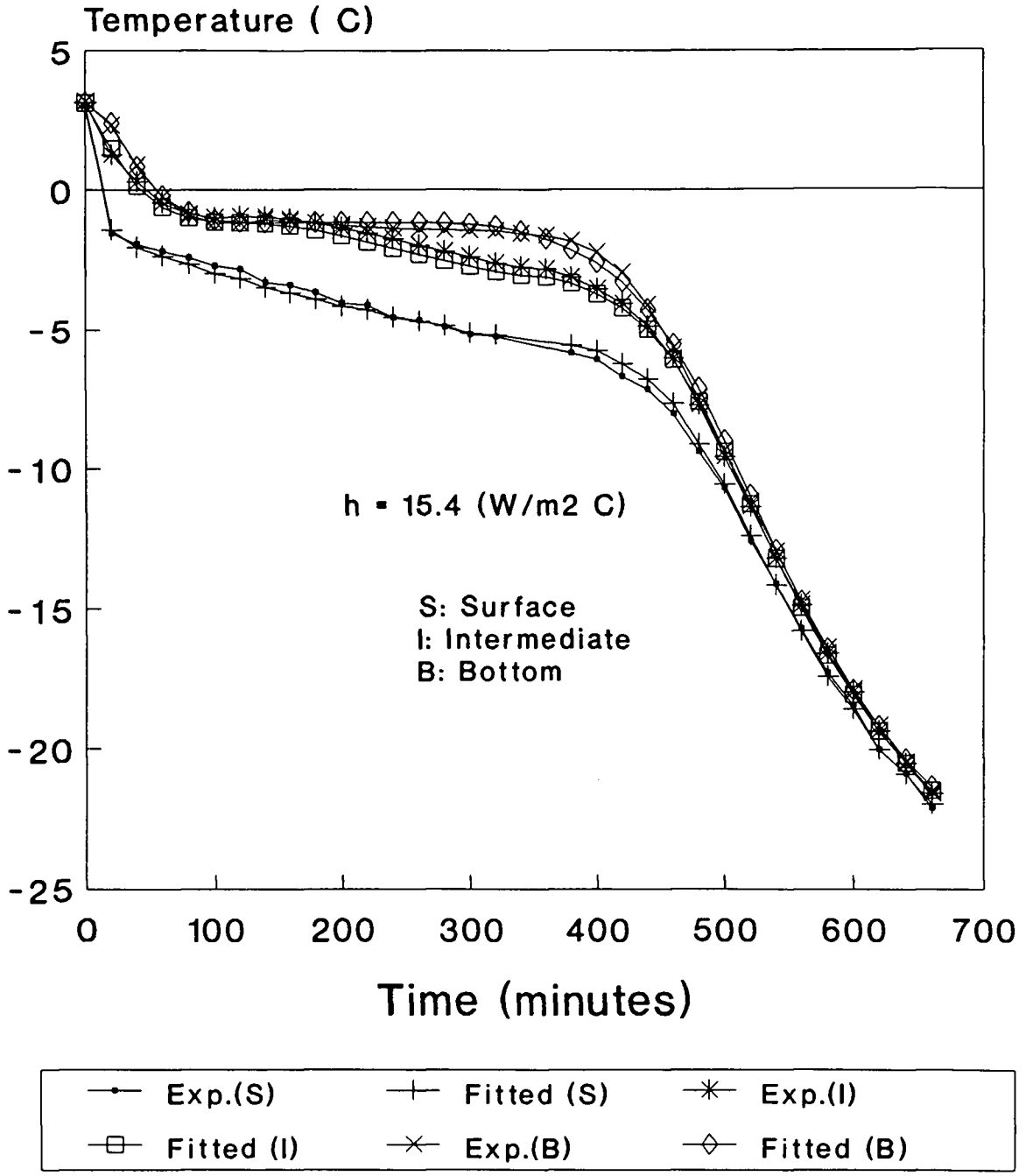


Figure IV.4 Thermophysical properties determination

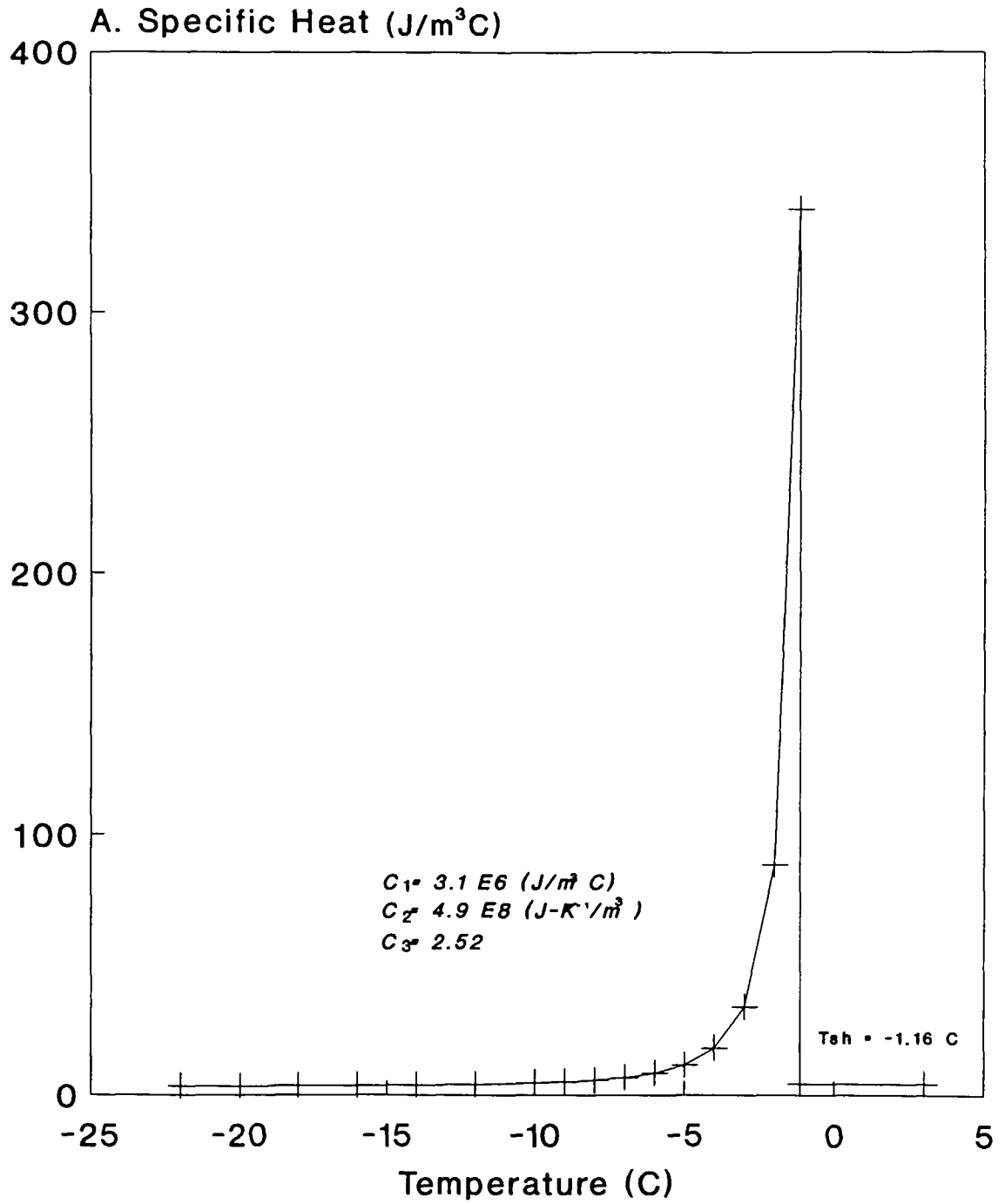


