STANDARDIZATION OF PROCESS PARAMETERS FOR READY TO EAT FISH PRODUCTS IN INDIGENOUS POLYMER COATED TIN FREE STEEL CANS

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By

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CERTIFICATE

This is to certify that this thesis entitled "**STANDARDIZATION OF PROCESS PARAMETERS FOR READY TO EAT FISH PRODUCTS IN INDIGENOUS POLYMER COATED TIN FREE STEEL CANS**" embodies the original work conducted by Mr.Sreenath P.G under my guidance. I further certify that no part of this thesis has previously been formed the basis of award of any degree, diploma, associateship, fellowship or any other similar titles of this or in any other university or Institution. He has also passed the Ph.D qualifying examination of the COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY,Cochin held in January 2007.

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DECLARATION

I, Sreenath P.G. do hereby declare that the Thesis entitled "**STANDARDIZATION OF PROCESS PARAMETERS FOR READY TO EAT FISH PRODUCTS IN INDIGENOUS POLYMER COATED TIN FREE STEEL CANS**" is a genuine record of bonafide research carried out by me under the supervision of Dr. RAVISHANKAR C. N, Senior Scientist, Fish Processing Division, Central Institute Of Fisheries Technology, Cochin-682029 and has not previously formed the basis of award of any degree, diploma, associateship, fellowship or any other similar titles of this or any other university or Institution.

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INTRODUCTION

Fish enjoys a prominent position in human nutrition. Seafood represents an excellent option as a major source of nutrients especially when used in combination with other muscle foods (Kinsella, 1988). As a rich source of protein, fish provides a good balance of protein, vitamins, minerals and a relatively low calorific content. In addition the PUFA content, especially the n-3 and n-6 PUFA have been considered as essential fatty acids and have been shown to have curative and preventive effects on cardiovascular diseases, neurodevelopment in infants, cancer and fat glycemic control (Conner,1997).

Fish constitutes a highly perishable group of foods (Cheftel and Cheftel, 1976). Fish deteriorates after death due to the action of different factors that can be summarized as microbiological, enzymatic and oxidative etc. Realy and Shewan, (1949) reported that among the various factors leading to fish spoilage, bacterial activity is the most important factor that produce the most striking and undesirable alterations in the flavour, odour and appearance. Due to the high perishable nature of fish, various preservation methods like drying, curing, canning, freezing etc have evolved over the period of time. Although each have their own advantages and disadvantages, these food preservation methods are aimed at preventing undesirable changes in the wholesomeness, nutritive value and sensory quality of food by controlling growth of microorganisms and obviating contamination by adopting economic methods.

Thermal processing is a food processing method involving the application of heat, the extent of which varies with the specific objectives and accordingly the thermal processing is classified into blanching, cooking, pasteurization, cooking and sterilization. In-container sterilization is the most common method of heat treatment. It involves

application of heat that is sufficient to destroy microbes that can cause spoilage or disease and the enzymes. The hermetic seal maintains an environment in the container that prevents the growth of other microbes of higher resistance and most importantly, prevents recontamination and pathogens from producing toxins during storage (Awuah et al., 2007). In all its forms of application, thermal processing persists as the most widely used method of preserving and extending the useful shelf life of foods.

Containers having the sufficient strength and rigidity to tolerate the high temperature and pressure of processing, impervious to air, moisture and microbes once sealed is one of prerequisites for successful canning operation. Technological innovations occurred in the field of thermal processing over the period had its impact on the containers and as a result, various types of containers have evolved at various points of time. Appert who established thermal processing as a method of preservation, conducted his pioneering work using glass jars sealed with cork. Shortly after this, many workers started to use metal containers for this technique. The metal can, the oldest form of packaging and preserving of foods for long periods, has contributed very significantly to the growth of food processing and food packaging technologies. Tinplate cans are one of the most popular and traditional containers for canned products. Tin resources are limited to certain geographical locations and hence countries like India which are lacking tin deposits have to import it which makes the tin containers expensive. More over these containers have other problems like poor lacquer performance, internal and external rusting, dissolution of the can material in the food during storage and the resultant development of metallic flavour in the product etc. all of which have lead to the decline of fish canning industry in India. These containers are three piece types and are coated on

their internal surface with epoxy and organosol type of resins. When the cans are heated at high temperature as in case of commercial canning, the components of these coatings like Bisphenol A (BPA) and and its condensation product with epichlorohydrin, Bisphenol A-diglycidyl ether (BADGE) may leach out of can coating. The health related impacts of ingesting contaminants like dissolved tin, lead, aluminium, BPA and BADGE have been reported by many workers (Krishnan et al., 1993; Kupier et al., 1997; Dewitte et al., 2001; Robertson, 1983). The world wide effort that started in the sixties for finding a suitable container for canned products that is free of tin resulted in the birth of Tin Free Steel in Japan. The chromium coated steel plate has been reviewed as an alternative to tinplate for canning food products by many workers (Barbeiri et al., 1970; Naresh et al., 1989). Recently chromium coated steel cans with polymer coating are available in the market. In these cans, the chromium coated steel is laminated with Poly Ethylene Terephthalate (PET) which prevents the direct contact between the metallic can and food material packed inside.

Sea food exports from India constitute one of the major sources of foreign exchange. But major portion of our seafood exports are done as conventionally frozen items. Recent export figures show a decline in the seafood exports from India both in terms of quantity and value (MPEDA, 2009). This decline is mainly due to the reduction in the quantity of fish available for export due to poor landings and disease out breaks. Switching over to the production and export of ready to eat convenience food which gives better unit value compared to conventional products can be adopted as an efficient method of improving the returns from export of sea foods.

Conventional canning operations have the tendency to induce permanent changes to the nutritional and sensory attributes of the foods. If we can develop a suitable method

of heating food rapidly to higher temperature than those used in conventional processing, we can sterilize the food while preserving its sensory and nutritional quality. High Temperature Short Time processing (HTST) as the name indicates involves sterilizing food at high temperature so that it takes less time to attain the fixed sterilization value in comparison to conventional canning.

The present study was undertaken with the following objectives

- To evaluate the suitability of indigenous polymer coated Tin Free Steel (TFS) containers for canning and storage of various fish and fish products.
- To compares the various commercially available rigid containers for the canning and storage of fish products.
- To develop ready to eat fish products that can be thermally processed and stored.
- Optimize the thermal processing parameters for ready to eat squid masala and shrimp curry in indigenous polymer coated TFS cans.
- Conduct shelf life evaluation of ready to eat fish products processed and packed in indigenous polymer coated TFS cans.
- Explore the possibilities of adopting High Temperature Short Time (HTST) processing in fish canning.
- Evaluate the effect of thermal processing at different retort temperatures on the heat penetration characteristics, sensory and nutritive parameters of Indian mackerel

2. REVIEW OF LITERATURE

2.1. TYPES OF THERMAL PROCESSING

Thermal processing is a food processing technique involving application of heat to food material. The heat treatment can be done as a single preservation technique or it can be used as one step in conjunction with other preservation techniques. The extent of heat treatment varies depending upon the specific objective concerning the preserving action of the heat treatment and the nature of the product. Thermal processing operations can further be divided into blanching, cooking, pasteurization and sterilization on the basis of severity of heat treatment, type of heat application, purpose of heat application etc.

2.1.1. Blanching

It is a mild heat treatment that is frequently applied to tissue systems prior to freezing, drying or canning. The objective of blanching process depends on the subsequent treatment of food stuffs. Blanching prior to freezing or drying is primarily done to inactivate enzymes. Pilnik and Voragen (1991) reported that the heat treatment of blanching fruits and vegetables in a water bath before their packing has as its main aim the activation and/ or inactivation of the enzymes present. (Eg. Oxidative enzymes in fruits and vegetables which would otherwise result in undesirable changes in colour, texture, flavour, nutritive value of the products during processing and storage). Blanching may also remove tissues gases, shrink the product, clean and stabilize colour (Barrett and Theerakulkait, 1995). In case of canning, it serves in wilting the tissues to facilitate the

packing, cleanses the tissue, remove the non- condensable tissue gases prior to container closing, activating or inactivating enzymes, improving colour and texture of foods. (Eg blanching helps in the generation of the characteristic curled shape and pinkish coloration of shrimp). Lund (1977) reported that a criterion frequently used to evaluate the adequacy of blanching operation regardless of the subsequent treatment is enzyme inactivation. Blanching is done in two ways, cold blanching and hot blanching. Cold blanching is done by immersing the food material in brine of sufficient strength for a predetermined period of time. The main objective of cold blanching is to enhance the color and texture of the product by the removal of excess moisture content and by the penetration of salt. Hot blanching is accomplished by heating the product in hot water or steam at temperature of less than 100 ° C (Lund, 1977). This helps in reducing the microbial load of the product in case of frozen products. An important problem regarding the hot water blanching is the leaching of water soluble components of the food like vitamins. Arroqui et al. (2001) reported that blanching may have some negative effect on product quality, such as excessive loss of texture, unwanted changes in colour, and nutritional losses. If applied under the appropriate temperature and time conditions, it may also minimize disruptive textural effects.

2.1.2. Pasteurization

It is also a mild heat treatment aimed at inactivating not all, but the selected vegetative microbes (mostly pathogens) present in the food and enzymes. Pasteurization involves preservation of foods by heating to temperature generally below 100° C (Ohlsson, 1977). The food is thus not sterile as the process does not eliminate all the vegetative forms and none of the spore formers. Thus the choice of target organism is of

utmost importance. In the pasteurization of meat products the choice of critical microorganism (also called reference micro-organism or indicator microorganism) has been the object of several discussions (Reichert et al., 1988). In principle, such microorganism should be the most heat resistant among undesirable vegetative pathogenic bacteria or other microbes potentially causing spoilage, discoloration, rancidity, flavour, etc. in meat and meat products. It is widely accepted that in the case of mild heat treatment below 90° C only, vegetative bacteria can be chosen for this purpose, because spores are hardly destroyed during pasteurization. The severity of the heat treatment and length of storage depends on the nature of the product, pH conditions, the resistance of the test organism or enzyme, the sensitivity of the product and the type of application of heat. Ramaswamy and Marcotte (2006) listed the typical processing conditions required for a range of products based on the purpose of heat treatment. Ohlsson (1977) classified the enzymes causing undesirable changes in foods into four groups and concluded that the destruction of enzyme activity is either by irreversible denaturation or by hydrolytic breakdown of the protein molecules.

The pasteurization process should be done in conjunction with other preservation methods like fermentation (pickles), refrigeration (milk), maintenance of anaerobiosis or must be used on products like high acid fruit juices where the environment is not suited for the growth of spoilage and health hazard microbes, as it does not involve the destruction of all the microorganisms (Lund, 1977). Many of the recent advances in pasteurized foods have been in combination with chilled distribution and storage as a means to extend the product shelf-life, or by utilizing additional hurdles such as acidity, low water activity, preservatives, modified packaging atmospheres or high sugar content.

This combination of technologies has given food companies the opportunity to produce foods of a high quality that would otherwise require the lengthy heat treatments associated with full sterilization regimes (Tucker et al., 2002). Since pasteurization involves mild heat treatment, it slightly affects the sensory and nutritive value of the food. The quality of the pasteurized product continues to deteriorate during storage as it is a temporary method of shelf life extension. The shelf life depends on the post pasteurization packaging and storage environment. Ohlsson (1977) reported that during pasteurization, loss of nutrients occur as a result of leakage of juices during coagulation of proteins, fat melting and breakage of cells in vegetables. Chai et al. (1984) reported an oyster pasteurization process using flexible pouch packaging for a product with properties similar to fresh oyster. The effect of pasteurization of oyster at different temperatures was studied by Chai et al. (1991). They found a decrease in moisture content, increase in hunter L (Lightness) value and shear force value with increase in temperature of pasteurization. The effects of high pressures and thermal pasteurization on the survival of microorganisms, enzyme inactivation and quality changes of guava puree during storage at 4°C were investigated and compared with untreated samples by Yen and Lin (1996). After treatment at a pressure of 600 MPa and 25°C for 15 min, the microorganisms in guava puree were inactivated to less than 10 cfu /mL and the product exhibited no change in colour, pectin, cloud and ascorbic acid content as compared with fresh samples whereas the microbial count was reduced to 200 cfu /mL and the product showed marked changes in viscosity, turbidity and colour when heated at 88–90° C for 24 s. They also reported that inactivation of enzymes in guava puree by thermal pasteurization was greater than by high pressures.

2.1.3. Cooking

Cooking is a heat treatment method, the primary objective of which is to improve the palatability of the food. It comprises several operations like boiling, baking, broiling, roasting, frying and stewing that differ in the method of heat application. Cooking can be considered as a preservation technique as cooked foods generally can be stored under proper refrigerated conditions longer than their uncooked counterparts if recontamination can be minimized. Gokoglu et al. (2004) studied the effects of different cooking methods (frying, boiling, baking, grilling, microwave cooking) on proximate composition and mineral contents of rainbow trout (*Oncorhynchus mykiss*). In all the cooking methods adopted, the moisture content was found to be decreasing and protein, ash and fat content were found to increase than raw material. Changes in dry matter, protein and ash contents were found to be significant for all cooking methods. The increase of fat content was found to be significant in fried fish mainly due to the absorption of fat by the fish. The Mg, P, Zn and Mn contents of fish cooked by almost all methods significantly decreased. The Na and K contents in microwave cooked samples increased, the Cu content increased in fried samples. Losses of mineral content in boiled fish were higher than those of fish cooked by other methods. The formation of heterocyclic aromatic amines (HAAs) has been shown to occur during cooking of protein-rich foods such as meat and fish at temperatures mostly over 150 °C (Knize et al., 1997; Solyakov et al., 1999). Many workers have reported that during the cooking of meat, HAAs are produced as a result of chemical reactions of creatine, sugars and amino acids, all common components of muscular tissue of animals (Jagerstad et al., 1983; Murkovic et al., 1997; Salmon et al., 1997). Oz et al. (2007) investigated The effects of cooking methods by deep-fat frying,

pan-frying, grilling and barbecuing on the formation of heterocyclic aromatic amines (HAA) of fillets of rainbow trout *(Oncorhynchus mykiss*) and brown trout (*Salmo trutta fario*). Ersoy et al. (2006) studied the effects of four cooking methods (baking, grilling, micro-waving and frying) on the heavy metal concentrations of sea bass fillets (*Dicentrarchus labrax*).The lead (Pb) concentrations of micro-waved and baked fish were significantly decreased. The Arsenic (As) concentrations of fried and micro waved samples were significantly increased. They recommended that micro-waving and frying are not suitable for sea bass. Retention of vitamins (retinol, thiamin, riboflavin, niacin and ascorbic acid) in earth-oven cooked samples was compared with the retention in micro-waved and oven-roasted chicken and lamb chops, microwave-cooked fish, boiled cassava and taro, and steamed cooked palusami, by Kumar and Aalbersberg (2006). The retention of retinol was found to be higher in microwave cooked samples than earth- oven cooked samples; Steam cooking was most detrimental to ascorbic acid. Samples cooked by microwave oven retained a higher percentage of thiamin than the oven-roasted or earth-oven cooked ones. Earth-oven cooked samples did not retain any detectable thiamin. Microwave cooking resulted in better retention with respect to niacin than the other methods of cooking adopted. A similar trend was observed in case of riboflavine. Puwastien et al. (1999) conducted studies on the changes on proximate composition, non protein nitrogen content of several species of Thai freshwater and marine fishes during different methods of cooking. They reported significant reduction in the moisture content and increase of crude protein, crude fat and ash in case of fishes cooked by many methods in comparison with the fresh ones. Changes in proximate, amino acid and fatty acid composition of farmed, commercially important rainbow trout (*Oncorhynchus*

mykiss) after conventional and microwave cooking were analysed by Nurhan Unusan (2006). Rainbow trouts cooked in microwave ovens had statistically significant higher total protein, total fat, and ash than electrical oven-cooked samples. The amounts of essential and nonessential amino acids were not different between cooking methods, but the difference between raw and cooked samples was significant. Lysine, leusine, methionine, threonine, valine, arginine and histidine were found most in microwave-cooked rainbow trouts whereas isoleucine, tyrosine and phenylalanine were found most in electrical oven-cooked samples. As total saturated fatty acid and total monounsaturated fatty acids amount were not statistically different between the cooking methods, the difference between raw and cooked fillets was found statistically significant.

2.1.4. Sterilization

It is a more severe heat processing technique intended to destroy microorganisms present in the foodstuff that can cause spoilage of the food or cause disease (Noronha et al., 1996). In commercial practice, the sterilization of food is accomplished after packing the food inside a hermetically sealed container.In-pack thermal processing of foods should deliver safe and high-quality products uniformly. Smout et al.(2000) reported that two main factors contributing to the nature of non-uniformity of safety and quality during thermal processing are (i) variability in heat delivery by the thermal process equipment to the food surface (heat distribution) and (ii) variability in heat delivery from the surface to the coldest spot of the food product (heat penetration).Sterilization of food stuffs in commercial point of view aims at attaining commercial sterility rather than absolute sterility. This is because targeting a food that is completely void of microbes would render the product wholesomeness or inferior in quality. During sterilization of low acid

foods, attention is given to *Clostridium botulinum* which can thrive comfortably under anaerobic condition resulting in the production of botulinum toxin. Brown (1991) reported that low acid foods must experience the minimum botulinum cook (F_0= 3 min) which is 12 D cycle reduction based on kinetic data for *C. botulinum.* However other heat resistant spores such as *Clostridium thermsaccolyticum, Bacillus stearothermophilus* and *Bacillus thermoacidurans* can survive this sterilization condition and can cause spoilage and economic losses if processed cans are stored under abused storage conditions of temperature. But processed cans are usually stored at temperature below 30 ^{0}C which is well below the optimum surviving temperature range of these organisms. Hayakawa (1977) reported that the effectiveness of the sterilization given is measured in terms of process lethality/ sterilization value which is given by,

$$F_o = \int_0^t 10^{(T-Tref)/z}$$

where t, z, T and T_{ref} represent the time (min), temperature sensitivity of the target microorganism, temperature at any given time, and reference processing temperature, respectively. The ultimate goal in achieving commercial sterility is to ensure that the ratio of targeted lethality (F_0) to required lethality (F_{req}) is at least , equal to unity (Awuah et al., 2007). Thermal process lethality is influenced by biological, physical and operational parameters. Several researchers have studied the influence of variability of various parameters on process lethality. The important parameters influencing the lethality are heat penetration parameters (j_h, j_c, fh and f_c) and bacteriological parameters (D and z values) Hicks (1961), pressure regulation in the retort (Thompson et al., 1979), heating time and the heat transfer coefficient (Varga et al., 2000). Although a food that has been

sterilized for a minimum sterilisation value of 3 min can be considered as commercially sterile, it is common to process the food to still higher sterilization value mainly to attain better textural and other sensory properties. The recommended F_0 value for meat products is a minimum of 6 min (Shapton and Shapton, 1997). Frott and Lewis (1994) recommended an F_0 in the range of 5–20 min for fish and fishery products. A common relationship for estimating the quality loss is the Cook/ C value, originally proposed by Mainsfield (1962) for aseptic processing of low acid foods. In terms of quality evaluation, the cook value is of little inertest since focuses on a single point (Awuah et al., 2007). They reported that the mass average cook value is preferred and more appropriate for characterizing the impact of different time-temperature combinations on heat sensitive nutrients. A maximum range in the region of 100-200 min is considered as the range beyond which quality is said to be impaired. Conventional canning operations have he tendency to induce permanent changes to the nutritional and sensory attributes of the foods. Hence, recent developments in food processing operations have aimed at technologies that have the potential to substantially reduce damage to nutrients and sensory components by way of reducing the heating times and optimized heating temperature. Some of tshe best examples of the systems that have evolved in the effort to improve the sensory and nutritive parameters of food are agitated retorting, thin profile packages, variable retort temperature processing.

2.2. EFFECT OF THERMAL PROCESSING ON THE QUALITY OF CANNED FOODS

The heat treatment delivered during thermal processing results in the destruction of nutritive and sensory quality of the food (Lund, 1975).The extensive heat treatment involved in the cooking and the sterilization steps substantially alters the nature of the raw material so that, a product with different characteristics is formed. The destruction of various sensory and nutritive parameters upon application of heat depends upon the thermal resistance of each component. The thermal resistance of various components in foods or associated with thermal processing is listed in detail by Lund (1975). Since the purpose of thermal processing is to lengthen the shelf life of the product and to ensure a nutritious food source, it should be designed to retain as much as possible of all the nutritional constituents present in the initial matter to serve human nutrition. The quality changes associated with canning can also be attributed to the changes occurring during the cooking stage also. The various factors affected by the thermal treatment can be broadly classified into chemical and physical parameters.

2.2.1. CHEMICAL PARAMETERS

2.2.1.1. Vitamin Content

Although processes in general could be expected to affect all classes of nutrients, by far the most widely studied group is the vitamins. Prediction of vitamin losses in thermal processing of conduction heated foods has been reviewed by many workers (Lund, 1977; Paulas, 1989; Ryley et al., 1990). Generally vitamin C and vitamin B_1 are used as indices of retention of water-soluble vitamins and fat-soluble vitamins

respectively (Lund, 1979). Bentereud (1977) reported that thiamine is the most thermo liable vitamin. In seafoods, nutrients affected by the time-temperature processes are especially vitamins B1 and C, but losses to other B vitamins occur, more than with freezing or home canning of seafood. About 70 % of thiamin is lost during canning, but seafood is considered only a moderately good source of this vitamin. Aubourg (2001) reported that heat liable vitamins like thiamine, riboflavin, niacin, pyridoxine and panthothenic acid are the vitamins most damaged by the sterilization process. Varying results have been reported for vitamin losses (5-80% for Thiamine; 71-73% for Niacin; 49-50% Riboflavin) by many workers. (Bentereud, 1977; Seet and Brown, 1983; Banga et al., 1993).

2.2.1.2 Protein and Amino acids

The nutritional value of a food protein depends on the distribution of the amino acids that can be absorbed in a bioavailable form. This bioavailability may be modified during processing and storage. Most phenomena involved in the improvement in or loss of both nutritional and physiological properties of food proteins result from the protein denaturation and chemical modification of amino acids (Finot, 1997). During canning process, the loss of proteins can be due to three possible reasons namely pre-cooking, thermal destruction and diffusion into the liquid in the can, No significant changes in total free amino acid content could be seen between raw and cooked tuna (Perez- Martin et al., 1988). However Seet and Brown (1983) reported some loss in case of total protein lysine during cooking.

Several studies have been published on the changes in individual amino acids caused by heating. Investigations on the amino acid content of several canned fish

products, and comparison with the results of raw materials have showed that there is no much significant loss, except for cystiene. Some losses on essential amino acids have been reported, except for histidine and sulfur containing amino acids (Tanaka and Kimura, 1988). Lysine, due to its highly reactive ε-amino group, is the most readily chemically modified essential amino acid. However in fish, due to smaller levels of available lysine, the loss of lysine is less (Hurrel and Carpenter, 1977).

2.2.1.3. Lipids and Fatty Acids

Marine lipid composition is highly unsaturated and oxidation during storage and processing is likely to occur, leading to quality loss (Pearson et al., 1977). Industrial and culinary processes can cause significant qualitative and quantitative alteration in fish fat contents. Changes in the palatability of the canned fish can result from the effects of canning and maturation processes. Gallalardo et al. (1989) have studied the effect of pre-cooking on the lipid classes at different loci of albacore. The study showed that there was an increase in PUFA and a decrease in saturated and mono unsaturated fatty acid contents. Triglyceride content did not vary much. A general decrease in total lipid content was noticed. Gallardo et al (1989); Garcia-Arias et al (1994) reported a relative increase in fat content of fish muscle after processing. They have attributed this to the loss of moisture content.

2.2.1.4. Minerals

Ackurt (1991) reported that mineral levels in some fish samples were affected by cooking methods. Slabyi and carpenter (1977) found that steaming of blue mussels reduced the iodine, potassium and sodium contents while freezing and canning produced

losses in magnesium and sodium. Schroeder et al (1967) found that the zinc content of lobster meat was increased by canning. Seet and Brown (1983) reported loss in minerals like sodium, potassium, magnesium, phosphorus, copper, iron and calcium from the muscle to the dipping medium during the canning of tuna. Reduced looses of minerals was associated with high fat content in the muscle, indicating a kind of interaction between the two constituents (Gall et al., 1983). During the canning of fishes, the bones become soft due to the heat treatment rendered. March (1982) reported that the soft textured bone can be consumed along with the meat thereby acting as an important source of calcium.

2.2.1.5. Indole

Indole is a metabolite released from degradation of amino acids Tryptophan by the bacterial enzyme tryptophanase. Duggan and Strasburger (1946) reported that indole level was not altered appreciably during cooking or extended storage at commercial holding temperatures in shrimps. Detection of indole is also desirable when sensory assessment is difficult and individual shrimp are very small (Ponder, 1978). Fresh uncontaminated shrimp contains indole at levels of 1μg/100g or less (Duggan and Strasburger, 1946; Chambers and Staruszkiewicz, 1981). The amount of indole produced in shrimp was proportional to the extent of decomposition that has taken place (Ponder, 1978), composition of the bacterial population, temperature, handling and storage (Chambers and Staruszkiewicz, 1981).

2.2.1.6. Volatile compounds

The changes in low molecular weight nitrogenous compounds can be used as an objective test for freshness evaluation (Slabyj and True, 1978; Yeannes et al., 1983). Assessment of TMAO decomposition and amine formation in albacore after cooking produced a significant increase in TMA and TVB contents (Gallardo et al., 1990). A gradual increase in volatile basses measured as TVB or as individual amines (DMA and TMA) has been observed by comparing the raw material and the final canned product (Yannes et al., 1983; Besteiro et al., 1993). Gallardo et al (1990) reported an increasing tendency in the order raw<cooked< canned for TVB and individual amines, while TMAO showed the inverse trend. They have reported that if a good quality raw material was employed and an appropriate sterilization treatment was carried out, canned samples would be within a satisfactory and acceptable limit of 40-45 mg TVB/ 100 g muscle.

2.2.1.7. Lipid Oxidation

The highly unsaturated lipids easily become oxidized, resulting in alteration in smell, taste, texture, colour and nutritional value. Oxidation starts immediately after the capture (Harris and Tall, 1989). Heidelbaugh and Karel (1970) have reported a lower degree of oxidation measured by peroxide values for pouched products compared to cans. The primary oxidized products easily break down into secondary products, such as aldehydes and ketones. Sinhuber and Yu (1958) reported a reduced TBA values in heat-processed products in pouches and cans, in which pouched products showed a smaller reduction after processing and during storage. Heidelbaugh and Karel (1970) reported a low TBA values for pouched products as compared to the cans. Chia et al. (1983) reported a faster rate of increase in TBA vales in canned samples as compared to the

pouches. In spite of some drawbacks, the TBA value for estimating the oxidative change remains the most widespread procedure for meat and meat products (Shahidi, 1994). Many workers have reported that the strong heat treatment and the presence of some catalysts in the fish muscle can favor non enzymatic lipid oxidation and hydrolysis so that the detrimental flavor and essential nutrient losses can be produced (Hsieh and Kinsella, 1989). Aubourg et al (1990) reported a significant formation of free fatty acids during the sterilization of different muscle zones of albacore tuna. A comparison of different time/ temperature sterilizing conditions (F_0 value =7 mins) showed that treatments with shorter times but higher temperatures lead to a higher hydrolysis development (Aubourg et al., 1997). Hale and Brown (1983); Aubourg et al (1990) reported that no significant change in PUFA concentrations could be noted on heat processing of various sea foods like sardine, mackerel, tuna and crab in sealed containers.

2.2.2. PHYSICAL PARAMETERS

2.2.2.1. Texture

Texture is one of the important quality parameters affecting the consumer acceptability of a food item. Various types of heating affect the fish muscle texture. Dunajski (1979) reported that cooking of fish muscle at about 60 ° C leads to the loss of original structure of collagen fibers and they become solubilised and thus any textural changes above this temperature are solely due to the heat denaturation of myofibrillar proteins. The collagen content of muscle was important role in the textural changes of muscle during heating. Sato et al. (1986) pointed out that the texture of cooked muscle is affected by the gelatin derived from the collagen. Ma et al. (1983) determined the textural

changes in canned shrimp by sensory and instrumental methods. They found a direct relationship between sensory perception of toughness and instrumental shear force measurements in canned shrimp processed at 124° C. Shrimp muscle toughened during initial stages of heating and softened during later stages. Ali et al (2005) studied the effect of thermal processing in retort pouch and aluminum cans to different F_0 values on the texture of oil sardine. They reported that product packed in retort pouch had better hardness, cohesiveness, springiness and chewiness than those in cans. They also reported that the various texture profile parameters decreased with increase of F_0 value. Tanaka et al. *(*1985) compared the firmness of mackerel canned at three different retort temperatures of 110,115 and 120° C and reported that thermal processing at higher temperature produce firmer products.

2.2.2.2. Colour

Colour is one of the main organoleptic characteristics used to establish the quality and acceptability of food products. Tarr (1952) reported a brown discoloration in white-fleshed fish upon heating. Changes in the salmon color pigments upon heating have been studied by Naughton et al (1956). Tarr (1958) stated that free ribose accounts for much of the Maillard type of reaction when fish is heated in presence of carbohydrates. Rainbow trout, Pollack, and shrimp processed to an equal lethality in cans developed a darker color when processed in cans than the ones in retortable pouches (Chia et al., 1983). This was attributed to the longer processing temperature needed in cans. Ali khayat (1978) examined the changes in the tristimulus color values of three tuna species, albacore, yellow fin and skipjack tuna. A significant loss in the tristimulus colour values of the samples during canning process noted and the greatest loss were found in albacore

followed by skipjack and yellow fin tuna. The same author has reported tat greater the amount of reducing sugar in the raw material, darker the color of the canned product. The effect of heating process, animal harvest location and position of meat within the container during thermal processing was evaluated by Requena et al (1999). It was found that the meat became darker with increasing heating process, crab harvest location had significant effect on the lightness (L* Value) and the meat located on the bottom of the can was darker than that in the top.

2.3. METHODS OF REDUCING THE PROCESS TIME

Conventional canning operations have the tendency to induce permanent changes to the nutritional and sensory attributes of the foods. Hence, recent developments in food processing operations have aimed at technologies that have the potential to substantially reduce damage to nutrients and sensory components by way of reducing the heating times and optimized heating temperature. Some of the best examples of the systems that have evolved in the effort to improve the sensory and nutritive parameters of food are agitated retorting, thin profile packages, variable retort temperature processing and High temperature short time processing (HTST).

2.3.1. Agitated retorting

Agitation during thermal processing is an effective means for providing induced-convection, which results in a higher heating rate and more uniform heating. During agitation, heat penetration is accelerated by the generation of convection current in the liquid phase and by the displacement of materials with densities different to that of filling liquid such as the head space bubble and solid food particulates. This mixing of contents

reduce the temperature gradient within the container and lead to better product through shorter process at higher temperature. There are currently two methods of inducing agitation in containers. The first involves horizontally oriented cans (i.e. axial rotation), the second involves cans loaded in a vertical position (i.e. end-over-end or EOE rotation). EOE rotation is a more effective means of improving heating rates because the headspace ``bubble" improves mixing and turbulence (Knap and Durance, 1998). The effect of end over end agitation on thermal softening of vegetable texture has been studied by Teherian and Ramaswamy (1996). The heat penetration during agitated retorting is influenced by many factors like rotational speed, system geometry, and headspace volume, product viscosity, off center axis of rotation, particle density and presence of particulates (Naveh and Kopel-man, 1980; Anantheswaran and Rao, 1985a; Anantheswaran and Rao, 1985b; Sablani and Ramaswamy, 1995, 1996; Ramaswamy and Sablani, 1997). Casales et al. (1988) reported that the movement of food within the can prevents burning of food contact with the wall of the container and higher sterilization temperature can be applied. Berry and Kohnhorst (1985) reported that burn-on at the surface of low viscosity foods can be substantially eliminated by inducing agitation Therefore, for low viscosity foods, rotation allows the application of higher processing temperatures and, leading to improved quality of the food (assuming agitation does not cause product damage). Rapid heating also has the advantage of increasing the throughput of process equipment and, hence, higher process efficiency and reduced production costs (Tattiyakul et al., 2002).

2.3.2. Thin profile packaging

The retortable pouch was developed during the 1960s in the USA, by a consortium of food packaging/processing companies working in conjunction with the US

Army Natick Laboratories (Herbert and Bettison, 1987). Gopakumar (1993) reported that the flexible laminated food package, the retortable pouch, which can withstand thermal processing and combines the advantage of the metal can and the boil-in-bag, can be used as an alternative to a metal can. Retort pouches have superior surface to volume ratio compared to metallic cans which along with its thin profile helps in faster heat penetration and thereby helps in attaining the required lethality value at the shortest time. Reduction of heating time while using pouches has been reported by a number of workers (Lampi, 1977; Chia et al., 1983; Durance and Collins, 1991). Chia et al. (1983) reported a reduction of 34%, 32% and 37% for trout, pollock and shrimps in pouches compared to cans. Durance and Collins (1991) reported a reduction of 48% process time for chum salmon in pouches than in cans. Various studies have shown the quality implications of the savings in terms of processing time. Dymit (1973) reported that shrimp in retort pouch were superior in flavour and colour to canned products. Mohan et al. (2007) compared the heat penetration characteristics and quality parameters of prawn kuruma packed in retort pouch and aluminum cans. They reported that shrimp kuruma processed in retort pouch took less time to attain the fixed sterilization value and had better sensory and nutritive parameters than those processed in aluminum cans. Other notable advantages of retort pouches are shelf stability, weight, storage space, ease of opening and preparation. Traditionally, retortable pouches are sterilized in batch-type retorts with custom designed racking systems. A method that allows continuous sterilization of flexible (soft) packaging materials (including retortable pouches) in a hydrostat has recently been patented by Brokaw et al. (2003).

2.3.3.Variable Retort Temperature (VRT) processing

Any retort process in which the environment temperature within the retort is modulated during the process, according to a predetermined temperature sequence, to alter the heating profile within the product may be described as a VRT process (Durance, 1997).In the case of VRT, the variable factors are the temperatures of the retort at different points in time during the heating and cooling phases of the process. Because a large number of different VRT's are possible for a given product, selection of an optimum process is most easily found with a computerized experimental search technique. In case of (constant retort temperature) CRT, the heating rate of the can centre is greater early in the process while the overall heating rate may be greater in the VRT process, owing to a higher final retort temperature. The VRT approach was not seriously considered in the earlier days of canning research, mainly because of the fact that the processes were cumbersome and unreliable when retort operation was strictly manual and VRT processes are difficult to study without the aid of computer simulations of heat transfer. The first comprehensive study regarding the VRT was conducted by Teixeira et al. (1975). They fixed thiamine as the specific quality attribute chosen for improvement. Only a slight improvement with respect to his specific attribute could be attained which lead them to suggest that VRT was not likely to be very useful. This in turn has lad to the development of research in the field of VRT. Banga et al. (1991) studied the VRT process from two angles; the optimum nutrient retention and the surface quality and process time. They attained small advantage only with respect to nutrient retention while they could attain 20 % improvement in terms of surface quality and 16.5% reduction in processing time as compared to the CRT process. Studies on the effect of variable retort

temperature on surface quality by Noronha et al. (1993) indicated that variable temperature profiles improved surface quality by up to 20% compared to a constant temperature retort profile. They have also found greater reduction in retort times with VRT process of low profile rectangular containers as compared to cylindrical cans examined in other studies. A change from constant to time-variable retort temperature could increase canning capacity by 20–50% depending on product specifications (Almonacid-Merino et al., 1993). Most of the studies regarding VRT have been based solely on computer simulations and only few have described the application of these principles to actual retort operations. Durance et al. (1996) applied VRT processing to a particular product, canned salmon, and confirmed with actual retort trials. VRT processes were shown to be capable of producing products of superior surface quality with equivalent F_0 values. Alternatively equivalent quality could be produced with a process time (i.e. steam-on time minus come-up time) of 54 min as compared with 64 min for the CRT process. Durance et al. (1996) concluded that the benefits of VRT may include improved nutrient and flavor retention, reduced heat damage to product surface, lower energy costs or shorter process times.

2.3.4. High Temperature Short Time processing (HTST)

HTST as the name indicates involves sterilizing food at high temperature so that it takes less time to attain the fixed sterilization value in comparison to conventional canning. The underlining principle of HTST is that the if a product is sterilized at two different temperatures but to the same bacteriological inactivation level, mostly negative changes in the quality will be smaller for the product sterilized at higher temperature (Ohlsson,1980).The basis of utility of HTST relies on the fact sterilization rates are

generally slower than cooking rates at low temperature and are higher than cooking rates at high temperatures and as one goes higher and higher in temperature, one obtains less and less cook effect at constant sterilizing values (Mansfield,1962). This implies that it is possible to go so high in process temperature that the resulting sterile product food may be inadequately cooked. Nutrient and quality factors are up to six magnitude resistant to thermal destruction than spores and vegetative cells and as a result, thermal death of bacteria generally undergo greater acceleration with increased temperature than concurrent reactions that lead to quality loss (Lund, 1977). HTST is applied mostly to liquid foods due to the fact the high temperature of processing imparts much greater heat than the centre leading to surface overcook and the related quality problems and thus particulate foods are still processed by the in container sterilization method But HTST can be applied to solid foods though the process of flame sterilization

2.3.5. Aseptic processing

This method of HTST is employed for the processing of milk, fruit juices mainly due to their low viscous nature. The heat treatment is done to a thin layer of the pumpable liquid food in a heat exchanger or by direct stem injection followed by holding to achieve required lethality and rapid cooling to minimise the impact of heat on nutrients. The product is subsequently filed into sterile containers in a sterile atmosphere. In contrast to in container sterilization where most of he lethal affect occurs at the end of the heating stage and beginning of the cooling phase, commercial sterility in HTST processing occurs in the holding tube at a constant temperature within seconds (Awuah et al., 2007). Smith and Ball (1955) described a new process for continuous milk sterilization and high temperature filling of low acid foods. Livingston et al. (1957) processed green beans,

beets, carrots, spinach, peas and soups by an HTST method and obtained during extended storage periods, retention of color and thiamine hat was higher than in foods canned by conventional methods. Eliot-Godereaux et al. (2003) developed a new Time-Temperature Integrator (TTI) in order to quantify the effects of High Temperature Short Time (HTST) processing on food quality. They selected a product of non-enzymatic browning as a potential marker and its formation was studied in a glucose/serine system, by means of absorbance measurements at 285 nm. Over the last decade, considerable research efforts and capital investments have focused on extending the aseptic concept to products containing large particles. These efforts somewhat paid off when the FDA approved a low acid soup containing large potato particles (Palaniappan, 1997). However the commercialization of aseptic processing to large particles is offset by the stringent regulatory demands for clear demonstration of achievable lethality. The process and machinery related issues that limit the extension of aseptic processing to particulate foods have been listed by Awuah et al. (2007).

2.3.6. Flame sterilization/ Steriflame process

It is a HTST method that is used for processing of filled close cans in which heating is achieved by the direct contact of cans with burner flame along with rapid rotation to induce convection (Leonard et al., 1975). It is a recommended method for particulate foods packed in brine, syrup or juice and for liquid foods. Flame sterilization was invented in France in 1957 (Cheftel and Beauvais, 1957; 1958 a, b, c) and first described in scientific literature in 1961 (Beauvais et al., 1961). Unlike conventional canning operations, flame sterilsation is done at atmospheric pressure and during processing a large pressure differential build up between the inside and outside of the can

and the can must act as its own pressure vessel. Due to the high internal pressure developed, Beauvais et al. (1961) recommended the use of heavier temper plates for cans. The method can be extended for cans having higher diameter by using stronger ends with single high expansion ridge (Casimir, 1972). The cans are agitated in order to attain better heat penetration (Richardson, 1987). Since flame sterilization causes the rapid destruction of microorganisms before extensive heat damage to the product can occur, the quality of the steriflamme products is superior to those from conventional retorts (Kieseker, 1972). Richardson (1987) reported that flame sterilization can be applied commercially to vegetables, milk shakes, cream, rice pudding, meat products and fish. Gillespy and Thorpe (1965) reported that flame sterilized strawberries and raspberries were firmer in texture but weaker in flavour than conventionally processed samples. Casimir et al. (1976) found that vacuum closed/ flame sterilized diced potato and whole kernel corn after 18 months of storage had better colour, texture flavour and acceptability than conventionally processed packs.

2.4. READY TO EAT FOODS

Ready to Eat (RTE) foods are pre processed foods which are normally packed and served or consumed when required. Technological innovations, particularly in the field of food processing equipment, processing and packaging materials have brought about revolutions in the field of RTE. Indian RTE food scenario is exhibiting tremendous growth rate in the recent years and today it has become a multi billion industry with large number of firms involved. The changes in the socio economic pattern of the society like the changing life style, increasing number of working women, increase in the family

income of people which makes the RTE foods affordable, awareness about healthy foods, changes in the meal pattern and existing food habits, desire to taste new food products have all contributed to the growth of RTE industry and we are in the midst of RTE revolution. Ready to eat thermally processed foods have the additional advantage that they can be stored for a period of more than one year without employing cold chain. RTE has now become an option to Home Meal Replacement (HMR) segment along with conventional options like restaurant, hotels, mess/ canteen, catering service etc. The development in the RTE industry had its reflections in the sea food sector also. The RTE industry has helped in the revival of the once collapsed sea food canning industry in India. Vijayan and Balachandran (1986) reported the development of canned sardine curry in metallic containers using two different types of curry medium. They found that, though the product was organoleptically acceptable upto 18 months of storage at room temperature, the curry acquired the lacquer taste and the cans exhibited rusting at the seam area. Srinivasa Gopal et al. (2001) standardised traditional Kerala style fish curry in indigenous retort pouch and reported a shelf life of not less than 12 months at room temperature. They have also reported that an F_0 value of 8.43 was satisfactory for fish curry products. Ravishankar et al. (2002) conducted studies on the heat penetration and storage characteristics of seer fish curry in retortable pouches. They reported that a sterilization value of 11.5 min is ideal for seer fish curry and the product is acceptable upto 24 months based on sensory attributes. Manju et al. (2004) reported studies on the heat penetration characteristics and shelf life studies of seer fish moilee, a traditional fish based product of kerala in retort pouch. They reported that the product stored at ambient temperature (27 ± 1^0 C) was acceptable up to 18 months and those stored at 37^0 C was

acceptable up to 10 months based on the sensory attributes. Ready to eat rohu curry in north Indian style processed to F_0 value of 46.42 min and cook value 102 min was found to be acceptable even after 6 months of storage at room temperature and at elevated temperature of 37^0 C with respect to sensory and chemical attributes (Mallick et al., 2006). Mohan et al. (2007) compared the heat penetration characteristics and quality parameters of prawn kuruma packed in retort pouch and aluminum cans. They reported that shrimp kuruma processed in retort pouch took less time to attain the fixed sterilization value and had better sensory and nutritive parameters than those processed in aluminum cans. The standardization of thermal processing parameters for ready to eat squid masala in tin free steel cans was described by Sreenath et al. (2007). They found that a sterilization value of 8 min with cook value of 91 min was ideal for squid masala based on sensory analysis and instrumental texture profile and shear force analysis.