Figure IV.5 Apparent specific heat of surimi sample

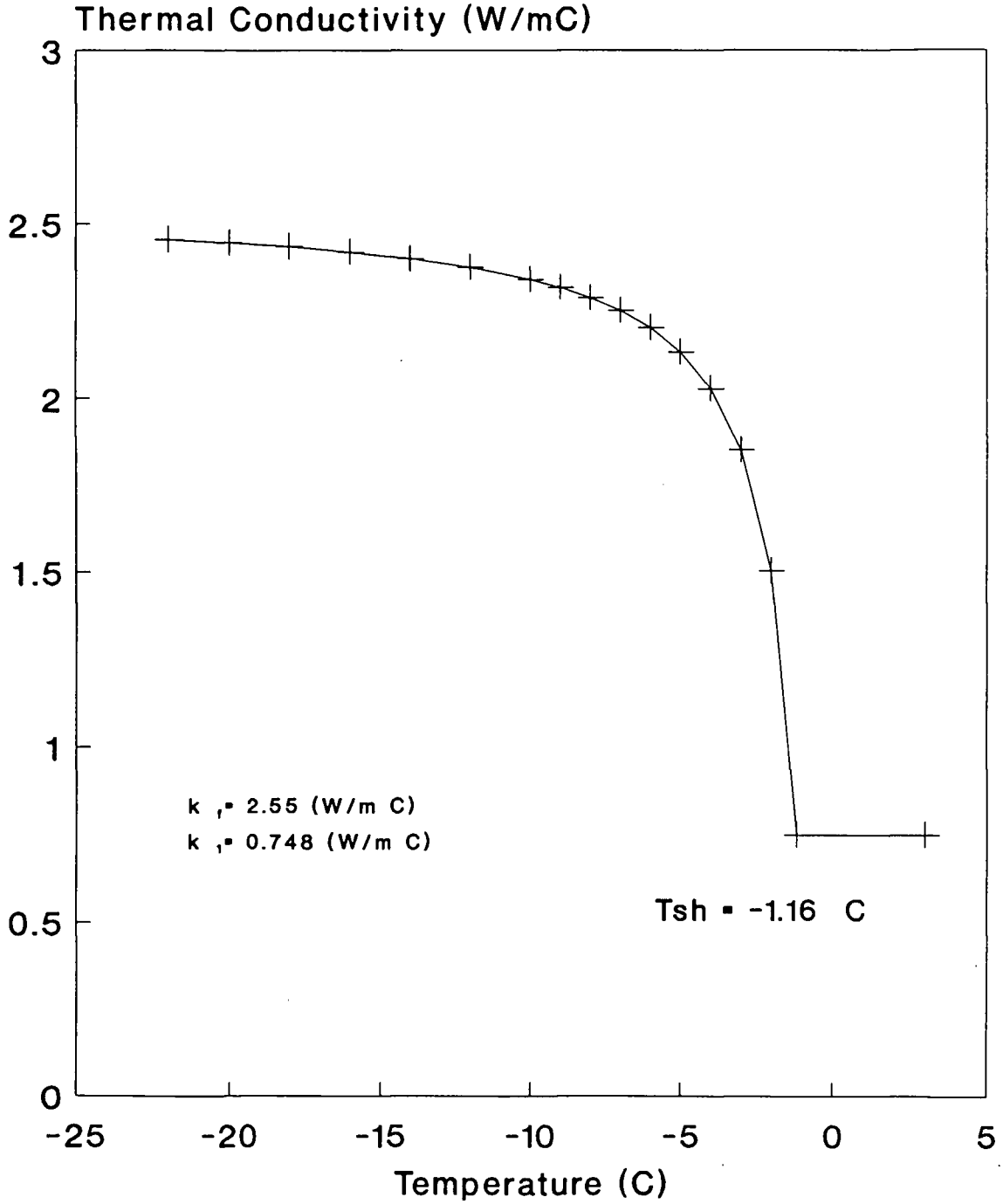


Figure IV.6 Thermal conductivity of surimi sample