2.5. STORAGE STUDY OF THERMALLY PROCESSED FISHERY PRODUCTS

One of the important advantages of thermally processed foods over foods processed by other methods is its longer shelf life at room temperature. Thus the thermally processed foods helps in avoiding the cold chain thereby avoiding the machinery and the operational costs involved in maintaining the cold chain. Taguchi et al. (1982) reported that canned products undergo changes in both sensory and nutritional value during long term storage due to chemical reaction within the food and also between the food and container metal. The rate of such changes are dependent on the storage temperature. Various studies have been conducted to assess the useful shelf life of hermetically processed foods. Most of these works were conducted based on the study of

the sensory and biochemical changes associated with long term storage. Bhandary (1971) while studying the keeping quality of common carps noticed considerable browning in mirror carp packs and this was attributed to high sugar content of the fish. Telles–Siqueira et al. (1975) have examined the organoleptic, chemical and bacteriological aspects of canned freshwater trout and sea trout during storage. Mai et al. (1978) concluded that lipid changes in cooked fish are least in fillets with high levels of lipids. Mai et al. (1978) reported that canning process followed by storage produced an increase in the proportion of FFA in the muscle lipids. Ribarova et al. (1991) reported that contents of lysine and leucine decreased gradually during storage whereas contents of glutamic acid and aspartic acid increased during storage of canned carp. Aurbourg et al. (1997) studied the effect on muscle lipid deterioration of initial cooking and of there time temperature processing combination after 4 months storage of albacore tuna canned in oil. Storage for 5 years resulted in slight decrease in SFA and MUFA and slight increase in n3 PUFA and no significant change in n6 PUFA in sardine canned in oil (Roso et al., 1998). No significant change in the muscle mass and moisture content could be noted during 5 weeks storage of tuna canned in water (Bell et al., 2002). Ravishankar et al. (2002) studied the heat penetration and storage stability of ready to eat seer fish curry processed in retort pouches. They found that the product remained in acceptable condition based on the analysis of sensory attributes of flavor, texture and overall acceptability. Manju et al. (2004) reported that seer fish moilee stored at room temperature and at 37^0 C in retort pouches had shelf life of 18 and 10 months respectively. Bindu et al. (2004) reported that vacuum packed and retorted ready to eat mussel meat remained in good condition based on taste panel results even after one year

of storage at room temperature. One of the important factor that limits the long term storage life of thermally processed products in tin and aluminium cans coated with lacquer is the development of metallic taste resulting from the dissolution of metal in the food and the leaching of the endocrine disruptors like BPA from the can coating to the food. Development of internal corrosion and bitter taste in sardine curry canned in tin cans after 15 months of storage was reported by Vijayan and Balachandran (1986). Gracia Arias (2004) reported that sterilisation and storage of tuna led to increase in lipid and decrease in moisture and protein. They also reported that protein digestibility and biological value did not show any deterioration.

2.6. CONTAMINATION OF FOOD MATERIALS FROM PACKAGING

Packaging makes food more convenient and gives the food greater safety assurance from microorganisms, biological and chemical changes such that packaging has become an indispensable element in the food manufacturing process. Despite of all these advantages, packaging has been the subject of many debates concerning environmental and health issues. This is due to its potential to contaminate the food that is coming into contact with it by the dissolution in the food that is coming into contact with the migrated substance. The term 'migration' is used to describe the process of mass transfer from packaging material to the food. It has been reported that diffusion is one of the main mechanism for the transfer and migration of substances from packaging material to food (Aravnitoyannis and Bosnea, 2004). Katan (1971) classified migration into 3 classes. Due to its various advantages, plastic and plastic based materials have emerged as the most widely used packaging material and nowadays more than 30 different plastic

materials are being used as packaging material (Lau and Wong, 2000). All plastics, apart from the basic polymer contain several non-polymeric components either inherent or added deliberately (Gopal and Ravishankar, 2003). They have classified these substances into polymerization residues, processing aids and end use additives. Since the polymers are of high molecular weight and are inert, they have limited solubility in aqueous and fatty systems. But non-polymeric substances may leach out form the plastic to food thereby contaminating the food with the consequent risk of toxic hazard to the consumer (Murthy and Raju, 1989; Crosby, 1981; Crompton, 1979). Lau and Wong (2000) separated the migration of additives or contaminants from polymeric packaging to food into three different but inter related stages: diffusion within the polymer, salvation at the polymer-food interface and dispersion into bulk food. One of the major decisive factors in the migration from the packaging material is the type of food that is coming into contact with it, it's composition, the prevailing temperature, pH, the physical state of the food, moisture content etc.. Hence, Robertson (1983) classified food items into 8 categories in order to determine the over all migration residue. Since the use of food stuffs for determination of migration is impractical mainly due to its perishable nature and varying composition, food stimulating liquids that can be used instead of actual food stuffs have been recommended by Crosby (1981); CEC (1985). The testing condition and the choice of simulating solvent are decided on the basis of various factors like the conditions under which the food is packed and stored (IS: 9845-1981). Two methods that have been recommended for carrying out the migration tests are the quantity in material (QM) which is the overall by quantity of substance which may be present in the packaging material and the quantity that could migrate to the food stuff i.e.; Specific

Migration limit (SML). A QM is more convenient than SML when the compound is shown to degrade in the food stimulant or if the QM is of such number that even if 100% of the compound migrates to the food, it would still be too low to become hazardous to public health (Aravnitoyannis and Bosnea, 2004).. Traditionally, migration data were obtained from the migration tests performed using food stimulating liquids like water, edible oils, ethanol water solutions etc. However, these tests are time consuming and expensive. Hence predictive migration models have been proposed to estimate the extent of migration. These models help in the identification of factors affecting migration which in turn allow the manufactures to improve the quality by determining the variables that have the greatest impact on the migration and also in controlling and limiting chemical contamination of food from packaging. Aravnitoyannis and Bosnea (2004) reported that Fick's first and second law can be applied since migration is actually a diffusion process. Crank (1975) provided a simple model to predict the extent of migration from polymer into extraction solvent. Barner et al. (1994) developed a model to predict the migration which is actually a modification of the Crank's model.

Since the overall migration tests cannot identify the exact chemical nature of the contaminant and its toxicity and official methods are time consuming, complicated and impractical for routine controls, more practical test methods have evolved. The analytical procedures typically involve sample preparation, extraction, clean up and final determination using chromatographic and spectrophotometric techniques. The common analytical procedures and the instruments used for the determination of chemical contaminants have been listed by many workers (Low and Wong, 2000).

Rigid metallic containers by themselves also are not free from the food contaminating potential though they don't present an array of contaminants like plastic packaging materials. In metallic containers, the contamination is contributed mainly by lacquer coating, the soldering compounds in case of three piece cans, tin coating and the base metal.

2.6.1. BPA and BADGE

Metal cans are traditionally protected against corrosion by the application of inner coatings based on epoxy and organosol type of resins (Frott and Lewis, 1995). Epoxy polymers are resistant to solvents and can bind to a variety of substrates especially metals. This property makes epoxy resins a popular choice for use in enamel coatings on the food contact surface of metal food and beverage cans. If the coating is inadequately formulated, they can be a source of contamination due to the migration of chemicals to food. Bisphenol A (BPA) and its condensation product with epichlorohydrin, bisphenol A-diglycidyl ether (BADGE) may remain unreacted if the curing process of lacquer coated can is insufficient (Mungia Lopez and Sato-Valdez, 2001). These residual BPA and BADGE can be a potential contaminant to the food that is packed. When the cans are heated at high temperature as in case of commercial canning, BPA may leach out of can coating. This statement is supported by the reports of BPA contamination in canned vegetables (Brotons et al., 1995), canned beverages (Horie et al., 1999), canned fish and meat (Imanaka, 2001).

BPA contamination is a serious issue for canned fish and meat products as various studies have shown that the leaching out of this compound is higher in fish and meat products than in other canned products (Brotons, 1995; Biles et al., 1997; Horie et al.,

1999; Yoshida et al., 2001). The oestrogenic activity of the BPA was accidentally discovered by Krishnan et al. (1993). Kupier et al. (1997) reported that BPA can interact with α and β oestrogen receptors. It is among the oestrogenic xenobiotics that may affect the reproductive system of animals and cause proliferation of breast cancer cells in vitro (Krishnan et al., 1993; Simal-Gandana et al., 1998). The toxicity of BADGE is related to cytotoxic effect in tissues with a high rate of cell division. The US National Institute of Occupational Safety and Health has listed BADGE as a tumorigen, mutagen and primary irritant. The migration limits for BPA and BADGE are 3 mg/kg (CEC, 1990) and 1 mg/ kg (Simal-Gandara et al., 1998) of food or food stimulant, respectively. BPA, BADGE and the related compounds are mainly determined by liquid chromatography using UV detection (Crathorne et al., 1986). However, fluorescence (Losada et al., 1991) or mass spectrometry could provide more sensitive and specific methods for the detection of these compounds.

2.6.2. Tin

Just under one third of the world's total tin production goes into the manufacture of tinplate, for which food packaging is by far the largest of many diverse applications. Tin coated containers are used for food packaging either with lacquer coating or as plain cans. As a result of the use of tinplate for food and beverage packaging, it is obvious that some tin will dissolve into the food content, particularly when plain uncoated internal surfaces are used. Tin dissolution from coated cans occur through the coating imperfections. Dissolution of metallic tin from the inside of a can body into the food content will result in it being present in the divalent form. The precise chemical nature of the divalent tin in a canned food product is important, as it is likely to have a major

influence on its ability to cause an acute toxicological response. However, the exact species present and their distribution will be different in each individual food type, since a number of factors have a role to play (Blunden and Wallace, 2003). The actual rate of dissolution of tin is dependent on a number of factors. Of these, the presence of oxidizing agents or depolarizers that corrode tin by direct chemical attack without evolution of hydrogen is probably the most significant. Other factors that have been attributed to favour the dissolution of tin are storage conditions, particularly investigated include temperature, can size (Marsal and Darre, 1976), types of base steel and the level of hydrogen in the base steel (Reznik, 1991). The effects of inorganic anions (NO_3^-, NO_2^-, Cl^-, CrO_4^{2-}, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, IO_3^-, and $B_4O_7^{2-}$) on the corrosion of tin in nitric acid has been investigated by Al-Suhybani (1989). It has been found that some of these anions inhibit corrosion while others accelerate it.

The Provisional Tolerable Weekly Intake for tin is 14 mg/kg body weight (JECFA, 1988a, 1988b) and recommended maximum permissible levels of tin in food are typically 250 mg/kg (200 mg/kg UK; MAFF, 1992) for solid foods and 150 mg/kg for beverages (Codex, 1998). Acute effects have been reported following the ingestion of inorganic tin via dietary products stored in tin cans. These generally take the form of digestive disturbances with symptoms of acute gastro-enteritis, i.e. nausea (97%), abdominal cramps (87%), vomiting (70%), headache (57%), diarrhoea (33%) fever (13%) (Piscator, 1979; Schafer and Femfert, 1984; Dewitte et al., 2001). To date, many spectrophotometric methods for tin determination have been reported. Kontominas et al.

(2006) reported the determination of tin using atomic absorption spectrophotometer having graphite furnace accessories.

2.6.3. Iron

Iron is the base metal for tin cans. Apart from being an ideal packaging medium, iron forms a potential source of contamination in tin coated metallic containers. The leaching of iron into the food materials occur through the areas of discontinuity developed on the internal surface coating of the cans due to improper application of tin and lacquer layer. Bernando et al. (2005) reported that during the double seaming operation due to friction, breakage occurs on the coating at the body hook and end hook. Product-package interaction occurs through this discontinuity leading to iron dissolution. The action of certain detinning agents also favors the dissolution of iron in the food. Farrow (1970) recognized inorganic nitrates in food products as a potential detinning agent. A potential detinning agent in case of fish cans is TMAO. Taguchi (1975) investigated the role of TMAO in the detinning process in case of fish cans and reported that the rate of tin liberation was proportional to the amount of TMAO added. The detinning action of TMAO increased at higher storage temperatures. The dissolution of iron in food results in the development of metallic flavor in the product. Sometimes the exposed iron may react with the sulfur containing compounds liberated from the product during retorting thereby forming iron sulphide (FeS) often seen as black spots on the internal container surface and in extreme cases, on the product surface. The control of iron migration is of great significance in case of tin plate beverage cans as even smaller levels of iron migrated to drink can affect the flavor of the drink (Hollander, 1998).

2.6.4. Aluminium

Due to its abundance, aluminium (Al) is distributed in the whole food chain (Lopez et al, 2000).Environmental aluminium is considered as non toxic, (Bunnig, 1984) and it has been regarded as harmless for healthy human beings until recently. But the possible connection between elevated tissue Al content and problems such as osteomalacia and neurodegenerative disorders has awakened interest in Al intake via the diet (Martyn et al., 1989; Storey and Masters, 1995).General possibilities of oral aluminium exposure of humans occur via food stuffs, use of aluminium containing food additives, migration of aluminium from food packaging into food and also drinking water. Due to various advantages over tin, aluminium has been used as a major container for canned fish and several other commodities like beer/ soft drinks, several types of food products and also collapsible tubes for different paste products (Balachandran et al., 1994). The major route of contamination of food packaged in aluminium containers is by leaching out of the aluminium from the can body. The leaching occurs mainly though the imperfections in the lacquer coating. Oduoza (1992) reported that the concentration of aluminium in canned seafood depends on quality of inside lacquer coating of the cans. The leaching of aluminium to the food that is packed depends upon a wide range of parameters like quality of the container, duration of cooking, pH level and presence of Cl^- ion (Jagannata and Murthy, 1990),oxygen concentration of the head space, storage time and the temperature and humidity of storage (Oduoza, 1992). Muller et al. (1998) surveyed the aluminium content of a variety of German foods including canned fish. The aluminium content of the canned fishes ranged from 1.2-5.5 μg/ FM. They also reported that the aluminium content of canned fish is comparable with those found in meat. The aluminium content of foods and beverage consumed in the Spanish diet was estimated by Lopez et al. (2000). Orally consumed aluminium is increasingly considered as a

contaminant of the food chain playing a role in the aetiology of neurodegenerative disorders like morbus Alzheimer and amyotrophic lateral sclerosis. An abundance of research has continued to link Al with Alzheimer's disease (Flaten, 1990). Animals loaded with Al develop both symptoms and brain lesions which are similar to those found in Alzheimer's disease (Lopez et al., 2000). The relationship of aluminium with various disorders has lead to the growing public concern regarding its consumption. The acceptable daily intake (ADI) of Al established by WHO-FAO is 60 mg/60 kg of body weight (WHO-FAO, 1989).Graphite furnace atomic absorption spectrometry is the method of choice for the determination of Al in food stuffs (Smeyers-Verbeke and Verbeelen, 1985, 1988).

2.6.5. Lead

Lead contamination is mainly associated with food packed in three piece cans. In case of three piece cans, the solder used to seal the side seam is composed 98% of lead and 2% of tin. Some amount of lead contamination may also originate from the tin coating in which it may be present as an impurity. Although attempts have been made to prevent the lead contamination by coating the interior of the can thereby preventing the can contents from coming in contact with food, little success could be achieved in this direction with respect to acidic foods. Bielig et al. (1978) found more than twice as much lead in orange and tomato juices stored in lacquered cans than in the identical juices stored in unlacqured cans. They have also reported that the rate of lead uptake in lacquered cans is temperature dependent whereas it is independent of temperature in unlacqured cans. The advent of two piece cans which are free from side seam has helped in reducing the contamination from this source. Rouseff and Ting (1980) studied the

effect of acidity, storage time and temperature on the lead content of canned grape juice employing flameless atomic absorption spectroscopy. They reported that acidity of the juice and exposed solder area of the side seam are the two important factors affecting the lead concentration in canned grape fruit juice. During early life, human infants are particularly susceptible to lead exposure, with a greater portion of the retained lead being distributed to bone and brain in infants than in adults (Robertson, 1983). Sub acute ingestion of lead by children results in encephalopathy, convulsions and mental retardation. Estimated daily dietary intake of lead for adults range from 0.015-0.1 mg, depending on the composition of the diet and where the consumer lives (Codex, 1996). The regulatory limits for lead in canned foods in almost all countries are now 2.0 ppm but only 0.5 ppm in baby foods and 0.2 ppm in soft drinks. The newer welded and two piece cans have eliminated the solder and has done much to reduce the led contamination. Capar (1978) noted that some foods which are stored in refrigerator after being opened for days accumulated increasing amounts of lead.

2.7. TIN FREE STEEL CONTAINERS

The world wide effort that started in the sixties for finding a suitable container for canned products that is free of tin resulted in the birth of Tin Free Steel in Japan. The steel for TFS is produced in much the same way as steel for tinplate and has the same specification for gauge and temper. The deposition of either chromium / chromium-oxide or chromium/ phosphate on the surface is done both in cathodic and anodic-cathodic manner. The various TFS material differs mainly with respect to surface treatments

applied to the steel and the resulting differences in corrosion resistance, appearance and enamel adhesion (Anon, 1974).

Commercial developments of chrome-plated and chromate-treated steels for food cans began in Japan and material of this type are now being manufactured in Japan, Europe and Britain. Typical examples of these materials are; 'Can Super' made by Fuji Iron and Steel Co. Ltd., and 'Hi-Top' made by Toya Kohan. The US Steel Corporation has developed 'TFS-210' which is made by a cathodic chromate phosphate process (Mahadeviah and Gowramma, 1996 a).

Naresh et al. (1989) have reviewed on the chromium coated steel plate as an alternative to tinplate for canning food products and in this report they have reviewed the manufacture of tin-free steel, fabrication of TFS Cans and different properties of TFS and have compared the economics of TFS with aluminium and tin cans. Barbeiri et al. (1970) studied the suitability of various type of chromium-coated steel against tinned steel for packaging food product.

Rice (1992) reported that microwaveable steel cans have a number of benefits including ensuring a 2 year non-refrigerated shelf-life for products contained with in them and being easy to secure and stated that it may be problem for consumer acceptance because of seemingly placing metal in the microwave. A new easy to open all steel can (TFS) offered by Continental Can Company was introduced in U.S.A. during 1970 for canning of number of vegetable, meat and fish products (Anon, 1971). Pielchowska and Chrzanowski (1972) studied the suitability of tin-free steel cans for canning various fish products and compared with anodized aluminium and electrolytic tin plate cans. Hottenroth and Verpack-Rdsch (1972) studied the suitability of chromium plated

'Ancrolyt' for packaging fish products and compared with electrolytic tin plate and reported that over a period of one year chromium plated cans were found suitable for packaging slightly or moderately corrosive fish products of low acidity.

Different types of tin free-steel plates developed in Japan are as follows (Mahadeviah and Gowramma, 1996b).

Can super - this is manufactured by electroplating coled-rolled steel sheet with chromic acid. Bending, drawn and impact tests show that the coated material on the plate doesn't peel off or flake. This type of container is used for mineral oils, gasoline tanks, paints, organic solution, dehydrated foodstuffs etc.

Hinac coat: - this is manufactured by treating cold-rolled steel strip with an emulsion containing chromic acid and an organic high polymer as main constituents with high-temperature baking for a short time. These types of containers have high corrosion resistance, supreme paintability great chemical and thermal resistance and good workability. It is used for packing sugar, cake, soap, motor oil, solvents, paint, ink electrical cases, crown caps, etc.

Hi-top: - the process of manufacture of this type of sheet was developed by Toya Kohan's technical research in co-operation with its affiliated firm, Toyoseikan Kaisha Ltd., in Japan. Hi-top is a tin free steel sheet manufactured by treating electrolytically, cold-rolled steel strip with chromic acid. Container prepared by these types of sheet can be used for packing beer and carbonated beverages.

Stainless weirchrome: - this is a steel plate deposited eletrolytically with metallic chrome on both sides. The chrome film coating ranges from 0.1x10 6 to 0.510 6 in thickness (0.1-0.5 micron in).

3. MATERIALS AND METHODS

3.1. CANNING FACILITY AND ACCESSORIES

3.1.1. Pilot scale retorting unit

The pilot scale mill wall model 24 rotary retorting system (John Fraser and sons Ltd, UK. Model.no.5682) was used for the experiments. This pilot scale retorting system performs laboratory scale thermal process in a manner which ensures close simulation with commercial scale equipment and which produces a high degree of process reproducibility and accuracy. Plate-1 shows the pilot retort used for the study. The model 24 system for pure steam, steam /air and over pressure water immersion process comprises three major components; the retort, the receiver and the control system. The retort provides a chamber in which the product is subjected to the required thermal process. The receiver provides a pressurized volume to balance the overpressure in the retort during super heated water cooks and during overpressure cooling. The control system provides the means to sequence process events, regulate energy flows and document retort temperature and pressure. Retort is constructed of mild steel and it can withstand a working pressure of 50 psig. It has got a dimension of 594mm inside diameter X 650 mm inside length on parallel portion. It has got a swing bolt type door with hinge on the left side. It has a standard square cage, which is perforated with side slots. The speed of rotation of cage ranged from 0 to 51 rpm and was electronically controlled. Instrument pockets are provided on the right side of the shell. These include pressure gauge, retort thermometer, pockets for thermocouple glands and petcock at the rear end. Sparge pipes are provided on the retort.They are four in number and provide on the bottom and top, left and right. Number of holes are 43 per sparge in 3 rows. The holes are of 4mm diameter. A water gauge is

provided on the right hand side of the retort, the gauge bottom indicates retort half full and the gauge top indicates retort is full. A pressure relief valve is provided on the retort which gas got a size of 1”and it will release if the pressure is above 55 psig. The pressure gauge, which is provided on the retort, has got a range of 0 to 60 psig. A 4-blade stainless steel fan is fitted to the retort for use during processing. The fan is designed to run at 1500 rpm and to displace in the order of 500 CFM free air and so create considerable turbulence within the retort during processing to ensure well mixing of steam and that no stagnant air pockets are allowed to exist.

The retort is connected to a very efficient cooling system. As soon as the process is over steam can be switched off and water can be allowed to enter into the retort with the help of a water pump from the water-storing tank. The same water can be recirculated with the help of a recirculating pump. This will provide a very efficient cooling mechanism by spraying water from the top of the retort. A high specification Myson MSK 50 –2/2090 pump suitable for use with super heated water up to 130 °C is fitted to recycle water through the retort.

The receiver is also constructed of mild steel and has got a working pressure of 50 psig. The dimension of the receiver is 594mm inside diameter X 850 mm on parallel side. It has got a water gauge with the gauge top indicates the receiver is full and the gauge bottom indicates receiver below over flow level. It has got a pressure relief valve and the setting is on 55 psig. It also has got a pressure gauge with a range of 0-60psig. The pressure in the receiver is hydraulically and pneumatically transmitted to the retort at the points in the sequence when the retort is required to be at over pressures. Two modulating valves control the receiver pressure, one regulates air into the vessel and the other acts on the vent and regulates air out. The controller is designed with a dual output to operate the

system. The pressure control valve is connected to the vent valves on the receiver and so the transfer line between the two vessels must be open when the pressure is controlled from the sensor mounted on the retort.

Networks of pipes are provided for the entrance of the steam, air and water into the retort and also discharge of the steam, air and water from the retort. All pumps are on the left side and the hand valves are on the right hand side. Incoming services are on the rear left, between upright members and outgoing discharges is on the rear center and right between upright members. Safety valve discharges are on the rear, between upright members and then to local drain.

The control systems specification sequence of all aspects of the retort operation is performed manually but with assistance from discrete electronic controllers on retort temperature and receiver pressure. The controllers and a number of other components are integrated into a PLC managed safety system.

The control system has got a digital temperature indicator and pressure indicator. A digital three-pin circular chart recorder is fitted to record retort temperature and pressure and receiver pressure. A Eurotherm digital indicator is fitted to display cage rotation speed. The instrument is connected to the 0-10 V output of the motor control unit and is scaled for 0-51 rpm. A digital electronic timer is provided to assist the timing of the cook period. The timer is integrated into the PLC monitor system and is used to prompt the operator to begin cooling. A Mitsubishi FI series 60 I/O Programmable Logic Controller is provided to monitor system safety. The PLC observes retort door interlocks and temperature and pressure alarms and acts upon the automatic valves pump and cage drive.

A set of 23 valves is fitted to isolate and regulate the services to and interconnections between the two vessels. Four styles of valves are fitted; they fall into two

categories, automatic and manual. The automatic valves include modulating valves on retort system receive air and receiver vent, air line link to the receiver and retort steam line and the transfer line between the retort and the receiver. The manual valves are all globe valves for local service isolation.

3.1.2. Ellab data recorder (Model TM 9608, Ellab A/S)

Temperature range of the instrument is –100.0 to +350.0 °C. Resolution of the instrument is 0.1°C. There are 8 channels with selective functions for product (Tc) and chamber (Ta) temperatures. These 8 channels are updated within 4 seconds with each channel getting updated within 30 seconds. The Fo constants are programmed T=121.1.1°C, Z=10 °C and Cook value constants T=100 °C, Z=33 °C. The print out interval from the instrument can be selected and it varies from 30 seconds to 60 minutes. The print out shows Tc and Ta min/max, peak temperatures, channel numbers and the actual process time they were measure and the corresponding Fo and Cook value of each channel.

3.1.3. Can punch

Holes were made in the containers to fit thermocouple glands using Ellab TC 89 can punch suitable for rigid containers (Plate-2).

3.1.4. Packing glands and accessories

Ellab A/S, Model No: GKJ 13009 C042 packing glands for all kinds of containers were used for the experiments (Plate-2). The GKM is as standard delivered with a GKM-U rubber oring. For special applications it can be used with wedge washers and silicon washers. Packing glands are usually made up of brass, stainless steel or polyoxymethylene

Plate-1. Overpressure autoclave (John Fraser Ltd, Model 24 Rotary Pilot Scale Retorting System

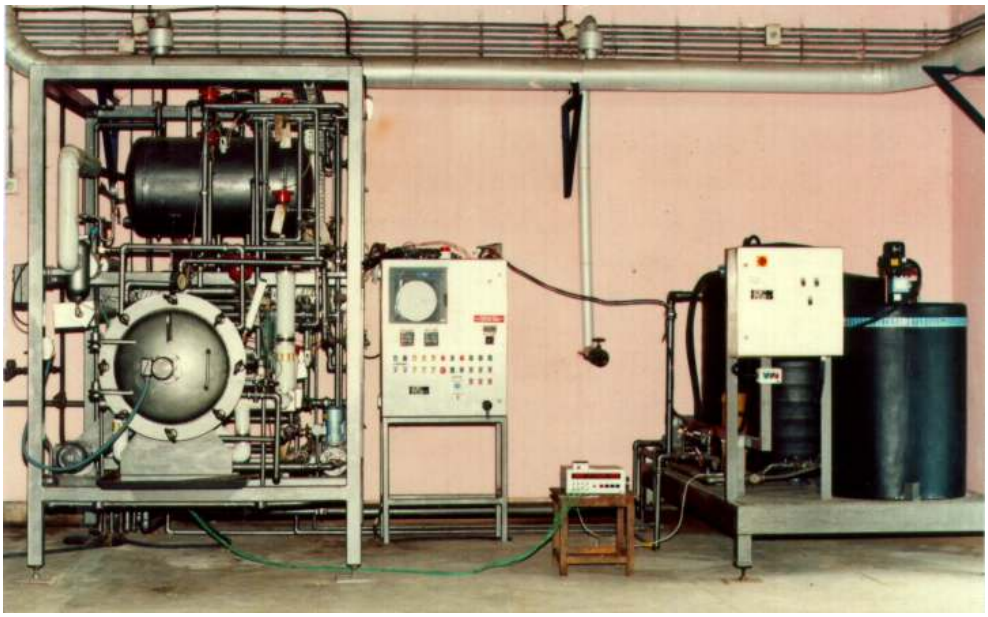
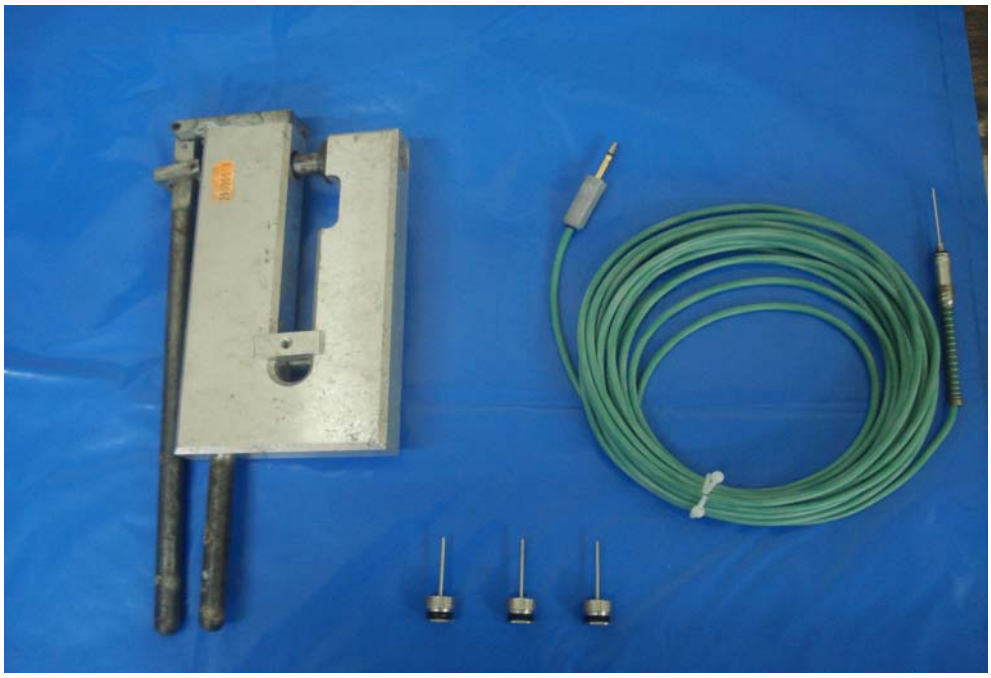


Plate-2. Can punch, thermocouple glands and probes



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3.1.5. Standard Thermocouple Probes

The probes used for the experiments are that of Ellab A/S, Model No: SSA 12040 G700 TS stainless steel electrode with a length of 40mm, diameter 1.2mm (Plate-2). These probes are copper/cupronickel thermocouples; they are sealed probes with the conductor being insulated from the process medium.

3.1.6. Exhaust line

The filled cans were exhausted using steam in an exhaust line (Can tech machines, Mumbai). It has a total length of 10 meters and can work on variable speed so that the exhausting time can be adjusted.

3.1.7. Double Seamer

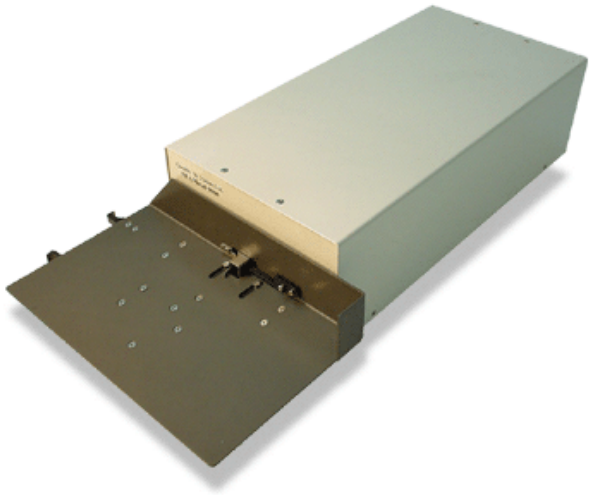
The cans were seamed immediately after exhausting using the semi automatic double seamer (Super Seam, Model No: 24 DS, Chennai). It can seam cans having diameter ranging from 51 to 178 mm and height 51 to 248 mm and has a maximum output of 40 cans per minute.

3.1.8. Double seam analyzer

The double seam parameters of cans were measured using SEAMetal 9000 system (Quality by Vision, Israel). It consists of seam saw, optical unit and the software (Plate-3). In order to accurately measure the seam parameters, a clean and precise section of the seam with little or no deformation should be made. This is done with the seam saw equipped with twin blade discs kept 12.9 cm apart and rotating at a speed of 500 rpm. Two cuts are made simultaneously. Once the cut is made, the inner portion is pushed inside using a no head screw driver so that the cut sections can be viewed through the seam analyzer.Usually three cuts are made in a can one after the other by rotating the can approximately 120°.

Plate-3. Double seam analyser (SEAMetal 9000 system (Quality by Vision, Israel)

Seam saw



Double seam analyser

The optical unit of the seam analyzer is equipped with a camera that catches the image of the cut section of the seam and forms a magnified image (50 times) of the latter in the screen. With the help of the software, the various parameters required for measuring the double seam parameters can be marked on the image thus formed.

3.1.9. Lacquer Coating Breakage detector

Lacquer Coating Breakage (LCB) detector developed by CIFT was used for testing the coating perfection of cans. It is easy to use without damaging the cans and can be easily incorporated to production lines. The checking time is 30 sec and the result is given as both audio and light indication.

3.2. INSTRUMENTS

3.2.1. Texture Analyser

It is a general-purpose material-testing machine manufactured by Lloyd instruments, UK , Model LRX plus (Plate-4a). The software used in the instrument is Nexygen. When used with Nexygen software, data output is to a computer display and printer. The main part of the instrument is a load cell. Standard cells are there with values of 5000 N, 500N and 50 N and each one can be used depending on the type. The LRX plus machines are fitted with two magnetically activating limit stops. Reaching magnetically activated limit stop will result in the machine stopping. The speed of the cross edge movement varies from .01-1016mm/min. The unit has a liquid crystal display (LCD) to show set up information, load and extension values and a key pad to input information for operating the machine when under the control of the console. The operating status of the machine is shown on and described on the display. The display, which has 4 lines of forty characters, is used to show or request information. The information displayed depends up on the status of the machine but generally; the top line displays title or help information for each display. The lower lines are split into four blocks, one block above each soft key to indicate the function of the key.

Plate-4 a. Food Texture Analyzer (Lloyd instruments, UK (Model LRX plus)

Plate-4 b. L,a,b colour solid

3.2.2. Coloriespectrophotometer

Colour measurements were done using a Hunter lab Colorimeter Model No D/8-S (Miniscan XE Plus) with geometry of diffuse /8° (sphere 8 mm view) and an illuminant of D65/10 deg. Samples to be analysed were homogenized and loaded inside the sample holder for determination of the CIE L*, a* and b* values. First step in measuring is standardization. Standardization sets the top and bottom of the scale for the neutral axis. During standardization the bottom of the scale was set first. This was done by placing the black glass or light trap at the sample port. The top of the scale was then set by using white tile. In order to measure the L*,a* and b* values, sample holder loaded with sample is placed at the instrument port with the side to be measured toward the port. Sample should be flat against the port and completely cover. When the read key is pressed the sample will be measured and its values saved in the instrument. In the Hunter scale, L* measures lightness and varies from 100 for perfect white to zero for black, approximately as the eye would evaluate it. The chromacity dimensions (a and b) give understandable designations of color as follows: a* measures redness when positive, gray when zero, and greenness when b* measures yellowness when positive, gray when zero, and blueness when negative (Plate-4 b.).

MATERIALS

3.3.1. Containers

3.3.1.1. Indigenous Polymer Coated Tin Free Steel Can and Easy Open Ends (EOE)

Indigenous Polymer Coated Tin Free Steel cans of size 307 X 109 (6 oz capacity) manufactured by M/s Amtech Packs, Mysore were used for the study (Plate-5 a). These are

2- piece cans manufactured by (Draw and Redraw) DRD process and are available along with Easy Open Ends (EOE). Both the can and EOE are made from Electrochemically Chromium Coated Steel (ECCS) plate coated with Poly Ethylene Terephthalate (PET) on either side (Plate-5 b). The PET coating substitutes the lacquer coating of conventional tin and aluminium cans is laid as a continuous layer over the chromium coated steel plates by the process of lamination. The EOE is also manufactured from electrochemically chromium coated steel plates with polymer coating and is provided with unique features like triple fold technology, scoring along the periphery, and pull up tab all of which facilitates the easy opening of the cans without employing a can opener. Cans and EOE were thoroughly washed before use to remove adhering impurities and dried well to remove traces of water.

3.3.1.2. Tin and Aluminium Cans

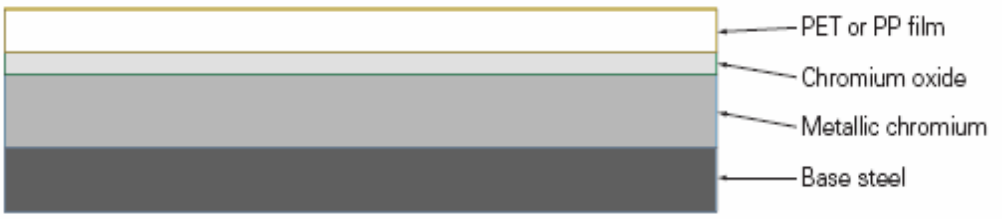
Tin cans of 8 Oz capacity and procured from M/s Sherton Industries, Bangalore, India and aluminium cans of 8 Oz capacity and manufactured by M/s Klass Engineering Company, Bangalore, India were used for the study. Tin cans were of 3-piece type while aluminium cans were of 2-piece type.

3.3.2. Fish

Fishes used for the study were yellow fin tuna (*Thunnus albacores*) and Mackerel (*Rastelliger kanagurta*), Indian white shrimp (*Feneropenaeus indicus*) and Squid (*Loligo dauvacelli d orbigny*). They were collected from fisheries harbor (Cochin), iced at the ratio 1:1 (raw material: ice) and transported to the laboratory under iced condition (0-4 °C). They were then washed using potable water to remove dirt. Mackerel was beheaded, degilled and made free of fins, washed thoroughly in potable water and cut into 2.5 cm size pieces, while shrimp was peeled and deveined followed by thorough washing in potable water. Squid was made free of viscera carefully without disturbing the ink sac and peeled off the skin and washed in potable water

Plate-6 a. Polymer coated Tin Free Steel (TFS) cans and Easy Open Ends (EOE)

Plate-6 b. Functional layers of TFS can



3.3.3. Oil

Double refined sunflower oil was used for the curry preparation.

3.3.4. Salt and other curry ingredients

Salt of edible quality confirming to IS: 594-1962 was used. All other ingredients used for the curry preprations were of good quality, food grade and fit for human consumption.

3.3.5 Squid masala curry

Squid masala curry was prepared following the recipe given in Table-1. Peeled squid were cut into rings of 0.8 cm width using a sharp stainless steel knife. The rings were then blanched in 8 % brine at 80 °C for 6 min. For curry preparation, chopped coconut was fried to a golden brown and kept aside. Sliced onions were light fried along with green chilly, curry leaves and ginger garlic paste. To this tomato paste was mixed along with chilly powder, turmeric powder, pepper powder and little salt. Blanched squid rings were added to this mixture along with fried coconut pieces and mixed thoroughly.

Table-1. Recipe for squid masala

Item	**Quantity**
Squid	1 kg
Green chillies	75 g
Ginger	50 g
Garlic	50 g
Onion	500 g
Coconut	2 ½ (chopped)
Chilly powder	10 g
Pepper powder	10 g

Salt	To taste
Coriander powder	10 g
Turmeric powder	5 g
Tomato	150 g

3.3.6. Shrimp curry

The peeled shrimps were hot blanched in 3% brine solution at 80 °C for about 7 min. After this they were cooled immediately to room temperature by keeping under fan. For the shrimp curry preparation, green chilly, curry leaves and ginger garlic paste were light fried along with sliced onions. To this tomato paste was mixed along with chilly powder, turmeric powder, pepper powder and little salt. Blanched shrimp was added to this mixture and mixed thoroughly. The recipe for shrimp curry is given in Table-2.

Table-2. Recipe for shrimp curry

Item	**Quantity**
Shrimp	1 kg
Green chillies	75 g
Ginger	50 g
Garlic	50 g
Onion	500 g
Chilly powder	10 g
Pepper powder	10 g
Salt	To taste
Coriander powder	10 g
Turmeric powder	5 g
Tomato	150 g

3.4. METHODS

3.4.1. ANALYSIS OF CAN

3.4.1.1. Determination of water capacity (IS: 6093, 1970)

Two holes of 3 - 4 mm diameter were drilled about 5 cm apart as close as possible to the countersink, from the inside surface outwards on a can end. This was attached by double seaming on the other end of the can body. The can was weighed to the nearest 1g and the container was filled with water at 27 °C employing a narrow water jet through one of the holes. Surplus water on the out side of the can was removed using a blotting paper and the filled can was weighed to the nearest 1g. The difference between the weights was noted and to this 0.45% of the value was added. This represents the capacity in milliliters.

3.4.1.2. Air pressure test (IS: 9396, 1979)

This test was performed to determine the pressure holding capacity of the cans and to check for any leakage through the double seam. The cans were pierced with a piercing type of pressure gauge and then air was pumped inside using a foot operated pump until any distortion of the can or any leakage through the double seam area was noticed. The double seamed cans have to be immersed in boiling water for 5 min prior to the test.

3.4.1.3. Determination of Vacuum (IS: 3336-1968)

The vacuum in the can was determined with a vacuum gauge of the piercing type.

3.4.1.4. Test for coating perfection

The perfection of the PET coating was analysed using the Lacquer Coating Breakage (LCB) detector. The can was filled with 10% brine and attached to the LCB

detector in such a way that one of the electrodes is in contact with the edge of the flange where the base metal is exposed and the other electrode is dipped in the brine. Presence of any discontinuity in the coating allows the circuit to complete which will be indicated by light and audio indicators.

3.4.1.5. Sulphide blackening test (Anon, 1977)

Resistance of cans to sulphide blackening was analyzed following the Cysteine test. For this, cans were filled with the test solution consisting of 0.5 g of cysteine chloride in 1 liter of buffer solution (3.56 g KH_2 PO_4 and NA_2H PO_4. 2 H_2O in 1 liter of distilled water). Filled cans were double seamed and retorted for 30 min at 125 °C. They were then left to cool down at room temperature for 24 hrs and were opened and evaluated for any blackening.

3.4.1.6. Test for delamination of PET coating

The polymeric coating of TFS can was subjected to delamination test using various organic solvents like acetone, carbon tetra chloride, chloroform, diethyl ether, ethyl acetate, n-heptane, methanol, and petroleum ether. Panels of 1 X 1 cm size were taken and immersed in organic solvents. They were taken out after 24 hrs and examined for any delamination of the PET coating. When there was no peeling they were kept immersed for another 12 hrs. The panels were taken out and heated in water bath for few minutes and examined for delamination of the coating.

3.4.1.7. Test for thickness of PET coating

The PET coating was first delaminated from the base metal by immersing in chloroform for 24 hrs. It was then dried in air at room temperature. The dried material was analyzed for its thickness using a digital micrometer.

3.4.1.8. Test for suitability of can for processing at different temperature and pressure

The cans were processed at different temperatures and pressures of 115 (10lbs), 121.1.1 (15lbs), 126 (20lbs) and 130 ^{0}C (25 lbs) in a pilot scale retort of model 24 rotary retorting systems (John Fraser and sons Ltd, UK. Model.No.5682) to determine it's ability to withstand different processing conditions.

3.4.1.9. Test for food contact application

Suitability of the can for food contact application was found out by determining the water extractives at 121.1 ˚C for 2 hrs and soluble chloroform extractives as per the methods of FDA (2003). The cans were filled with 200ml of hot glass distilled water and immediately heat-sealed. The sealed cans were heat processed at 121.1.1 °C for 2 hrs. After processing the processed water was transferred into clean beakers and evaporated up to 50ml.The contents of the beaker were transferred into another clean pre weighed tared platinum dish and evaporated to dryness. After cooling the weight of the dish is again taken to the nearest 0.1 mg to find out the amount of water extractives. To those dishes containing water extractives 50 ml of chloroform is added to dissolve all the chloroform extractives. The contents are filtered and evaporated to dryness in a clean pre weighed tared platinum dish. After drying the weight of the dish is again taken to the nearest 0.1 mg to determine the amount of chloroform extractives.

3.4.1.10. Test for seam integrity

The seam integrity of the polymer coated tin free steel cans was analysed following the cut out analysis (Balachandran, 2003) and using the semi-automatic Double seam analyser (Quality By Vision, Model SEAMetal 9000M, Israel). For cut out analysis, double seamed cans were selected at random and three equidistant points were marked on the circumference of the seam of the can. Using a micrometer, the Seam length (L), Seam thickness (T_s), Body hook, Cover hook, Body plate thickness (T_b), Cover plate thickness (T_c), were measured. From these parameters, the % overlap was calculated using the formula.

$$\% \text{ Overlap} = \frac{BH + CH + 1.1tc - L}{L - (2.2tc + 1.1tb)}$$

Where

BH = Body hook length

CH = Cover hook length

tc = Cover plate thickness

tb = Body plate thickness

L = Seam length.