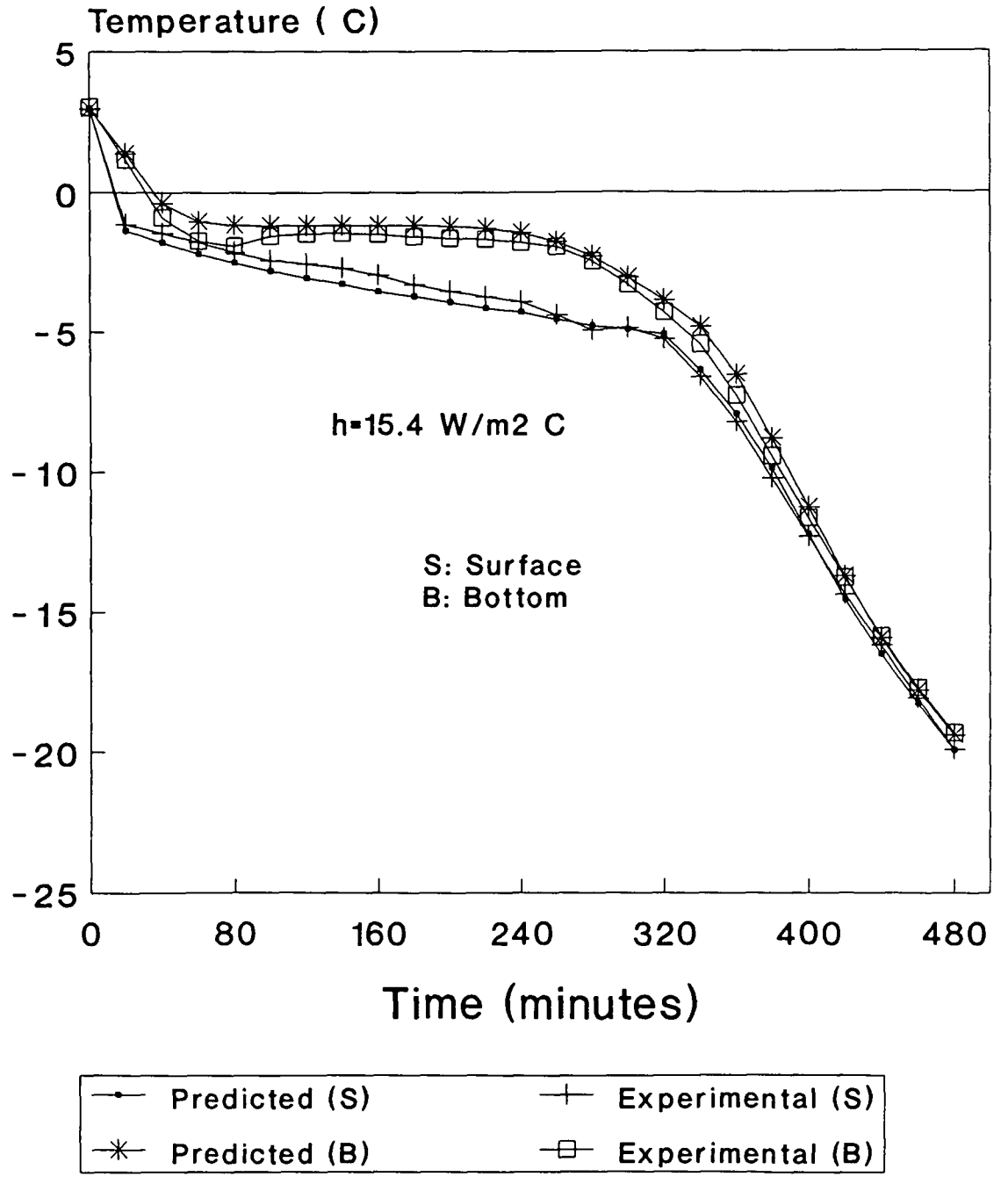


Figure IV.7 Predicted and experimental temperatures for validation #1

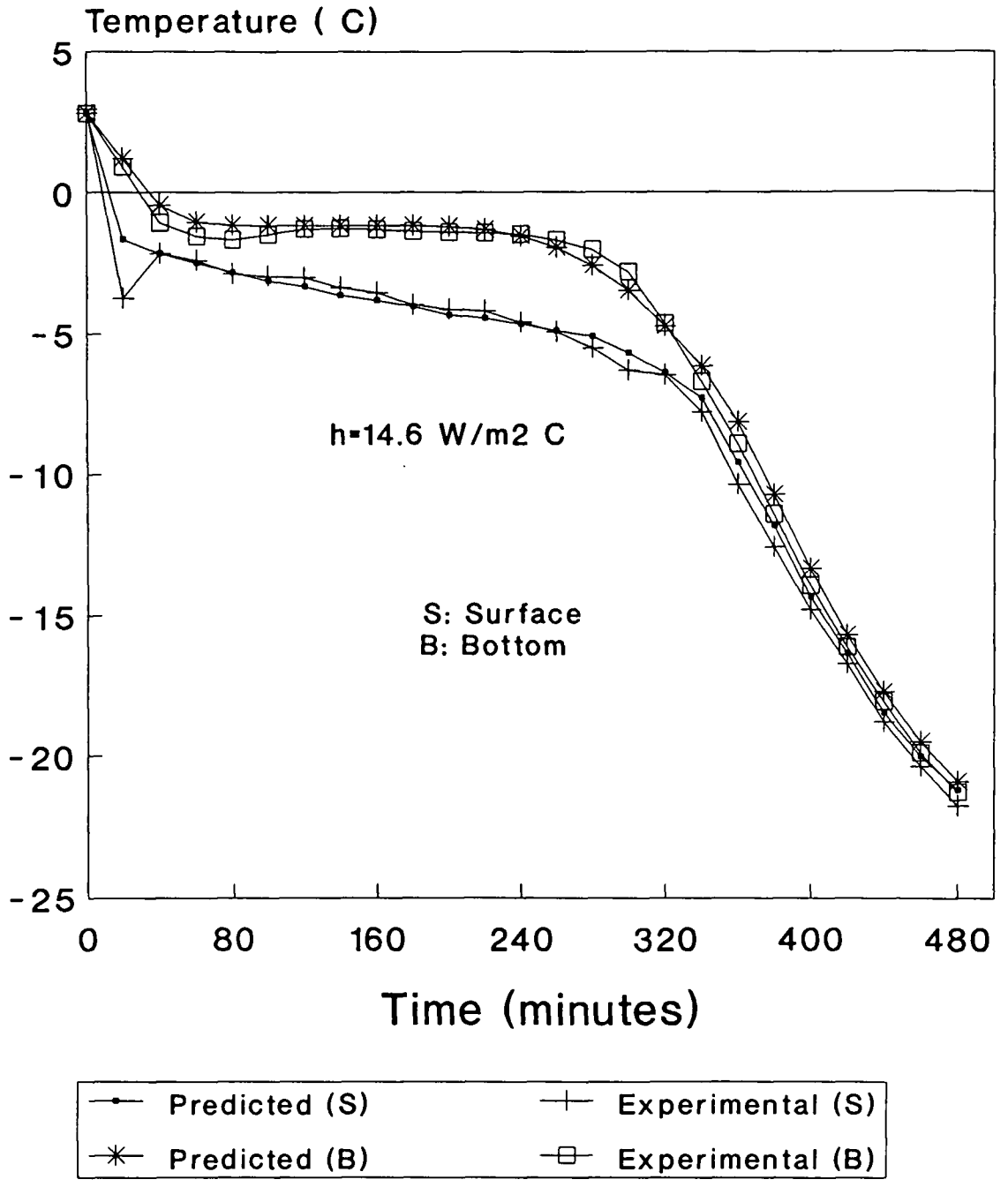


Figure IV.8 Predicted and experimental temperatures for validation #2

Nomenclature

C : apparent volumetric specific heat ($J/m^3°C$)