For the purpose of seam analysis using the double seam analyser, double seamed cans were selected at random and three cut sections were made on the double seam one after the other using the twin blades of the seam saw which are rotating at a speed of about 500 rpm. The cut width is 12.9 mm, which accurately fits to the camera of seam analyser. The double seam parameters such as Seam length (L), Seam thickness (T), Body hook (BH), Cover hook (CH), Body thickness (t_b), End plate thickness (t_c) etc were measured using the seam analyzer SEAMetal 9000M.

3.4.2. THERMAL PROCESSING

3.4.2.1. Prepration of test cans

Adequate number of test cans were prepared to trace the thermal history during the heating and cooling phases of the canning operation. For this the cans were perforated from the side by using the can punch which can form holes through which the packing gland can be inserted into the can. The perforation was done in such a way that the thermocouple tip will be pointed towards the centre of the can at one third height from the bottom which is recognised as the slowest heating point. The packing gland was then tightly screwed into the can body with the rubber gasket which helps in forming leak proof joint.

3.4.2.2. Standardisation of optimum process parameters for ready to eat fish products in polymer coated tin free steel cans

Heat penetration studies were conducted with the purpose of standardizing the optimum process condition for various ready to eat fish products in tin free steel cans. The heat penetration studies of Squid masala and shrimp curry were carried out seperately by thermal processing at 121.1 ^{0}C to F_0 values of 7, 8 and 9 and 6, 7 and 8 respectively in a stationary retort. In both cases, about 160 ±2 g of product was packed in washed and dried 6 Oz polymer coated easy open-end TFS cans, maintaining headspace of 0.4 mm. During can filling, care was taken to avoid the curry from contaminating the sealing area of the cans. Adequate numbers of test cans were prepared by fixing with thermocouple glands at about one third height from the bottom of the can with the tip of the gland pierced into the core of the meat. The cans were exhausted under steam in an exhaust box for 10 min and immediately double seamed in a double seaming machine. The sealed cans of squid masala

and shrimp curry were divided into 3 batches and were loaded inside the retort (John Fraser and sons Ltd, UK. Model.No.5682) separately on perforated stainless steel trays. The themocouple probes were attached to the thermocouple glands that were already attached to the test cans. The lead wire from the thermocouples were attached to the Ellab data recorder (Model TM 9608, Ellab A/S). Three test cans were employed for each trial run of each product. Care was taken to maintain the initial product temperature at 35 °C. Squid masala was processed at 121.1 °C to three different F_0 values of 7, 8 and 9 min while shrimp curry was processed to F_0 6, 7 and 8 min. Triplicate runs for each F_0 value was also conducted. The cans were cooled rapidly by spraying water under pressure to a core temperature of 40 °C so as to prevent the proliferation of thermophiles and the product from getting overcooked. The cooling water was maintained with constant chlorine residual level of 2 mg/L. Graves et al. (1977) recommended a residual chlorine level of 1–3 mg/L to maintain bacterial control in cooling water. The thermal history of the retort and the test cans during the entire thermal process operation was collected at every 30 sec using Ellab data recorder (Model TM 9608, Ellab A/S) evaluated as described in section 3.4.2.4. The cans were then dried, labeled and stored. The cans were stored at room temperature for about 15 days and then subjected for the analysis of commercial sterility, instrumental colour, texture, shear force and sensory parameters for the selection of optimum process conditions.

3.4.2.3. Canning of mackerel in brine (MIB) at different retort temperatures

In order to determine the effect of different retort temperatures on the heat penetration parameters, sensory and biochemical characteristics, Mackerel in brine was thermally processed at different retort temperatures of 115, 121.1 and 130 ^{0} C in a

stationary retort to the standardized F_0 value of 8 min. Many workers have reported that F_0 value of above 9 min was not satisfactory for canned mackerel products based on the sensory characteristics (Srinivasa Gopal et al., 1998 and 2001). Triplicate runs for each tmeperature was conducted and the average values were taken.

Freshly cut mackerel pieces were blanched in 10% brine for 15 min and then about 140± g of fish pieces were filled into the cans. Test cans were fixed with fish piece with the tip of the thermocouple gland piercing into the core of the meat. Precooking was done at 100 °C for about 20 min. The precook exudate was drained off and the cans were filled with 60ml of hot brine solution. The filled cans were then steam exhausted in free flowing steam for 10-12 min and immediately double seamed in a seaming machine. The filled and sealed cans were divided into three batches and thermally processed to a F_0 value of 8 min at 115, 121.1 and 130 ^{0}C (John Fraser and sons Ltd, UK. Model.No.5682). Care was taken to maintain the initial product temperature at 35 °C. Triplicate run for each temperature was conducted. At the end of the process cans are cooled immediately. Thermal data during heating and cooling phases of the thermal process operation was collected and evaluated as described in section 3.4.2.4. The cooled cans were dried, labeled and stored. (IS: 3849-1976). The cans were kept for maturation for about 14 days and analysed for commercial sterility, instrumental colour, texture and shear force, sensory and biochemical parameters.

3.4.2.4. Thermal process evaluation

The recorded data were analysed using a computer. The lethality accumulated during the entire processing (heating and cooling) was calculated from the temperature history inside by numerical integration based on the original work of Ball (Ball and Olson, 1957).

$$F_o = \int_0^t 10^{(T - Tref)/z}$$

where t, z, T and T_{ref} represent the time (min), temperature sensitivity of the target microorganism, temperature at any given time, and reference processing temperature, respectively.

The cook value, originally proposed by Mansfield (1962) for aseptic processing of low-acid foods which is measure of heat treatment with respect to nutrient degradation and textural changes that occur during processing, was determined according to the relationship

$$C = \int_0^t 10^{(T - Tref)/z}$$

where t, z, T and T_{ref} represent the time (min), z value of the heat liable component (taken as 33 °C), temperature at any given time, and reference processing temperature for the heat liable component (100 °C), respectively.

The heat penetration data was plotted on an inverted semi log paper with product Temperature deficit (RT-CT) on vertical log scale (Y-axis) against time on the linear horizontal scale (X-axis) as described in NCA manual (1968). The lag factor of heating (jh), lag factor of cooling (jc), slope of heating curve (fh), time in minutes for sterilization at retort temperature (U) were determined. Cooling curve was plotted and cooling process parameters were determined as described by Ramaswamy and Singh (1997). Using these

parameters the process time (B) was calculated according to mathematical method (Stumbo, 1973). The total process time was calculated by adding 58% of come up time (CUT) to B.

Process time (B) = fh [log I x Jh – log g]

Total Process time (T) = B + 58% of come up time

3.4.3. STORAGE STUDY

Ready to eat squid masala and shrimp curry were prepared and processed in large scale according to the chosen F_0 values and kept for storage studies at room temperature (30±20C) during which samples were taken on monthly basis and were analyzed for instrumental color, TPA, shear force, TBA, pH and sensory characteristics for a period of one year following standars methods.

3.4.4. ANALYSIS OF FISH MEAT

3.4.4.1. Physiochemical Parameters

3.4.4.1.1. pH (IS: 2168-1971)

5g of the sample was dispensed in 10ml of distilled water and pH was measured by using pH meter.

3.4.4.1.2. Instrumental colour

The L*, a* and b* or CIE Lab colour values of the samples were analyzed using Hunter lab colorimeter (Model No: Miniscan-XE plus, Hunter associates laboratory, Virginia, USA). Squid muscle and shrimp pieces were finely homogenized in a food

homogenizer (Kenstar Kitchen Appliances India Limited, Aurangabad, India.) and loaded inside the sample holder while fish meat was made free of skin and bones before homogenising.

3.4.4.1.3. Texture profile attributes

The texture profiles of samples were analyzed using a food texture analyzer (model LRX Plus, Lloyds Instruments, Hampshire, U.K.) and Nexygen software (Lloyds Instruments). The sample was placed on a flat platform and was subjected to double compression by a cylindrical probe with a 50-mm diameter. The test was conducted at a speed of 12 mm/min using a 50-N load cell. The sample was allowed for a double compression of 40% with a trigger force of 0.5 kg during which the various textural parameters like hardness1, hardness2, cohesiveness, springiness, gumminess, chewiness were determined.

3.4.4.1.4. Warner –bratzler shear force

The shear force of samples was determined using the Food texture analyzer (Lloyds Instruments, Model LRX Plus, Hampshire, UK) and software Nexygen. The test was done with a load cell of 50N fitted with the Warner-Bratzler shear attachment, which is a 3mm thick steel blade with a V-cut at the lower edge. The blade edge was not sharpened and fitted loosely into the slit in the table. The sample to be tested was placed on the table under the blade and was allowed to be cut by the blade that was moving downwards at a constant speed of 50mm/s through the slit of the table. The shearing direction was set perpendicular to the orientation of the muscle fibers.

3.4.4.2. Biochemical parameters

3.4.4.2.1. Proximate composition

3.4.4.2.1.1. Determination of moisture (AOAC, 2000)

A known weight of sample (10 gm) was weighed in a preweighed clean petridish on an electronic balance. The samples were allowed to dry until uniform weight by placing in a hot air oven at 100 °C for 6 hrs. Then cooled in a desiccator and weighed. The moisture content was calculated and expressed as percentage.

3.4.4.2.1.2. Determination of crude protein (AOAC, 2000)

About 0.5- 1 gm of the minced sample was transferred into a Kjeldahl flask of 100 ml capacity. A few glass beads and a pinch of digestion mixture and 10 ml of concentrated sulphuric acid were also added. It was then digested over a burner until the solution turned colourless. To the digested and cooled solution distilled water was added in small quantities with intermittent shaking and cooling until the addition of water generated no heat. It was transferred quantitatively into a1 00 ml standard flask and made up to the volume. With a 2 ml pipette, the made up solution was transferred to the reaction chamber of the Micro-Kjeldahl distillation apparatus. 2 drops of phenolphthalein indicator and 40% sodium hydroxide were added till the indicator changed to pink. Distillation was done for 4 minutes and ammonia liberated was absorbed into 2% boric acid containing a drop of Tashiro’s indicator. The amount of ammonia liberated was determined by titration with 0.01 N standard sulphuric acid. Crude protein was calculated by multiplying total nitrogen content with conversion factor of 6.25 and expressed as percentage.

3.4.4.2.1.3. Determination of ash content (AOAC, 2000)

About 1-2 gm of the sample was transferred into a preweighed silica crucible. The samples were then charred by placing in a muffle furnace at 550 °C for 4 hrs until a white ash was obtained. Crucibles were weighed after cooling in a desiccator and percentage of ash was calculated.

3.4.4.2.1.4. Estimation of crude fat (AOAC, 2000)

About 2-3 gm of accurately weighed moisture free sample was taken in a thimble plugged with cotton and extracted with petroleum ether (Boiling point 40-60 °C) in a soxhlet apparatus for for about 10 hrs at a condensation rate of 5-6 drops per second. Excess solvent was evaporated and the fat was dried at 100 °C to constant weight. The crude fat was calculated and expressed as percentage.

3.4.4.2.2. Amino acid profile (Ishida et al., 1981)

Reagents

1. 6 N HCl	
2. Buffer A	Tri Sodium Citrate 32.7g, Distilled Ethanol 140 ml, Perchloric acid 16.6 ml, pH 3.2. Make up to 2 liter with distilled water.
3. Buffer B	Tri sodium citrate 117.6 g, Boric acid 24.8 g, 4 N NaOH 45 ml, pH 10. Make up to 2 lire with distilled water.
4. Buffer C	0.05 N HCl.
5. OPA Buffer	Sodium carbonate 40.7 g, Boric acid 13.57 g, Potassium sulfate 18.8 g. make up to 1 liter.

6. O-phthalaldehyde reagent	OPA 80 mg, Methanol 1.4 ml, 2 Mercapto ethanol 0.2 ml, Brij 0.15 ml. make upto 100 ml with OPA buffer.
7. Sodium hypochlorite reagent	0.3 ml sodium hypochlorite make up to 100 ml.

Procedure

About 100-150 mg of sample was weighed accurately into a heat sealable test tube. 10 ml of 6 N HCl was added and the tube was heat sealed after filling with pure nitrogen gas. Hydrolysis was carried out in a hot air oven at 110 °C for 24 hrs. After hydrolysis, the contents were removed quantitatively and filtered into a round bottom flask through whatman filter paper No 42. The contents of the flask were flash evaporated to remove the traces of HCl and the process was repeated for 2-3 times with added distilled water. The residue was made upto 10 ml with 0.05 N HCl. The sample thus prepared was filtered through a membrane filter of 0.45 µm and 20 µ ml of this was injected to Shimadzu HPLC-LC10AS consisting of column packed with strongly acidic cation exchange resin i.e. Styrene divinyl benzene copolymer with sulfonic group. The column used Na type i.e. ISC-07/S1504 Na having a length of 19 cm and diameter 5mm. The mobile phase consists of two buffers, Buffer A and buffer B. The oven temperature was maintained at 60 °C. The amino acids were eluted from the column by stepwise elution i.e. acidic amino acids first followed by neutral and then basic amino acids. The amino acid analysis was done with non-switching flow method and fluorescence detection after post column derivatisation with O-phthalaldehyde. In the case of Proline and Hydroxy proline, imino group was converted into amino group with odium hypochlorite. Amino acid standard was also run to

calculate the concentration of amino acid depending upon the standard chromatogram. The results were quantified and represented as gram amino acid per 100 g proteins.

3.4.4.2.3. Determination of Tryptophan (Sastry and Tummru, 1985)

Reagents

5% NaOH	6 N HCl
2.5% Sucrose	0.6% thioglycolic acid
50 % H_2SO_4	0.1 N HCl
Standard tryptophan (10 µ g/ml)	

Procedure

About 200-250 g of fish muscle was accurately weighed and was hydrolyzed with 10 ml 5% NaOH at 110 ^{0}C for 24 hrs in a sealed tube filled with pure nitrogen. The hydrolysate was neutralized to p H 7.0 with 6 N HCl using phenolphthalein indicator. The volume was made up to 100 ml with distilled water. The solution was then filtered through whatman filter paper No. 1 and filtrate was used for the estimation. To a test tube containing 4 ml of 50 % H_2SO_4, 0.1 ml of 2.5 % sucrose and 0.1 ml of 06 % thioglycolic acid were added and these tubes were kept for 5 min in water bath at 45-50 ^{0}C and cooled The sample was then added to the test tubes. A set of (0.1-0.8 ml) standard tryptophan (10µ g/ ml) was run in this way the volume was made up to 5 ml with 0.1 N HCl and allowed to stand for 5 min for the development of color. The absorbance was measured against a reagent blank at 500 nm in a spectrophotometer.

3.4.4.2.4. Estimation of minerals and metallic contaminants using Atomic Absorption Spectrophotometer (AOAC, 1980)

Reagents

1. Nitric acid

2. Perchloric acid

Reagents 1and 2 were mixed in the ratio 9:4

Stock solution of sodium, potassium and calcium were prepared by diluting concentrated solution of 1000 mg/l (Merck).

Procedure

Samples size of 200mg of fish muscle and gravy was used for the experiment. To the sample containing flask, 7ml of nitric acid and perchloric acid (9:4) mixture was added, covered with a watch glass and left at room temperature over night. The sample was then digested using a microwave digester (Milestone ETHOS PLUS lab station Closed Vessel Microwave Digestion System). The completely digested samples were allowed to cool at room temperature, filtered (glass wool) carefully and transferred into a clean 50 ml volumetric standard flask and then diluted to the mark with ultra pure water (Milli Q, Millpore). The digested samples were analyzed using Varian Spectra-220 AA, Atomic Absorption Spectrophotometer equipped with a deuterium back ground corrector for the determination of minerals and metallic contaminants.

3.4.4.2.5. ATP breakdown products

The ATP breakdown products were determined according to the method of Ryder (1985) using High Performance Liquid Chromatography (HPLC). Merck Hitachi Li

Chrome HPLC fitted with L-7100 quaternary gradient pump, L-7400 UV detector and C18 stainless steel column was used for the analysis. Merck Hitachi Model D-7000,Chromatography Data Station Software HPLC System Management (HSM) was used in the study.

3.4.4.2.5.1. Standard preparation

The standard nucleotide solution was prepared individually so as to give a concentration of 10 mM. For this, 27.755 mg ATP, 23.5585 mg ADP, 17.36 mg AMP, 17.4105 mg IMP, 6.805 mg Hx and 13.41 mg HxR was dissolved in 5 ml milli Q purified (0.22 µm Millipore) distilled water separately. Initially, Hx and HxR were dissolved in 0.1 N NaOH and made up to known volume using milli Q purified distilled water. From this 10 mM stock solution, 0.01, 0.05, 0.1, 0.5 and 1.0 mM mixed standard solutions were prepared by diluting with milli Q purified distilled water and used for obtaining standards curve area.

3.4.4.2.5.2. Sample preparation

Fish extract used for the analysis was prepared by homogenizing 5 g of fish muscle (without skin) with 25 ml chilled 0.6 M perchloric acid in a laboratory homogenizer (ART modern Labortechnik, Zienkener Str. Muellheim, Germany) at 00 C for 1 min. The homogenate was centrifuged at 6000 rpm for 20 min at 40 C. The supernatant was then decanted and immediately neutralized to pH 6.5 - 6.8 with 1 M potassium hydroxide solution. After standing at 1-20 C for 30 min, the precipitated potassium perchlorate was removed by filtration through a syring of pore size 0.45 µm.The filtrate was stored at -700 C until analysed. High Performance Liquid Chromatography (Merck Hitachi Li Chrome HPLC fitted with L-7100 quaternary gradient pump, L-7400 UV detector, set at 240 nm)

was used for quantitative analysis of ATP breakdown compounds of prepared samples. 20 µL aliquots of the sample extracts were injected into the HPLC and the separation of the nucleotide products was achieved by a 5 µm pore size column (C18 stainless steel column with size 250 x 4 mm, length x dia). Integration was carried out using Chromatography data station software, HPLC System Management (HSM) programme installed into the computer system. The mobile phase of 0.04 M potassium dihydrogen orthophosphate and 0.06 M dipotassium hydrogen orthophosphate dissolved in Milli Q purified distilled water was used at a flow rate of 1.5 ml/min. The peaks obtained from fish muscleextracts were identified by comparing against the standard solutions. ATP breakdown products, comprising ADP, AMP, IMP, Hx and HxR were measured and K value was calculated using the formula described by Saito et al. (1959).

$$\text{K-value (\%)} = \frac{[\text{HxR}] + [\text{Hx}]}{[\text{ATP}] + [\text{ADP}] + [\text{AMP}] + [\text{IMP}] + [\text{HxR}] + [\text{Hx}]} \times 100$$

3.4.4.2.6. Biogenic Amines

The biogenic amines content in fish was determined using rapid HPLC method as described by Ozogul et al. (2002). The gradient system and the flow rate were modified depending on the retention time of the standard amine solution to get good resolution within a short time.

3.4.4.2.6.1. Preparation of standard amines solution

16.57 mg of histamine di-hydrochloride, 18.29 mg of putrescine di-hydrochloride, 17.14 mg cadaverine dihyrochloride, 17.52 mg of agmatine sulphate, 12.67 mg of tyramine

hydrochloride, 17.20 mg of spermine tetrahydrochloride and 17.53 mg of spermidine tri-hydrochloride were dissolved separately in 10 ml of HPLC grade water. The final concentration of free base for each amine was 1 mg/ ml solution. From this, 2.5, 6.25, 12.5 and 18.75 µl of each standard was taken and made up to 250 µl using HPLC grade water and derivatized to get a concentration of 10, 25, 50 and 75 µg/ml (ppm) respectively.

3.4.4.2.6.2. Preparation of sample

Fish muscle (5 g) was taken and made free of and transferred to a centrifuge tube. The sample was homogenized with 25 ml 6% TCA for 3 min, centrifuged at 12000 rpm for 10 min at 40 C and filtered through Whatman No. 1 filter paper. The aliquot was made up to 25 ml with 6% TCA and stored at -200 C until analysis.

3.4.4.2.6.3. Derivatisation procedure

A stock solution of 2% benzoyl chloride in acetonitrile was prepared to enhance the reaction with amines. For derivatization of standard amine solution and fish sample, 50 µL and 2 ml was used respectively. One milliliter of 2 M sodium hydroxide was added, followed by 1 ml benzoyl chloride (2%), and mixed on a vortex mixer for 1 min. The reaction mixture was left at room temperature (25 0C) for 30 min. The benzoylation was stopped by adding 2 ml of saturated sodium chloride solution and the solution was extracted two times with 2 ml of diethyl ether. The upper organic layer was transferred into a clean test tube after mixing and evaporated to dryness in a stream of nitrogen or using vacuum drier. The residue was dissolved in 500 µL of acetonitrile and stored at -20 ^{0}C untill use and 20 µL was injected into the HPLC.

3.4.4.2.6.4. Chromatographic condition

Merck Hitachi Li Chrome HPLC fitted with L-7100 quaterinary gradient pump and L-7400 UV detector was used for the analysis. Merck Hitachi Model D-7000, Chromatography Data Station Software HPLC System Management (HSM) was used in the study. The column used was Li Chrome CART® 250-4 C18 RP of size 250 x 4 mm (length x dia) with pore size of 5 µm. Chromatographic separation was done by continuous gradient elution with acetonitrile (solvent A) and HPLC grade Millipore water (solvent B) as described by Ozogul et al. (2002). The gradient started with 50% acetonitrile and increased to 80% in 10^{th} minute. The pressure was maintained between 1300 to 1500 psi throughout the separation period.

3.4.4.2.7. Determination of sulfhydryl content (Sedlak and Lindsay, 1968)

This method is based on the development of a yellow colour when DTNB is added to compounds contained sulfhydryl groups to form 2-nitro 5- mercaptobenzoic acid.

3.4.4.2.7.1. Prepration of tissue extract

About 800 mg of sample was homogenised with n16 ml 0.02 M EDTA in a tissue homogeniser for 2 min @ 10,000 rpm. Tubes were kept in ice bath to avoid heat generation during homogenisation. The homogenate was kept in ice bath until used.