$C(T)$: apparent volumetric specific heat as a function of temperature ($J/m^3°C$)

C_e : empirical constant ($J/kg°C$)

C_{pa} : apparent specific heat ($J/kg°C$)

C_n^i : apparent volumetric specific heat at node n and time $i\Delta\theta$ ($J/m^3°C$)

C_1 : empirical constant ($J/m^3°C$)

C_2 : empirical constant ($J-°K^{n-1}/m^3$)

C_3 : empirical constant

D : empirical constant ($J-°K^{n-1}/kg$)

e_i^j : temperature error at thermocouple i and time indicator j (°C)

F : objective function

h : heat transfer coefficient ($W/m^2°C$)

k : thermal conductivity ($W/m°C$)

$k(T)$: thermal conductivity as a function of temperature ($W/m°C$)

k_n^i : thermal conductivity at node n and time $i\Delta\theta$ ($W/m°C$)

k_r : empirical constant ($W/m°C$)

k_1 : thermal conductivity above the initial freezing point ($W/m°C$)

k_f : thermal conductivity in the fully frozen state (Schwartzberg's original equation), parameter in our search (W/m°C)

L : thickness of surimi sample for heat transfer experiments (m)

n_c : empirical constant

S_d : empirical constant (kg/m^3°C)

S_k : empirical constant (W/m)

T : temperature (°C)

T_a : ambient temperature (°C)

T_i : initial temperature of surimi sample for heat transfer experiment (°C)

T_n^i : temperature at node n and time $i\Delta\theta$ (°C)

T_{sh} : initial freezing point of food material (°C)

T_{sw} : normal freezing temperature for pure water (°C)

$T(x,\theta)$: temperature as a function of position and time (°C)

x : position in x-axis (m)

x_i : position of thermocouple i (m)

Greek letters

α : thermal difussivity (m^2/s)

ρ : density of food material (kg/m^3)

ρ_r : empirical constant (kg/m^3)

ρ_l : density of food material above the initial freezing point (kg/m^3)

θ : time (s)

θ_j : time at indicator j (s)

$\Delta\theta$: time increment (s)

Δx : space increment (m)

τ_i^j : experimentally recorded temperature at thermocouple i and time indicator j (°C)

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APPENDICES

APPENDIX I

Identifiability

The identifiability condition will be analyzed by two examples. A mathematical derivation of this criterion can be found in Beck and Arnold, (1977).

The derivation for the identifiability condition showed that linear dependence occurs when for n parameters the relation:

$$\lambda_1 \frac{\partial y_i}{\partial P_1} + \lambda_2 \frac{\partial y_i}{\partial P_2} + \ldots + \lambda_n \frac{\partial y_i}{\partial P_n} = 0 \qquad \text{AI.1}$$

is true for all i observations and for not all the λ_j values equal to zero.

The derivation can be described by the following two examples. The examples have been chosen to discuss the parameter estimation problem in two different situations.

Example 1. In this example, we will analyze a mathematical model where the linear dependence among parameters is not straightforward. The mathematical model is:

$$y_i = ae^{-(b + cx_i)} \qquad \text{AI.2}$$

Where

$$\frac{\partial y_i}{\partial a} = e^{-(b + cx_i)}; \quad \frac{\partial y_i}{\partial b} = -ae^{-cx_i}e^{-b}; \quad \frac{\partial y_i}{\partial c} = -x_i ae^{-cx_i}e^{-b} \qquad \text{AI.3}$$

Replacing in AI.1 and reducing terms:

$$\lambda_1 - a\lambda_2 - ax_i\lambda_3 = 0 \qquad \text{AI.4}$$

If $\lambda_3=0$, linear dependence exists between parameters a and b ($\lambda_1 = a\lambda_2$).