3.4.4.2.7.2. Determination of total sulfhydryl group

Aliqots of 0.5 ml of tissue homgenate was mixed in 15 ml stoppered test tube with 105 ml 0.2 M tris buffer, ph 8.2 and 0.1 ml 0.01 M 5,5-dithiobis-2-nitrobenzoic acid (DTNB). A reagent blank (without sample) and a sample balnk (without DTNB) wre prepared in similar manner.the test tubes were stoppered and allowed to stand with

occsional shaking for 30 min, then filtered through Whatman filter paper No.2, thereby attaining clear filterate. Then the absorbance was read in a Spectronic 20 Genesys at 412 nm.

3.4.4.2.7.3. Prepration of standard curve

Standard solution of concentration 2X10–4 cystine ranging from 0.1-0.5 ml was pipetted in duplicate. The volume was made upto 0.5 ml with 0.02M EDTA. To this 1.5 ml tris buffer was added, followed by 0.1 ml 0.01 M DTNB and made upto 10 ml with absolute methanol and then proceeded as given above for sample.

A graph was drawn taking concentration along the X-axis and absorbance along the Y-axis and the concentartion of the sample was calculated from the standard graph. The sulfhydryl content was estimated acoring to the formula

$$\text{1 mole SH/g DM} = \frac{\text{Conc. in the volume taken for estimation X 16}}{\text{Wt: of the sample X \% DM X volume taken for estimation}}$$

3.4.4.2.8. Determination of Indole in shrimp (Cheuk and Finne, 1981)

About 35-40g of the muscle was homogenized with 80ml ice cold 6% TCA solution in a Laboratory mixer emulsifier (Euro Turrax T20b Ika Labortechnik) for 1 min. and 80ml ice cold petroleum was added and blended once more for 1 min. The homogenate was transferred to centrifuges tubes and centrifuged for 10 min. at 10,000 rpm in a refrigerated centrifuge (REMI cooling Centrifuge). Supernatant was filtered through Whattmann no.1 filter paper under slight suction and was transferred to a separatory funnel. After the

formation of two layers, the lower acid layer was transferred to a second separatory funnel and was re-extracted with 40ml light petroleum as described above. The procedure was repeated thrice and the light petroleum extracts were combined into one separatory funnel and indole was extracted with exactly 10ml freshly prepared Ehrlich's reagent by vigorous shaking for 1min. When layers were separated and cleared, the lower coloured layer was transferred to a cuvette and absorbance was read at 570 nm against a reagent blank solution. Concentrations of indole in the samples were determined from a standard curve.

3.4.4.2.8.1. Preparation of Ehrlich's reagent

To 9 g of paradimethylaminobenzldehyde (Sigma Chemicals Co., St. Louis, USA) 45 ml of concentrated hydrochloric acid was added in 250 ml volumetric flask and was then made up to volume with ethanol.

3.4.4.2.8.2. Preparation of Standard Curve

A stock solution of indole was prepared by accurately weighing 10mg indole (sigma chemicals Co., St.Louis, USA), and dissolving it in 100ml light petroleum. Then 0.1 to 0.5 ml stock indole solution was accurately pipetted to separatory funnels and 80 ml 6% TCA and 80 ml light petroleum were added. Indole was then extracted by the procedures described above and absorbance was read at 570 nm in a spectrophotometer. A standard curve was constructed as concentration (μg) versus absorbance.

3.4.4.2.9. Volatile compounds

3.4.4.2.9.1. Preparation of Trichloro Acetic Acid (TCA) Extract

About 10 g of accurately weighed sample was extracted with 10% trichloro acetic acid (TCA) by grinding in a mortar and pestle, the content was filtered quantitatively

through Whatman Filter paper No.1. Filter paper was thoroughly washed with TCA and filtrate was made up to 100 ml. The TCA extract was used to measure Trimethyl amine and Total Volatile base nitrogen of fish.

3.4.4.2.9.2. Total Volatile Base Nitrogen (TVB-N) (Conway, 1950)

Conway unit were cleaned in chromic acid, soaked in water, washed and dried. Cover plates were coated on underside with wax grease. The units were kept ready before preparing the extract.

One ml of the supernatant was taken from the TCA extract prepared and was put in the outer chamber of Conway micro diffusion unit, spreading it around the chamber as much as possible. One ml of standard acid is taken in the central chamber and one ml saturated potassium carbonate solution in the outer chamber. Cover plate was put on ensuring that no leak occurs. Solutions in the outer chamber were gently swirled with great care to mix them. Unit was left overnight. Acid in the central chamber was titrated against 0.01N sodium hydroxide using 2 drops of Tashiro's indicator. A reagent blank was also titrated by taking standard acid at central compartment and 10% TCA in the outer chamber. Total volatile base nitrogen (TVB-N) was calculated and expressed as mg N/100 g.

3.4.4.2.9.3. Tri-methylamine nitrogen (TMA-N)(Conway 1950)

1ml of standard 0.01N sulfuric acid was taken in the inner chamber of the diffusion unit. To the outer chamber 1ml of TCA extract and 1ml of neutralized formaldehyde and 1ml of saturated potassium carbonate were added. The unit was then sealed, gently swirled and kept overnight undisturbed. The amount of non-reacted acid in the inner chamber was determined by titration against standard 0.01N sodium hydroxide using Tashiro's indicator.

Blank was simultaneously carried out with 1ml of 10% TCA solution. TMAN was calculated as mg N/100 g of the muscle.

3.4.4.2.10. Determination of Thiobarbutyric acid (TBA) value (Tarladgis et al., 1960)

10 g of fish meat was mixed with 100 ml 0.2 N HCI and homogenised to make slurry. Slurry was poured to a round bottom flask and connected to the TBA distillation apparatus. Distillation was done until 50 ml of the distillate was collected within 10 minutes. 5 ml of distillate was taken in a test tube, 5 ml TBA reagent was added and heated for 35 mins. A blank was also done with distilled water. Colour developed was measured in a spectrophotometer at 538 nm and TBA value was determined and expressed as mg malonaldehyde/kg of fish sample.

3.4.4.3. Microbiological Analysis

3.4.4.3.1. Total plate count (Hitching et al., 1995)

10 g of the sample was weighed aseptically into a sterile sample dish and transferred into a sterile polythene pouch and soaked in 90 ml normal saline for 15 minutes, after which it was blended in a Stomacher blender(Stomacher 400 Circulator) for 60 seconds at normal speed. Using a sterile pipette, 1 ml of the supernatant was aseptically transferred into a 9 ml saline tube and mixed well using Vortex mixer. Similarly further dilutions were prepared for the inoculation. 1 ml each of the appropriate dilutions was pipetted to appropriately marked sterile petridishes taken in duplicates for each dilution. About 15-18 ml of molten plate count agar medium cooled to 45 °C, was poured to each plate, mixed well with the inoculam and allowed to set for 30 minutes. The plates were incubated at 37 °C for 48 hours in an inverted position. After the incubation period, the

individual bacterial colonies were counted. The average counts of the triplicates were taken and TPC/g of the sample was calculated.

3.4.4.3.2. Commercial sterility (IS: 2168-1971)

About eight cans were selected at random from each batch processed to different F_0 values. Four cans from each batch were incubated at 55 °C for 4 days and another four were incubated at 37 °C for 14 days. The incubated cans were opened under aseptic conditions and the samples were transferred to sterile thioglycollate broth tubes. Then a layer of sterile liquid paraffin was applied in each tube so as to create anaerobic condition. The tubes were then incubated at 37 °C for 48 hrs and observed for any development of turbidity, which indicates survival of microorganisms. Tubes not showing any turbidity were incubated for further 48 hrs at 37 °C to ascertain the sterility.

3.4.4.4. Sensory evaluation

Sensory characteristics of the squid masala and shrimp curry processed to different F_0 values amd mackerel procesed in brine at different retort temperatures were evaluated by a panel of 10 trained judges on a 10-point scale (IS 6273 (II) 1971; Vijayan 1984).The characteristics covered under the taste panel were color, flavor, texture and overall acceptability. Attributes studied under texture were chewiness, succulence, toughness and fibrosity. The overall impression of the product on the assessor was scored in overall acceptability. Samples were served to the panelists after warming in a microwave oven for 3 min on a coded dish. The panelists were asked to assign a score of 1–10 as prescribed by Vijayan (1984). A sensory score of 4.0 was taken as the margin of acceptance. The sensory score card used in the study is given in Annexure-1.

3.4.5. Statistical analysis

Experiment results are expressed in mean±standard deviation. Multiple comparisons of the significant analysis of variance were performed by Duncan's multiple comparison test.AP < 0.05 was considered statistically significant. All data were analyzed with the aid of statistical package program SPSS 10.0 for Windows (SPSS, Inc., Chicago, IL) (SPSS 2000).

4. RESULTS AND DISCUSSION

4.1. STUDY ON THE SUITABILITY OF INDIGENOUS POLYMER COATED TIN FREE STEEL CANS FOR THERMAL PROCESSING AND STORAGE OF FISH PRODUCTS.

Any container that is used for thermal processing should satisfy certain quality criteria that make it suitable for the purpose it is intended for. Some of the characteristics of an ideal container as prescribed by Balachandran (2003) are capability to form hermetic seal, sufficient strength and rigidity to withstand the severe conditions of high temperature while being thermally processed, impervious to air, moisture, dust and microbes once it is sealed, should not impart any toxicity to the contents, should be inexpensive to discard after use and should have a pleasing and sanitary appearance. The indigenous polymer coated tin free steel cans were subjected to the analysis of various quality parameters adopting standard methods.

4.1.1. Physical properties of tin free steel cans

4.1.1.1. Water holding capacity

The 307x 109 cans have a water capacity of 180 ml. Determination of water holding capacity is important from commercial point of view in case of products packed in oil and brine medium. IS standards suggests that the drained weight of the product should not be less than 70 and 65 % of the water holding capacity in case of products like sardine in oil and mackerel in oil respectively (IS: 2421, 1963; IS:2420,1985). Thus the packer has to adjust the filling weight in such a way that the customer gets a drained weight of 65-70% of the water holding capacity.

4.1.1.2. Pressure holding capacity (Air pressure test)

The polymer coated tin free steel cans were found to withstand internal air pressure of 30 psi for about 15 seconds without undergoing any bulging or leakage through the double seam area. This is well above the standard which prescribes that the cans should withstand air pressure without any leakage through the double seam area and should not undergo any bulging at an internal pressure of 25 psi (IS 2471, 1963). The containers were checked for its capability to withstand internal air pressure by pumping air into the container which was immersed in water and holding for a fixed period of 15 seconds. The head space gases may heat faster than the product and exerts a pressure within the container as soon as the retort temperature exceeds that of head space thereby applying strain on the container wall and double seam area. As heating progresses, the entrapped gases are expanded out of the product cellular structure and joins the gases of the head space that are already expanded and acting on the container wall. When the product temperature exceeds 100 ^{0}C, the water inside the container turns steam again adding to the pressure on container wall and seal area. If the container wall is not of sufficient strength and rigidity, this can lead to bulging of the container and in extreme cases, the container burst. Any leakage on the double seam results in the uptake of water during the cooling process and loss of vacuum. The result of air pressure test indicates that the TFS cans have the sufficient strength and rigidity to resist the internal pressure developed during the thermal processing.

4.1.1.3. Vacuum

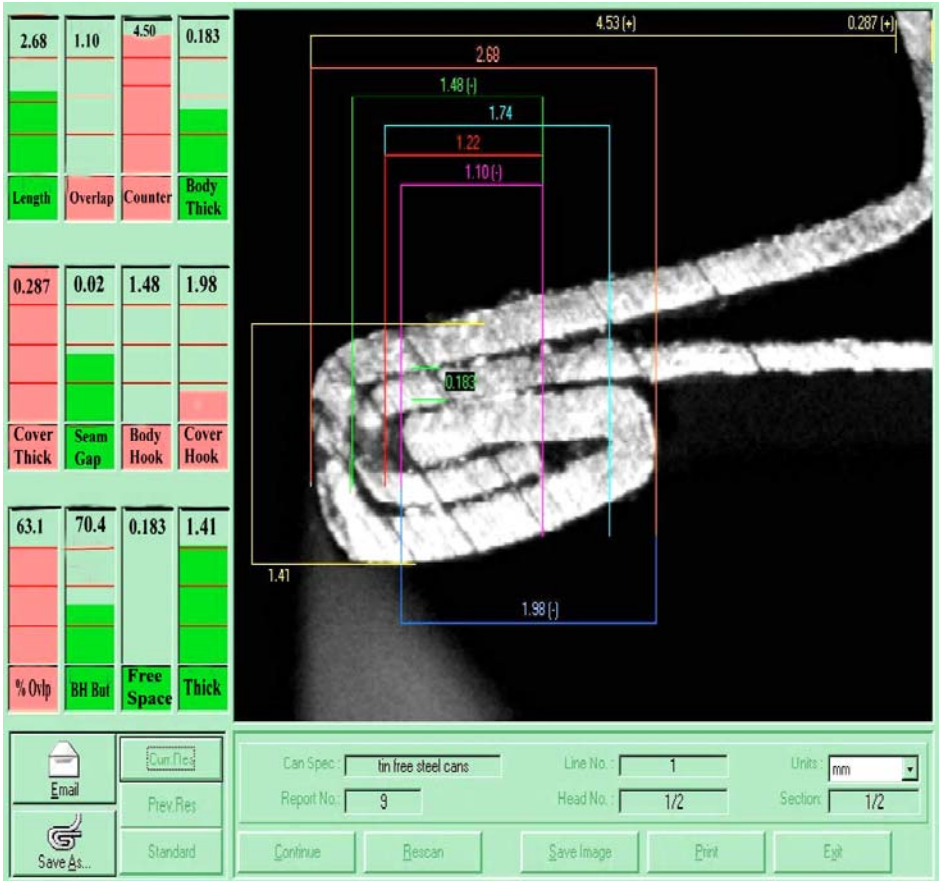
It is a term used in the canning industry to denote the difference between pressure inside and pressure outside the container (NCA, 1968). TFS cans were found to maintain

a vacuum of 100-120 mm Hg upon testing using vacuum gauge which indicates that the double seam is free from any leakage (IS 2420: 1985). Good vacuum is one of the important factors indicating the soundness of processed cans. Important factors contributing to loss of vacuum involve leakage through the faulty seam and perforations on the can body, gas formation due to microbial or chemical spoilage.

4.1.1.4. Cut out analysis

The results of the cut out analysis of polymer coated tin free steel cans are given in Table-3. The base plate thickness and end plate thickness of polymer coated tin free steel cans are 0.19mm (0.15 mm of base steel + 20 μ PET coating on either side) and 0.28 mm (including PET coating on either side), respectively. One of the important factors affecting the success of canning operation and the subsequent storage life of the thermally processed food is the integrity of the double seam. Polymer coated tin free steel cans had a % overlap of 63 %.This is higher than the ideal % overlap value of 45% suggested by Balachandran (1993). Hermetic seal formed in metallic cans performs several functions. It prevents recontamination of the canned products with microbes, leakage of liquid and vapors in and out of the can and maintains desired vacuum or pressure inside the can. Evolution of automatic/ semi automatic double seam analysers have made the analysis of double seam easier and more accurate which makes it a versatile instrument when it comes to online checking of cans in a commercial cannery. The results of cut out analysis was cross checked with the results of double seam analyzer SEAMetal 9000M. The double seam parameters of polymer coated TFS cans are given in Plate-6**.**

Plate-6. Double seam parameters of indigenous polymer coated tin free steel cans (Quality by Vision, Model *SEAMetal 9000M, Israel).*



4.1.1.5. Analysis of lacquer coating integrity using LCB detector

Testing for lacquer coating integrity of polymer coated TFS cans using LCB detector indicated that 97% of the tested cans had polymer coating free from any defects. Coating integrity is of significant importance as imperfection of the lacquer coating is one of the main problems associated with the rigid metallic containers like tin and aluminum cans. The product that is packed comes in direct contact with the metallic layer in areas of coating failure. On prolonged exposure, the metal gets dissolved by the food material and imparts metallic taste to the product in addition to the harmful health effects of ingesting the metallic contaminants along with the canned food.

4.1.1.6. Test for sulphide blackening

The indigenous polymer coated tin free steel cans did not develop any blackening in its interior when subjected to sulphide blackening test indicating that they are resistant to sulphide blackening. This is mainly due to the integrity of the polymer coating that prevents the iron sulphide formation due to the reaction between the product and the metal. Kontominas et al. (2006) reported that one of the important problems encountered in case of canned products is the development of black discoloration on the internal surface of can body and the product surface. They have attributed this to the formation of iron sulfide (FeS).

4.1.1.7. Delamination test for PET coating

Dealmination test using different solvents showed that the PET coating is resistant to delamination by solvents except chloroform and carbon tetra chloride. In case of panels immersed in chloroform, the PET coating peeled off completely from either

surfaces of the base plate after 12hrs whereas, in case of panels immersed in Carbon Tetrachloride, the PET coating did not show any peeling after 36 hrs of immersion but blisters appeared on the coating when put into boiling water. The peeled off PET layer was analyzed for its thickness using a digital micrometer. It was found that it has a uniform thickness of 20 μ. The cans are also provided with an external coating of PET that along with the underlying layer of chromium gives it a smooth, greyish and glistening appearance.

4.1.1.8. Suitability for thermal processing at higher temperature and pressure

Thermal processing of foods is done at higher temperature and pressure and thus one of the important requirements for an ideal container for thermal processing is its ability to withstand the conditions of high temperature and pressure. When processed under different temperatures of 115 ^{0}C (10 lbs), 121.1 ^{0}C (15 lbs), 126 ^{0}C (20 lbs) and 130 °C (25 lbs) and the cans were found to retain their original shape without undergoing any distortion. This shows that they are suitable for high temperature and pressure processing and do not require any overpressure during processing.

4.1.1.9. Test for food contact applications/ global migration test

The over all migration of components from the lacquer coating to the food material is one of the main issue regarding the packaged foods that has attracted the interest of global scientific and legislative communities in the recent years. It involves movement of substances from the packaging material to the food that is packed inside, mainly through the mechanism of diffusion. Thus the packaging that is intended to protect the contents represents the primary source of contamination (Lau and Wong,

2000). The values of water soluble, chloroform soluble and n-heptane soluble extractives of polymer coated TFS cans were 6.9, 0.64 and 25.0 mg/liter respectively. This is much below the maximum limit of 60 mg/ liter prescribed by FDA (2002).

These results of indicate that the indigenous polymer coated tin free steel cans are suitable for thermal processing and storage of fish and fish products.

Table-3. Cut out parameters of indigenous polymer coated TFS cans.

Sl. No:	Parameter	Result
1.	Body plate thickness	0.18 ± 0.001 mm
2.	Endplate thickness	0.28 ± 0.002 mm
3.	Seam length	2.68 ± 0.005 mm
4.	Seam thickness	1.41 ± 0.021 mm
5.	Body hook	1.48 ± 0.02 mm
6.	Cover hook	1.98 ± 0.035 mm

Salient features of indigenous polymer coated tin free steel cans

- Two piece can.
- Easy open end, which can be opened easily by pulling the tab that, is attached to the lid by a lid-rivet joint.
- Does no require any can openers.
- Triple fold technology that avoids any possible injury to fingers from the edges of the opened cans.
- The polymeric coating that is applied by the lamination process forms a continuous layer over the base metal.

- The polymer coated tin free steel cans are free of BPA and the related compounds.
- Smooth, greyish, glistening appearance provide by the PET coating along with the underlying layer of chromium.
- The bottom of the can is designed for better stackability so that it can be stacked vertically without risk of toppling on the shelf. This also helps to reduce the storage space requirement for the cans.
- Economically cheaper to other commercially available containers. The cost of the can is 4.5 INR as against 14 -15 INR for tin cans of the same capacity.

4.2. COMPARATIVE ANALYSIS OF VARIOUS COMMERCIALLY AVAILABLE CONTAINERS FOR THERMAL PROCESSING AND STORAGE OF FISH AND FISH PRODUCTS

One of the important factors affecting the success of a canning operation is an efficient container. The technological innovations occurred in the field of thermal processing over the years had its impact on the packaging materials also. As a result, various types of containers both rigid and flexible have evolved at various points of time. Of the various materials available for can making, tinplate is the most widely used one which accounts for about 80% of the total (Catala et al. 1998). But tin which is used to coat the steel base in case of tin cans is limited to certain geographical areas of the world which made tin containers expensive. This has resulted in search for alternative materials for tin cans all over the world (Leymarie, 1972). The important alternatives presently available for tin cans are aluminium and tin free steel cans. But a comparative study regarding these containers with respect to the container cost and suitability for the thermal processing and storage of fish products is still lacking. Commercially available rigid containers like tin, aluminium and TFS cans were analysed following standard methods for their suitability for thermal processing and storage of fish products.

4.2.1. Seam analysis

A double seam may be defined as that part of the can formed by joining the body and end components, the hooks of which interlock and form a strong mechanical structure (Balachandran, 1993). During double seaming, the can ends/ lids are attached to the can body using a double seaming machine. Maintenance of seam integrity is of prime importance in the success of canning and the subsequent storage life of canned product.

The minimum over lap prescribed for metallic cans is 45% (Balachandran, 1993). A faulty seam can make the entire canning operation unsuccessful. Percentage Overlap for tin, aluminium and TFS cans as determined following the manual method was 63, 59 and 62 respectively (Table-4). Thus all the three types of cans tested were found to have good seam integrity. The results of double seam parameters as recorded by the automatic double seam analyzer are given in Plate-7.