Example 2. This example is a case where the parameters cannot easily be estimated if measurements are made only over a certain range of the independent variable or at certain values. The mathematical model is:

$$y_i = \frac{ax_i}{bx_i + 1} \qquad \text{AI.5}$$

Where

$$\frac{\partial y_i}{\partial a} = \frac{x_i}{bx_i + 1}; \quad \frac{\partial y_i}{\partial b} = \frac{-a\ x_i^2}{(bx_i + 1)^2} \qquad \text{AI.6}$$

Replacing in AI.1 and reducing terms:

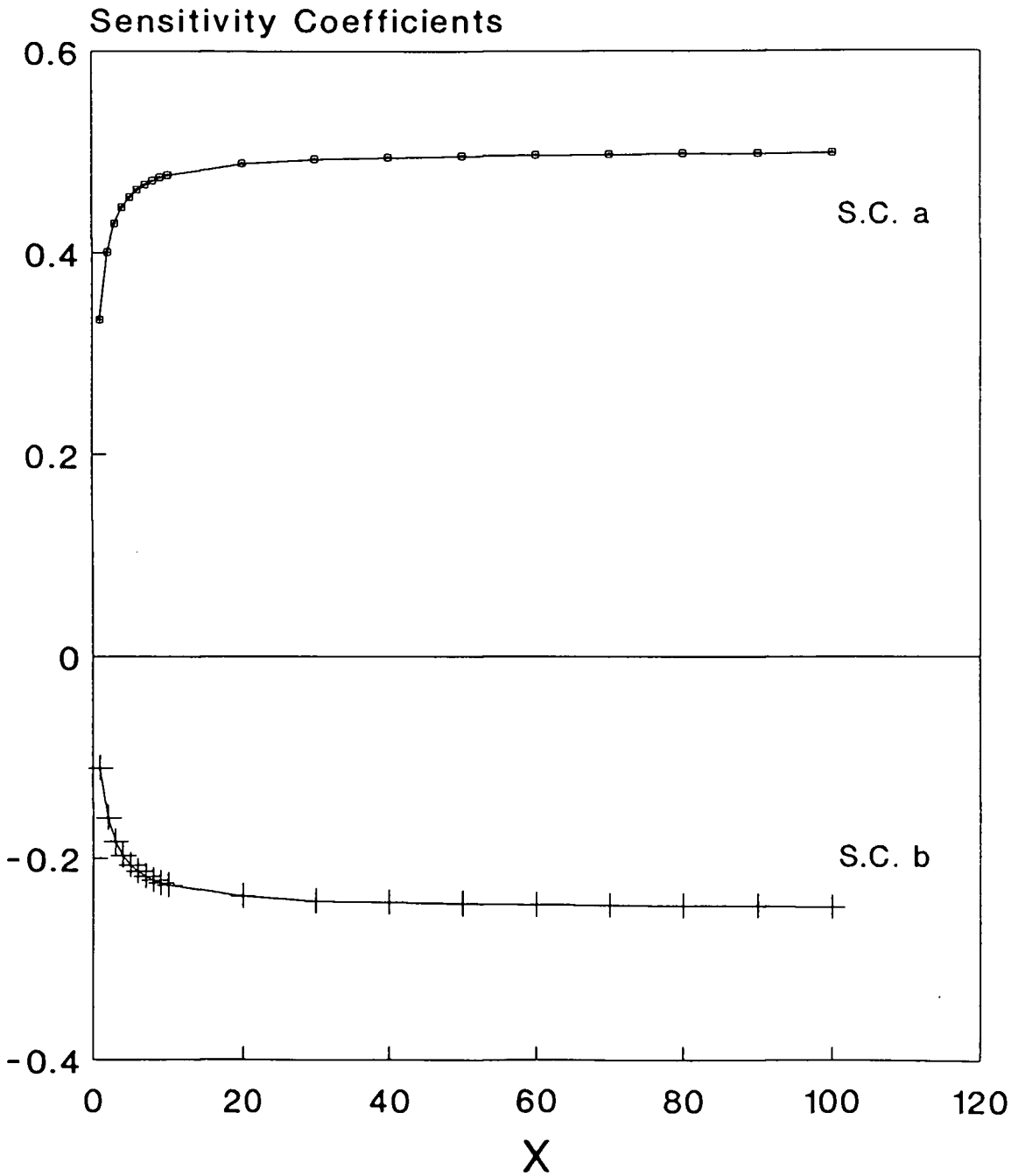
$$\lambda_1 = \frac{ax_i\lambda_2}{bx_i + 1} \qquad \text{AI.7}$$

This shows that parameters a and b can be independently

determined, the relationship between λ_1 and λ_2 depends on x_i. An analysis of Equation AI.7 shows that for large values of x_i Equation AI.7 can be reduced to:

$$if \ x_i \to \infty; \quad \lambda_1 \approx \frac{a}{b}\lambda_2 \qquad \text{AI.8}$$

This shows that for large values of x_i, parameters a and b cannot be independently determined. Figure AI.1 shows a plot of sensitivity coefficients assuming $a=1$ and $b=2$ (Equation AI.5).



• S.C., Sensitivity Coefficient

Figure AI.1. Sensitivity coefficients for a and b, Equation AI.9

APPENDIX II

COMPUTER PROGRAM FOR HEAT TRANSFER PROCESS

A computer program developed in BASIC language was implemented for the heat transfer process presented in Equations IV.1 to IV.6. The following was the nomenclature used in the computer program:

CA : Apparent volumetric specific heat in node N at time TIE (s) ($J/m^3°C$)

C00 : Apparent volumetric specific heat above the initial freezing point ($J/m^3°C$), (defined as C in Chapter IV)

C11 : Empirical constant ($J/m^3°C$) (defined as C_1 in Chapter IV)

C12 : Empirical constant ($J-°K^{n-1}/m^3$) (defined as C_2 in Chapter IV)

C13 : Empirical constant (defined as C_3 in Chapter IV)

DT : Time increment (s)

DTT1 : Time counter

DX : Space increment (m)

H : Heat transfer coefficient ($W/m^2°C$)

KA : Thermal conductivity at position N-1/2, time TIE, evaluted at temperature TA ($W/m°C$) (defined as k in Chapter IV)

KD : Thermal conductivity at position N+1/2, time TIE, evaluated at temperature TD (W/m°C) (defined as k in Chapter IV)

K00 : Thermal conductivity above the initial freezing point (W/m°C) (defined as k_l in Chapter IV)

K11 : Empirical constant (W/m°C) (defined as k_r in Chapter IV)

K12 : Empirical constant (W/m) (defined as S_k in Chapter IV)

K13 : Defined as k_l-k_f (Schwartzberg's model) or k_l-k_r (Succar-Hayakawa's model). For details refer to Chapter IV.

N : Node N. 0, 1,...,N,...,NI

NI : Number of partitions

TAM : Ambient temperature (°C) (defined as T_a in Chapter IV)

TIC : Initial freezing point of food material (°C) (defined as T_{sh} in Chapter IV)

TIW : Normal freezing temperature for pure water (°C) (defined as T_{sw} in Chapter IV)

TF : Final temperature at the center of the infinite slab (°C)

TO : Initial temperature of the product (°C) (defined as T_i in Chapter IV)

T1(N): Temperature at node N time TIE-DT (°C) (defined as T_n^i in Chapter IV)

T2(N): Temperature at node N time TIE (°C) (defined as T_n^{i+1} in Chapter IV)