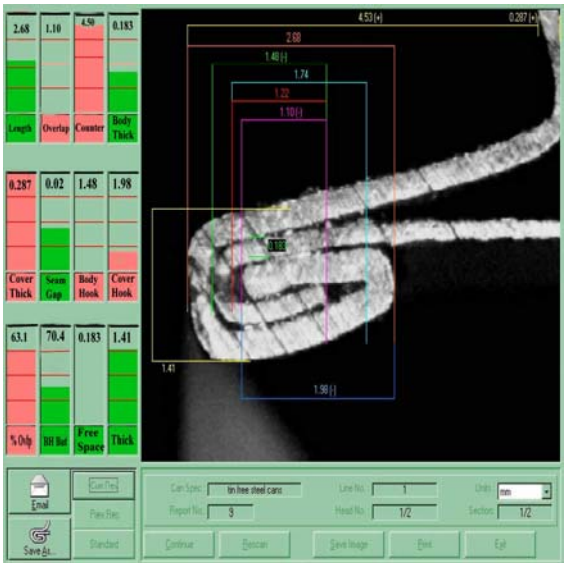
4.2.2. Pressure holding capacity (Air pressure test)

Tin, TFS and aluminium containers were checked for their capability to withstand internal air pressure by pumping air into the container which was immersed in water and holding for a fixed period of 15 seconds. Both tin and TFS cans were found to withstand an internal air pressure up to 30 psi without showing any bulging for the prescribed period of 15 seconds while the aluminium cans bulged at 27 psi (Table-4). According to the prescribed standards, the cans should withstand air pressure without any leakage through the double seam area and undergoing any bulging at an internal pressure of 25 psi (IS 2471, 1963)

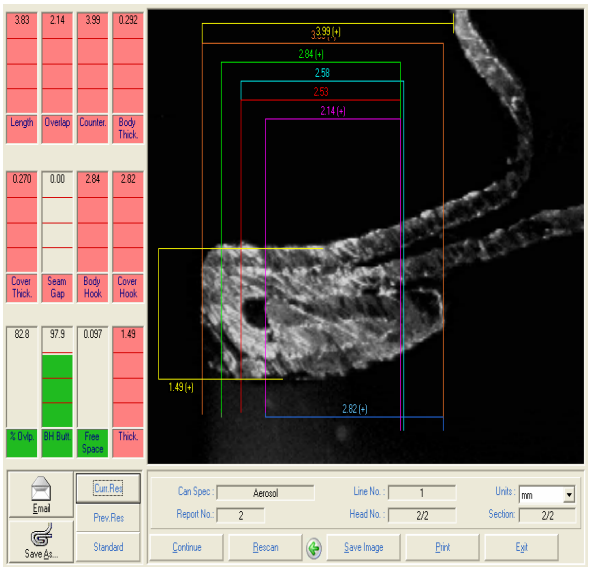
4.2.3. Vacuum

IS standards suggests that vacuum inside processed food cans should not be less than 100 mm Hg (IS 2420, 1985). All the three types of cans were found to maintain vacuum of 100-120 mm Hg (Table-4). Usually loss of vacuum results from leakage through the faulty seam and perforations on the can body, gas formation due to microbial or chemical spoilage.

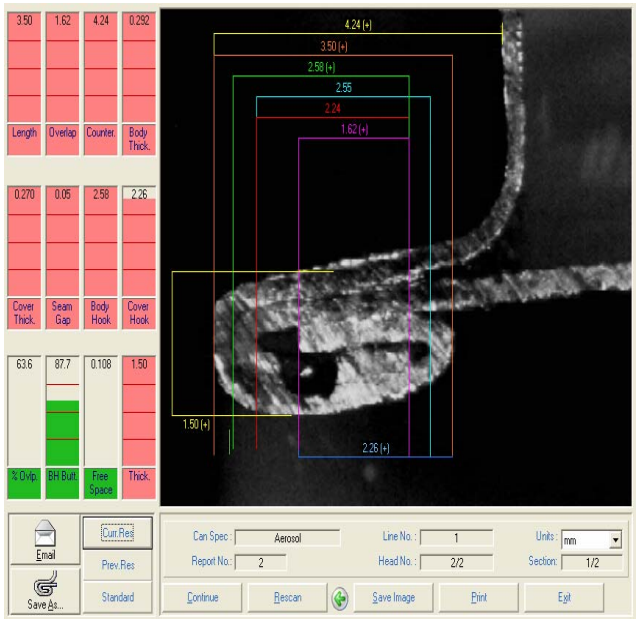
Plate-7. Double seam parameters of TFS, Aluminium and Tin cans



Double seam parameters of TFS Cans



Double seam parameters of aluminum cans



Double seam parameters of tin cans

4.2.4. Analysis of lacquer coating integrity using LCB detector

Metallic cans are protected from the action of the food material that is packed inside by the application of certain protective coatings that prevents the metal from coming in direct contact with the food. But if the coating is non uniform or if there are areas of discontinuity in the coating, then the metal will be exposed to the food leading to the problems like discoloration of the food material, dissolution of metal in food leading to metallic taste and health impacts. The cans were tested for the integrity of coating using LCB detector and results are given in (Table-4). Upon testing using the LCB detector, 85 % of the tin and 77 % of aluminium cans failed the test, indicating the poor coating integrity of these cans. In some cases, the imperfections on the coating were even visible to naked eye in the form of scratches. On the contrary, about 97 % of the TFS cans tested were found to pass the LCB test indicating the perfection of the polymer coating. Thus it can be seen that the success rate with the TFS cans is 6.5 and 4 times higher than tin and aluminium cans. If cans with poor lacquer coating are selected for thermal processing and storage of fish products, the food material will be exposed to the metal leading to discoloration of the product and can surface, generation of metallic taste in the product and the more serious health related issues arising for the ingestion of metal contaminated food. In humans, acute effects resulting from tin consumption of tin contaminated foods and drinks results in gastrointestinal symptoms including abdominal distention and pain, vomiting, diarrhoea and head ache (Anon, 2005). Berthlof et al. (1988); Storey and Masters (1995) reported a possible correlation between high aluminum content in the human tissues and appearance of certain neurodegenerative disorders like Alzheimer disease and other Encephalopathies and Osteomalacia.

Table-4.Physical properties of Tin, Aluminium and TFS cans

	Parameter	Results		
		Tin cans	**Aluminum cans**	**TFS cans**
1.	% overlap	63 ±0.72	59 ±0.54	62 ±0.38
2.	Pressure holding capacity	Withstand up to 30 psi	Bulged at 27 psi	Withstand up to 30 psi
3.	Vacuum (mm Hg)	102 ±0.54	105 ±0.26	110 ±0.18
4.	Lacquer coating perfection (%)	15 ±1.5	23 ±2.0	97 ±1.0
5.	Test for food contact applications a)Water soluble extractives (ppm)	16.4 ±0.46	12.2 ±0.32	6.9 ±0.18
	b)Chloroform soluble extractives (ppm)	0.80 ±0.03	0.72 ±0.01	0.64 ±0.04
	c)n-Heptane soluble extractives (ppm)	48.2 ±1.02	34.5 ±0.88	25.6 ±0.92

4.2.5. Test for Food contact applications/ Global migration test

The global migration is the sum of all individual constituents of the food contact surface that migrate to food or food simulant. Global migration is normally measured as the difference of the packaging weight before and after the contact (N. de Kruijf et al. 1983). The analysis of overall migration values using different simulants immediately after the cans were processed at the prescribed temperature shows significant difference between the containers ($p<0.05$). The extractive value for tin, aluminium and TFS cans using distilled water as simulant was 16.4, 12.2 and 6.9 ppm, respectively whereas the chloroform soluble extractives for the same were 0.80, 0.72 and 0.64 ppm respectively.

The overall migration values of tin, aluminium and TFS cans using n-Heptane were 48.2, 34.5 and 25.6 ppm respectively. Although these values are well below the maximum permissible limit of 60 ppm fixed by FDA (2002), a quantity wise examination of the extractives released by the cans shows that tin cans released the largest quantity of migrants upon testing using simulants, followed by aluminium cans. Although regulatory bodies prescribe a maximum permissible limit for extractives, no references regarding the effect of storage on the levels of extractives are available.

4.2.6. Storage study in different containers

Mackerel in curry medium was processed in tin, aluminium and TFS cans and kept for storage at room temperature (28±2 ^{0}C) for a period of 18 months. These cans were checked once in two months for visual signs of external rusting and other parameters like internal appearance of can walls, adhesion of product to the can walls and internal rusting were checked after opening the cans. Samples of both gravy and fish meat were subjected to analysis of various metallic contaminants after microwave assisted pressurized acid mineralization.

4.2.6.1. External appearance of the can

One of the major draw back of metallic containers is the development of corrosion on its external surface that leads to bad appearance of the cans thereby affecting the marketability of the product. Processed cans were examined once in two months for any signs of external rusting for a period of 18 months. Tin cans started exhibiting signs of external rusting on the 6th month of storage especially at the double seam area and the side seam area and this became more prominent on the 10th month of storage study

(Plate-8). Chatterji (2000) reported that the extent of external rusting depends on the thickness of tin coating and the quality of lacquer film. Thus the rusting noted on the external surface of tin cans can be attributed to the improper tin and lacquer coating especially at the side seam area that permitted the direct contact between the metal steel and atmospheric oxygen. But polymer coated TFS cans was free from any external rusting even on the 18^{th} month of storage. This resistance against the rusting is provided by the polymer coating that is applied on the base metal either through film coating or through direct extrusion process in which a thin layer of PET is extruded onto the ECCS plate (Boelen et al. 2004) as a continuous layer as against the electrochemical tin deposition followed by application of lacquer paint in case of conventional tin cans. Mahadeviah (1984) reported that TFS has much better resistance to corrosion as compared to tin Plate. Aluminium cans although had a smooth external surface, lost its characteristic appearance on the latter stages of the storage. This can be attributed to the formation of aluminium oxide layer on the can surface. Aluminium when exposed to oxygen in the air, develops a dense oxide layer of approximately 0.005 μm thickness consisting mainly of amorphous Al_2O_3 and aluminium oxide hydrate (AlOOH) and some physically and chemically bound water, depending on the moisture content of the air. The oxide layer of aluminium is colourless, tough and non-flaking (Beliles, 1994), impervious and seals off oxygen, preventing further oxidation or chemical reaction, and adheres strongly to the metal underneath. It provides excellent protection to the base metal (Rajwanshi et al. 1997).

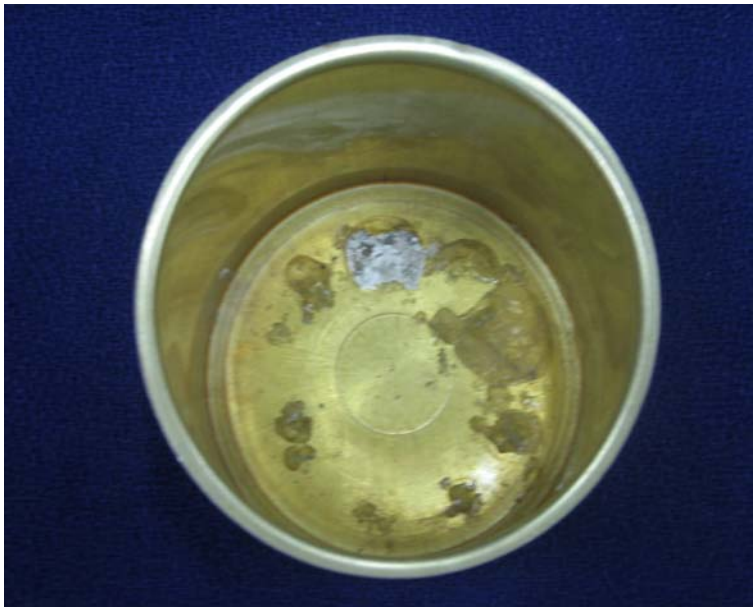
Plate-8. External corrosion on tin cans

4.2.6.2. Internal appearance of cans

Internal appearance of the processed cans is a function of the internal can coating. Many problems associated with the canned products like development of discolouraton, internal rusting, metallic flavour in product etc. arise from poor lacquering, mechanical damage to the lacquer layer during handling and transportation of the empty containers and during the double seaming operation (Bernardo et al. 2005). After opening, the cans were analyzed for appearance of the inner container wall after removing the product. In case of tin and aluminium cans, it was noticed that the fish pieces were attached to the can wall and exhibited poor content releasing property whereas the PET coated TFS cans were found to have excellent content release property. The content release property is correlated to the surface energy at the interface between the content and the can material. Content release property improves with the lowering of surface energy (NKK, 2002). Content release property is dependent on the level of stickiness between the content and film, and is mostly governed by the wettability of the film surface (surface energy). The surface energy can be divided into two components: dispersion part and polar Part. The latter is correlated to the effect of the PET film's surface energy on the stickiness. Focusing on the polar part of PET polymer, the film surface was depolarized. In PET coated plates, an excellent content release property is achieved by adding a minute amount of natural vegetable oil which helps in depolarizing the surface. This oil has the effect of activating the surface of the PET resin, thus affecting the polar part of the PET polymer on the film surface and lowering the surface energy (Jitsukawa and Yamashita, 2003). Another major problem with the tin cans was the development of blackening on the internal surface of the container in the form of black spots and marks.

Plate-9 a. Internal rusting of tin cans on storage

Plate-9 b. Lacquer failure in aluminium cans in the form of blisters and peel off



These marks appeared in the cans soon after the heat processing and in its extreme case, the products also took black discoloration on storage, as visible from the 6th month of storage. The reason for this is the formation of iron sulfide (FeS) and tin sulfide (SnS) respectively (Kontominas et al. 2006). PET coated TFS cans and aluminium cans on the other hand were free from any such discolouration. This may be due to the non availability of any iron and tin in case of aluminium cans and the perfection of the inner PET coating that prevents food-metal interaction in case of TFS cans. Examination of the interior surface of the Alumnium cans revealed appearance of blisters on the lacquer coating and lacquer peel off in some areas coating (Plate-9 b) which started appearing on the 7th month of storage.

4.2.6.3. Test for metallic contamination

Internal corrosion of food cans and the dissolution of metals in food have been attributed to limit the popularization of ready to eat foods in metallic containers (Vijayan and Balachandran, 1986). Tait (1989) reported that long term shelf life performance test have been used to evaluate packaging performance. This testing involves storing large number of cans for a period of about one year and periodically opening individual cans to check for visual signs of corrosion. The cans packed with mackerel curry were free of any visual signs of internal corrosion on the initial months of storage. On the 7th month of storage, tin cans started developing internal corrosion particularly at the areas near double seam and side seam and on the 10th month, the rusting became severe (Plate-8). This can again be attributed to the imperfections in the lacquer and underlying tin coating that facilitated the food material to react with the base metal. Similar incidence of internal rusting in fish curry cans on storage was reported by Vijayan and Balachandran (1986).

Aluminium and TFS cans were free from any visual signs of corrosion even at the end of 18 months of storage. Charbonneau (1997) reported on the different types of corrosions encountered in case of metallic containers. Corrosion, in addition to damaging the appearance of the product, affects the nutritional value and healthiness of the canned food.

Lacquer failure and the associated food metal interaction in addition to modify the appearance of the can interior and product, have the more serious effect of metallic contamination in the product and the associated health implications. Many workers have reported on the toxicological effects of metallic ingestion as a result of canned food consumption (Anon (2005); Berthlof et al. (1988); Storey and Masters (1995). Mackerel in curry packed in tin cans were analyzed for tin, lead and iron while those packed in TFS cans were analysed for chromium and iron whereas aluminium was the targeted compound in case of products packed in aluminium cans. The contents were analysed as gravy and fish muscle separately to find the level of contamination in them. The determination of all these metals were conducted in graphite furnace atomic absorption spectrometer after microwave assisted pressurized acid digestion of the sample. Colina and Romero (1992) reported that the transformation of solid sample to solutions is an important pretreatment step in order to avoid serious underestimation of analyte. Microwave assisted pressurized acid mineralization which is carried out in closed vessels with relief valves has the advantages like faster rate of mineralization, prevention of metal loss by volutilisation during digestion as in case of volatile analyte elements like lead and mercury (Tahan et al. 1995). The results of the periodic analysis for metallic contamination in canned foods packed in tin cans are shown in Figures.1-3.

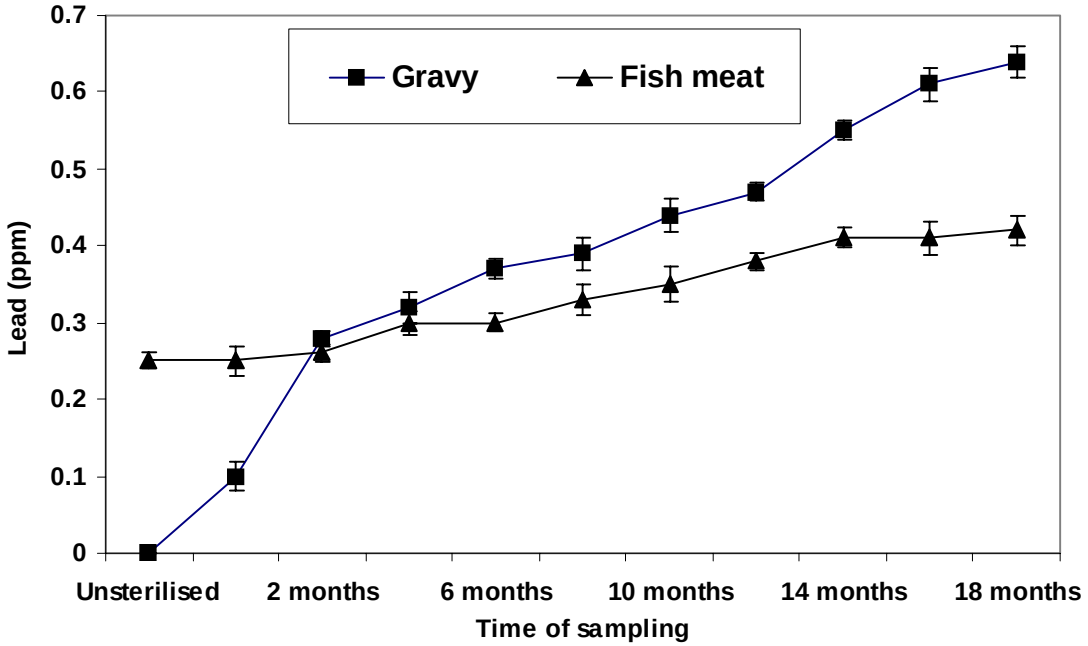


Fig-1.Change in the tin content of gravy and fish meat stored in tin cans

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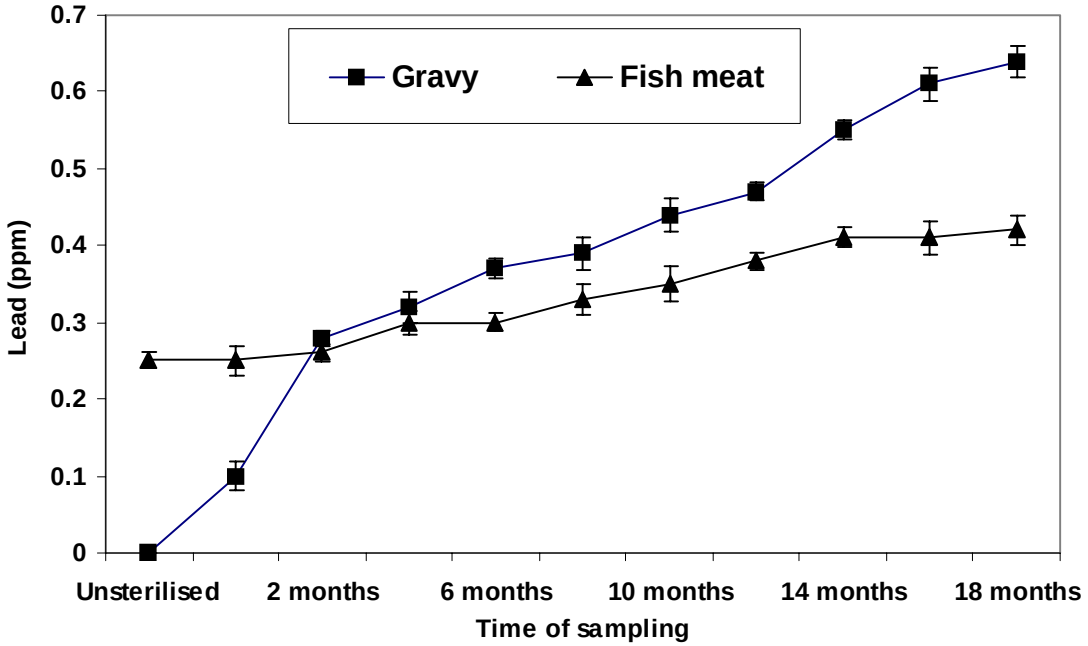

Fig-2.Change in the lead content of gravy and fish meat stored in tin cans

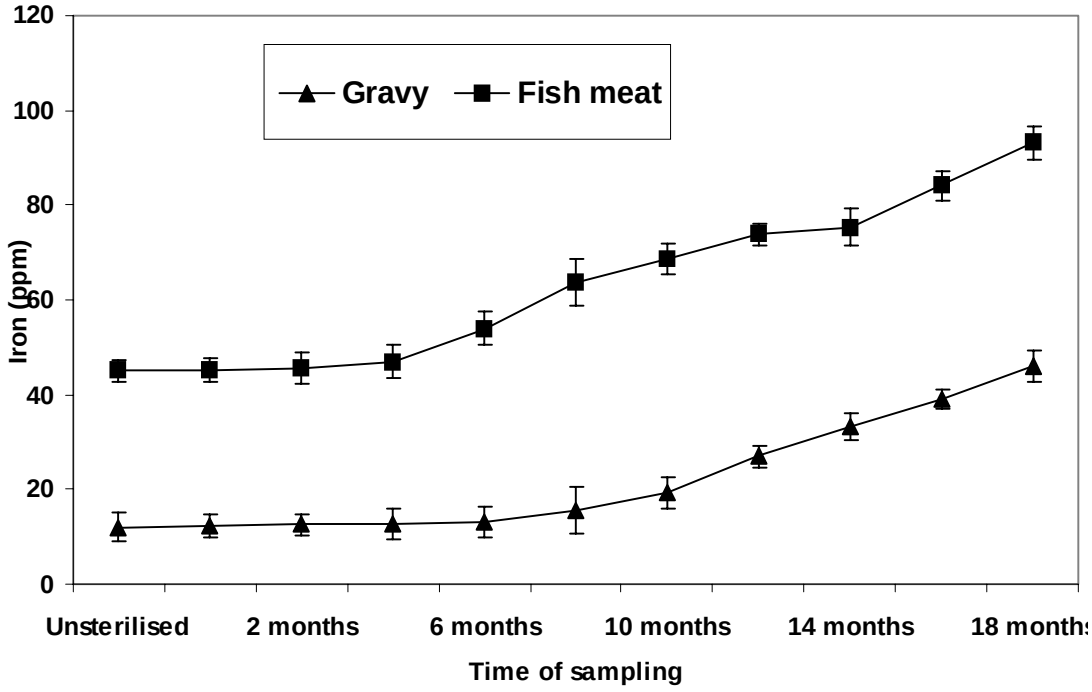

Fig-3.Change in the iron content of gravy and fish meat stored in tin cans

Tin content of the gravy and fish meat did not exhibit any significant difference prior to sterilization ($p>0.05$). While no lead could be found in pre sterilized gravy, the fish muscle had 0.25 ppm of lead prior to sterilisation. Many workers reported on the lead content of fish meat (Dugo et al. 2006; Ersoy et al. 2006). The iron content of gravy and fish prior to sterilisation were 12.12 and 45.10 ppm. The tin content of both sterilized gravy and fish meat although showed slight increase as compared to presterilised samples, did not vary significantly between each other. Lead which was not detected in case of unsterilised gravy increased to 0.10 ppm after heat processing while its content in fish meat did not show any significant change ($p>0.05$). As reported by Voegborlo et al. (1999) solder consisting of 98% lead and 2% tin and applied in the side seam of 3 piece tin cans can be considered as the source of contamination of food by lead during canning.