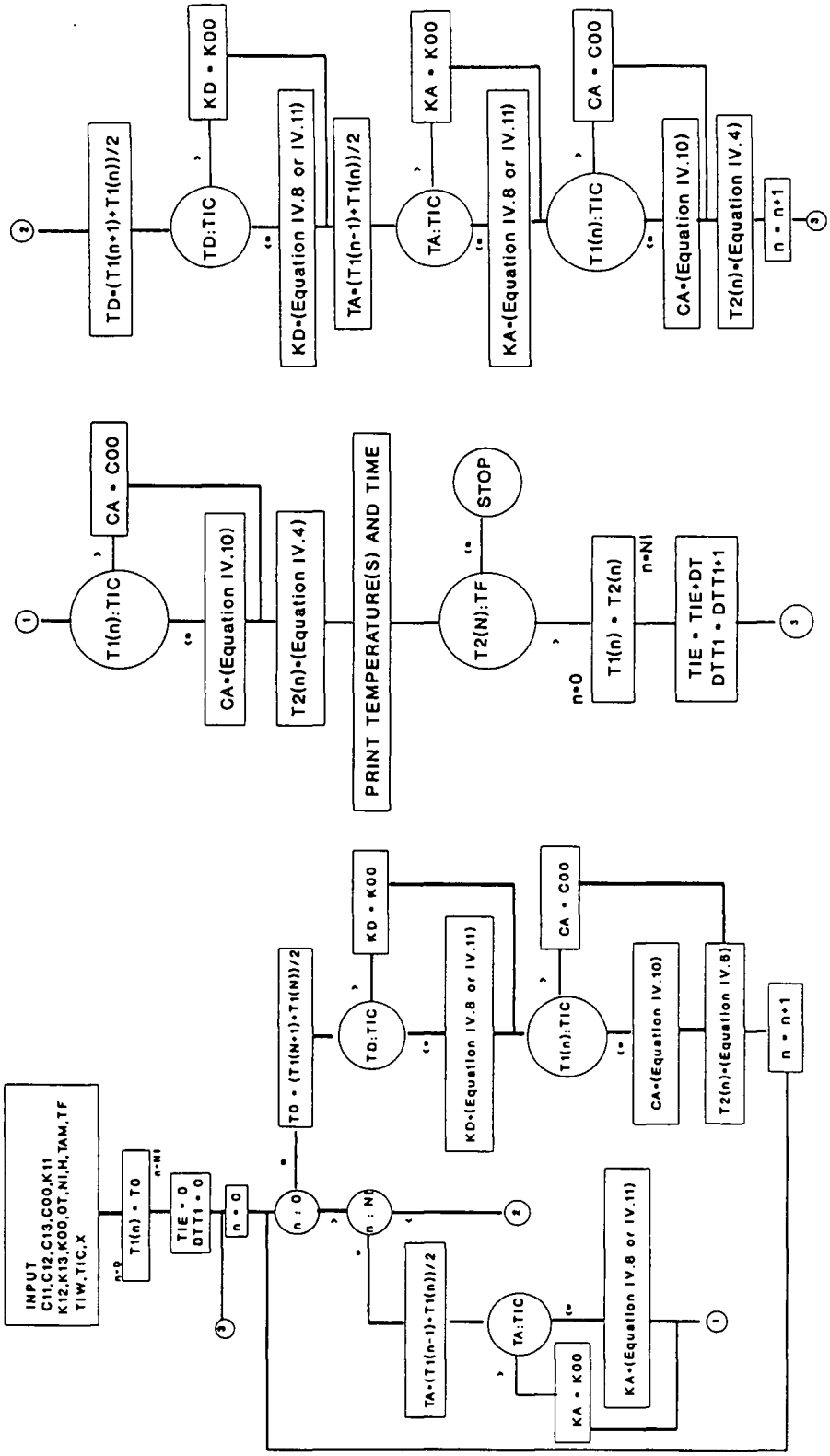


Figure AII.1 Flow chart

CUMPUTER PROGRAM

```
 10 DIM T1(20),T2(20)
 20 REM "PROGRAM TO SIMULATE HEAT TRANSFER PROCESS"
 30 TIE=0:DTT1=0
 40 C00=4000000!:K00=.5
 50 H=30:DT=.1:X=.03:NI=10:DX=X/NI:T0=3:TF=-20:
    TAM=-26.4:CTE=DT/(DX)^2:TIW=0:TIC=-1.16
 60 FOR II=0 TO NI
 70 T1(II)=T0
 80 NEXT II
 90 INPUT "kf or kr        ",K11
100 INPUT "Sk              ",K12
110 INPUT "k1-kf or k1-kr  ",K13
120 INPUT "C1              ",C11
130 INPUT "C2              ",C12
140 INPUT "C3              ",C13
150 REM CALCULO DE T2(N)
160 DTT1=DTT1+1
170 TIE=TIE+DT
180 FOR N=0 TO NI
190 IF N<>0 THEN 250
200 TD=(T1(N+1)+T1(N))/2
210 IF TD>=TIC THEN  KD=K00:GOTO  230
220 KD=K11+K12*(TIC-TD)+K13*(TIW-TIC)/(TIW-TD)
230 IF T1(N)>=TIC THEN  CA=C00:GOTO 260
240 CA=C11+C12/(TIW-T1(N))^C13:GOTO 260
250 IF N=NI THEN 380 ELSE 280
260 T2(N)=DT*(((KD/DX)*(T1(N+1)-T1(N))-H*
    (T1(N)-TAM))/(.5*DX*CA))+T1(N)
270 GOTO 440
280 TD=(T1(N+1)+T1(N))/2
290 IF TD>=TIC THEN  KD=K00:GOTO  310
300 KD=K11+K12*(TIC-TD)+K13*(TIW-TIC)/(TIW-TD)
310 TA=(T1(N-1)+T1(N))/2
320 IF TA>=TIC THEN  KA=K00:GOTO  340
330 KA=K11+K12*(TIC-TA)+K13*(TIW-TIC)/(TIW-TA)
340 IF T1(N)>=TIC THEN  CA=C00:GOTO 360
350 CA=C11+C12/(TIW-T1(N))^C13
360 T2(N)=(CTE*(KD*(T1(N+1)-T1(N))-KA*
    (T1(N)-T1(N-1)))/CA)+T1(N)
370 GOTO 440
380 TA=(T1(N-1)+T1(N))/2
390 IF TA>TIC THEN  KA=K00:GOTO  410
400 KA=K11+K12*(TIC-TA)+K13*(TIW-TIC)/(TIW-TA)
410 IF T1(N)>=TIC THEN  CA=C00:GOTO 430
420 CA=C11+C12/(TIW-T1(N))^C13
430 T2(N)=(CTE*2*KA*(T1(N-1)-T1(N))/
    CA)+T1(N):GOTO 450
440 NEXT N
450 IF INT(DTT1/600)<>DTT1/600 THEN 480
460  PRINT ;TIE/60;T2(0);T2(10)
480 IF T2(NI)<=TF THEN 530
490 FOR N=0 TO NI
500 T1(N)=T2(N)
510 NEXT N
520 GOTO 160
530 PRINT USING "###.#";TIE/60;T2(0);T2(10)
540 END
```