Lead from the solder is usually taken up by the food depending upon the amount of solder exposed and the acidity of the food. The iron content of heat processed gravy and fish meat did not show any significant change ($p>0.05$). Storage at room temperature resulted in significant increase in the tin content of both gravy and fish meat ($p<0.05$). On the 2nd month of storage, the tin content of gravy and fish meat were 22.4 and16.5 ppm respectively which on the 4th month, rose to 40.6 and 32.8 ppm respectively there by recording a doubling in its content in both gravy and fish meat. This agrees with the findings of Davies et al. (1980) and Rouseff and Ting (1980) that the accumulation of tin in canned products is affected by duration of storage. Cameron and Brittain (1971) reported that canned beans stored in tin cans accumulate 31 ppm of tin on the first week of storage. Thus the levels of tin accumulation in the present study is much lower than the findings of Cameron and Brittain (1971). The lead content on the 2nd month of storage, although recorded significant increase in gravy did not vary significantly in case of fish meat. The lead content of gravy and fish meat on the 4th month storage were 0.32 and 0.30 ppm respectively ($p<0.05$). Significant increase in the lead content of grape fruit juice was reported by Rouseff and Ting (1980) on the 4th month of storage. Iron contents of gravy and fish muscle on the 2nd month of storage were 12.61 and 45.54 ppm respectively which on the 4th month reached 12.74 and 46.95 ppm. Lall (1995) reported that the Fe content of processed fish and fishery products may be influenced by the widespread possibilities of contamination from ferrous metals during cooking and processing. Tin and lead content of gravy and fish meat on the 8th month of storage were 64.2 and 54.0 and 0.39 and 0.33 ppm respectively ($p<0.05$). The level of iron in gravy and fish meat on the same period was 15.62 and 63.82 ppm ($p<0.05$). This drastic

increase in the levels of these metallic contaminants is favored by the imperfections in the inner lacquer coating of the can that permits food metal interaction. Greger and Baer (1980) reported that the main factor that affects the amount of metallic contaminants accumulated in canned foods during storage is the extent to which the interior surface of the cans are coated with lacquer. After one year of storage, the tin and lead content of gravy and fish meat increased to 78.1 and 70.0 and 0.47 and 0.38 ppm respectively ($p<0.05$) while the contents of iron in gravy and fish meat were 26.92 and 75.92 ppm respectively. The tin, lead and iron contents of gravy and fish meat increased significantly on the subsequent storage months and reached 109.5 and 96.0, 0.64 and 0.42 and 45.94 and 93.09 ppm respectively at the end of 18 months of storage study. Greger and Baer (1981) reported significant increase in the tin and iron content of products stored in lacquer coated cans.

The periodic analysis of tin, lead and iron in the gravy and fish meat of canned mackerel stored in tin cans coated with lacquer indicates that the levels of these elements increases on storage. Tin contamination can be believed to have occurred through the imperfections on the lacquer coating while the source of lead is the solder of the side seam and the level of uptake of these elements is a factor of storage time, area of exposure and pH of the product (Ikem and Egibor, 2005). Ranken (1988) reported that in addition to the quantity of metals like tin, lead, iron added inadvertently during processing, internal rusting and etching of cans could be the possible source of these heavy metals in food. Iron although showed slight increase in the initial periods, increased significantly only after the 8^{th} month of storage. This can be attributed to the fact that during the initial months, the tin coating along with the lacquer provided little

chance for iron to interact with the food and with the dissolution of tin with time, more and more iron started leaching to the food as indicated by its increased levels in both gravy and fish meat towards the latter part of the storage. A high tin value suggests extent of corrosion of canned food container (Tarley et al., 2001). Mackerel curry in tin cans although underwent metallic pick up, the levels of contaminants in gravy and fish meat were lower than the permitted levels of 250 and 2.0 ppm for tin and lead respectively (Oduoza, 1992) .

The results of the analysis of aluminium in the gravy and fish muscle of product packed in aluminium cans and chromium and iron in products packed in polymer coated TFS cans and subjected to storage at room temperature for a period of 18 months is given in Figures.4-6. The aluminium content of pre sterilised gravy and fish muscle were 0.05 and 0.15 ppm respectively. Gravy was prepared in aluminium free vessels and this is evident from the low aluminium contents in gravy prior to packing in cans. The aluminium content of gravy and fish meat increased with sterilization with gravy having more aluminium levels than fish meat. This can be attributed to the leaching of aluminium from the can walls through the discontinuities of the lacquer layer into the gravy during the heat processing. The aluminium content of retorted gravy and fish muscle were 0.20 and 0.23 ppm respectively. A quantitative estimation of the aluminium levels in the retorted gravy with that of the pre sterilised samples shows that the level of contamination in the sterilized gravy is four times that of un sterilised samples ($p<0.05$). This is in agreement with the reports of many workers on the increased aluminum levels in foods after cooking in aluminium vessels (Evenshtein, 1971; Liukkonen-Lilja and Piepponen, 1992).

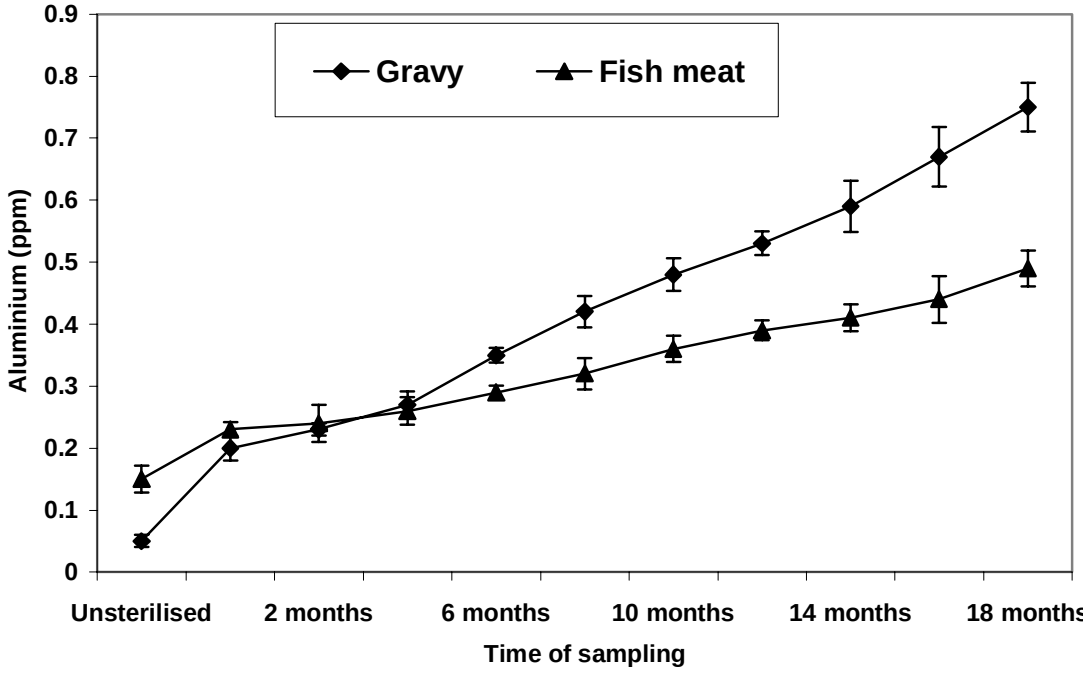

Fig-4.Change in the aluminium content of gravy and fish meat stored in aluminium cans

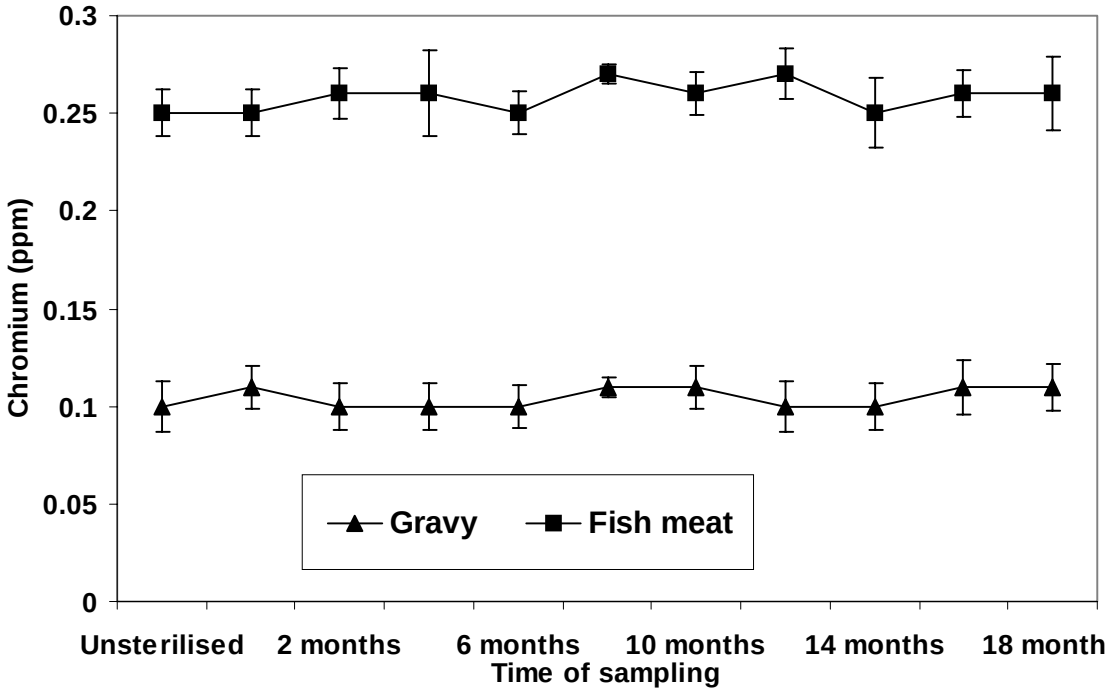

Fig-5.Change in the chromium content of gravy and fish meat stored in polymer coated TFS cans

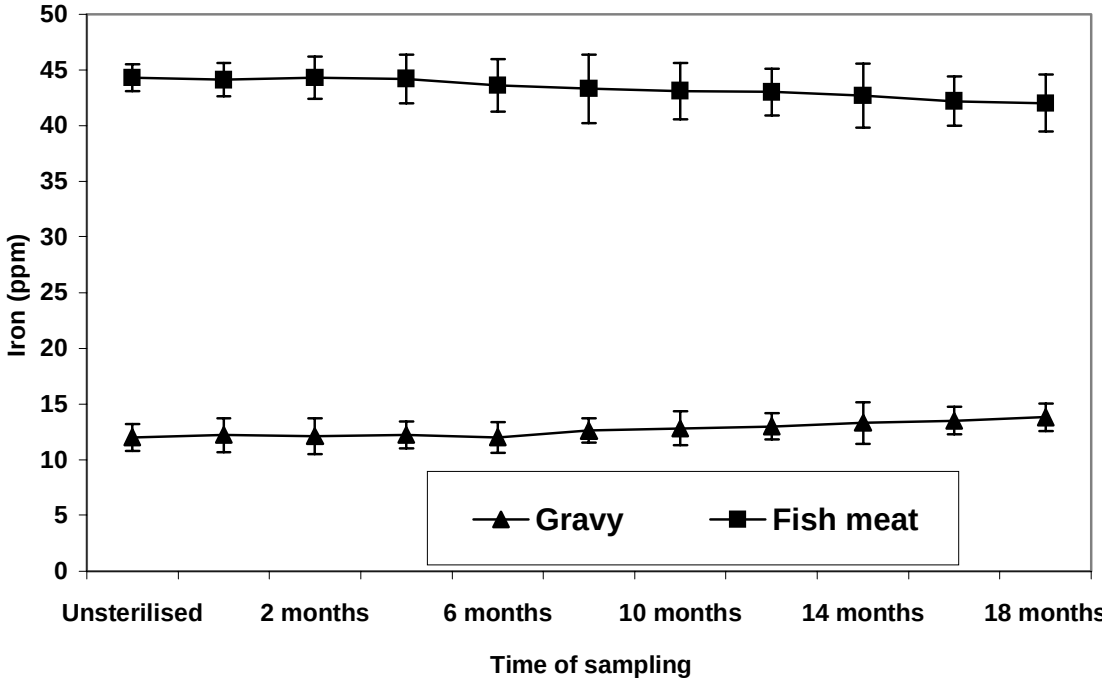

Fig-6.Change in the Iron content of gravy and fish meat stored in polymer coated TFS cans

Products packed in polymer coated TFS cans on the other hand, did not show any significant changes in the contents of the target elements i.e., iron and chromium in both gravy and fish meat after heat processing. The levels of chromium in gravy and fish meat before and after canning were 0.10 and 0.25 and 0.11 and 0.25 ppm respectively. Gravy and fish meat had iron content of 12.0 and 44.03 ppm prior to canning which on heat processing did not vary significantly ($p>0.05$). Fish along with vegetable oil and fruits are reported to contain smaller amounts of chromium (Codex, 1995). Most foodstuffs contain less than 0.1 mg chromium per kg (NCM, 1995). Reported values for chromium in raw fish flesh ranges form 0.11- 0.24 ppm (Topcuoglu et al., 2002; Ersoy et al., 2006). Nettleton (1985) reported that the levels of iron found in sea foods can range from 0.3-7.0 mg/100g. During storage, the products packed in aluminium cans showed significant increase in the aluminium contents. On the 2nd month of storage the contents of

aluminium in gravy increased to 0.23 ppm while that of fish meat remained more or less the same (0.24 ppm). Thus on the 2nd month of storage, the aluminium contents of both gravy and meat were same. Analysis of chromium and iron levels in products packed in polymer coated TFS cans did not indicate any significant changes in both gravy and fish muscle ($p>0.05$). The contents of aluminium in gravy and fish meat on the 6th month of storage was 0.35 and0.29 ppm respectively ($p<0.05$). No significant change in the contents of chromium and iron of both gravy and fish meat could be noted in polymer coated TFS cans between the 2nd and 6th months of storage. On the 8th month of storage, the iron content of gravy exhibited a significant increase as compared to the initial values and analysis of the fish meat revealed a decreasing trend in the iron content. This may be due to the diffusion of his element from the fish muscle to the packing medium. This trend in both gravy and fish muscle continued in the subsequent sampling months and on the 10th month, the levels of iron in gravy and fish meat were 12.8 and 43.1 ppm respectively ($p<0.05$). Analysis of the canned products in aluminium and polymer coated TFS cans on the 12th month of storage showed that the aluminium content of both gravy and fish meat significantly increased to 0.53 and 0.39 ppm respectively ($p<0.05$) while the chromium contents of both gravy and fish meat remained unchanged ($p>0.05$) and the iron contents continued to decrease in fish muscle with a subsequent rise in its level in gravy. The levels of aluminium in the gravy and fish meat at the end of 18 months storage were 0.75, 0.49 ppm respectively while the chromium remained more or less unchanged in both gravy and fish meat as compared to the previous months ($p>0.05$). Tuzen and Soylak (2007) reported aluminium contents in canned fish ranging from 0.45 ppm in canned tuna to 1.50 ppm in canned *Trachurus trachurus*. While gravy attained

iron content of 13.8 ppm, its level in the fish meat decreased to 42.0 ppm on the 18th month. The lowest and highest chromium levels of various canned fish products reported by Tuzen and Soylak (2007) ranges from 0.97 ppm to 1.70 ppm. Chromium contents in the literature have been reported in the range 0.0–0.30 ppm in canned fish samples (Ikem and Egiebor, 2005). The chromium levels of both gravy and fish muscle are much lower than these reported values. According to the Institute of Medicine (2002), the upper tolerable intake level for chromium for women and men aged 51– 70 years is 20 and 30 mg/ day respectively.

The leaching of aluminium from the can body to the food through the imperfections of the lacquer coating can be attributed as the main reason for the occurrence of this metal in both gravy and fish meat and the increase in its content with storage at room temperature. This fact is supported by results of the analysis of lacquer coating integrity of empty aluminium cans prior to filling and seaming using LCB detector in which 77% of the cans failed. With storage, the lacquer failure became even more pronounced and examination of opened cans showed presence of blisters and in extreme cases, areas where the can material completely exposed without any lacquer coating (Plate-9). Other factors that contributes to the leaching are the duration of storage and storage temperature, low pH of the food (Joshi et al., 2003), presence of salts like sodium chloride (Rajwanshi et al., 1997). The product was found to have pH of 5.5. Although aluminium levels increased with storage, its level is well below the provisional tolerable daily intake of 1.0 ppm per day recommended by WHO (Ranau and Oehlenschlaeger, 1997).

In case of TFS cans, the intact polymer coating prevented any possible interaction between the food and the can metal as evident from the unchanged levels of both chromium and iron even after 18 months of storage as compared to initial levels. This again supports the high success rate of 97% for coating integrity obtained with polymer coated TFS cans.

Canned foods are normally stored for 12-18 months prior to consumption. Unlike conventional canned products packed in media like brine and oil where the media is normally decanted prior to consumption, ready to eat fish products are consumed along with gravy. At all stages of storage; the levels of various metallic contaminants except iron in tin and aluminium cans are higher in gravy than fish meat. This can be attributed to the fact that gravy being in close contact with the container walls attains more metallic pick up than fish meat. This makes the situation even more alarming in that a consumer taking a ready to eat product packed in gravy in metallic can happens to ingest higher levels of heavy metals like tin, lead, aluminum etc along with the product. Products packed in polymer coated TFS cans on the other hand had chromium levels stable at 0.10- 0.11 ppm for gravy and 0.25 – 0.26 ppm for fish meat. The iron content on the other hand showed significant increase in gravy and decrease in fish meat with storage. This is due to the diffusion of this element from the fish meat to gravy. Results of this experiment clearly indicates the effectiveness of polymer coating which is applied as a continuous layer and substitutes the conventional lacquer of tin and aluminium in preventing the corrosion and the metallic contamination in product. Although the levels of tin, lead and aluminium of fish curry stored in tin and aluminium cans increased with

storage, their levels were lower than the maximum permissible level prescribed by various food and standards committee.

4.2.7. Health significance of tin, lead, iron, aluminium and chromium

Tin-Many workers have reported depressed hematocrits, hemoglobin levels and serum iron levels among rats fed with higher levels of tin (de Groot, 1973 and de Groot et al. 1973). Yamaguchi et al. (1980) noted that rats given oral doses of tin retained less calcium in bones. In humans, acute effects resulting from consumption of tin contaminated foods and drinks results in gastrointestinal symptoms including nausea (97%), abdominal cramps (87%), vomiting (70%), headache (57%), diarrhea (33%) and fever (13%). (Piscator, 1979; Schafer and Femfert, 1984; Dewitte et al. 2001). Baker and Runete (1972) reported that the incubation period averages 15-30 min and the symptoms can last from half an hour to 3 weeks of consumption. Other important harmful effects associated with tin ingestion involve abdominal distention and pain vomiting, diarrhoea and head ache (Anon 2005).

Lead- It is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities,2001).The most common form of acute lead poisoning is gastrointestinal colic (Beliles, 1994).

Iron- though iron is an essential nutritive element deficiency of which can lead to anemia, excess concentration in food can be detected by taste (Oduoza,1992). Vijayan and Balachandran (1986) reported development of internal corrosion and metallic taste in canned sardine curry stored in tin cans.

Chromium- Chromium (III) is an essential nutrient that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. However, Cr(VI) is carcinogenic (Ikem and Egiebor, 2005;Tuzen and Soylak, 2006).

Aluminium- Berthlof *et al*. (1988); Storey and Masters (1995) reported a possible correlation between high aluminum content in the human tissues and appearance of certain neurodegenerative disorders like Alzheimer disease and other Encephalopathies and Osteomalacia. Romero (1991) reported on the aluminium induce pathological dysfunction in hemodyalised individuals.

4.3. RAW MATERIAL CHARACTERISTICS

The raw materials used for the study were Indian Mackerel (*Rastrelliger kanagurta*), Indian white shrimp (*Fenneropenaeus indicus*) and squid (*Loligo dauvaceli*). The average body length and weight of raw materials (whole) is given in Table-5.

Table-5. Physical characteristics of the raw materials

	Average total length (mm)	Average body weight (g)
Mackerel	181.0±5.0	110.0±3.0
Shrimp	125.0 ±2.5	22.0±2.0
Squid	155.0±4.5	98.0±1.5

4.3.1. Proximate Composition

The proximate composition of the raw materials is given in Table. 6. Moisture is the principal component of fin fish and shellfish muscles. Stansby (1962) reported that the moisture content of shell fish and fin fish muscles ranges from 28 to 90% by weight. The moisture content of Indian mackerel, shrimp and squid were 72.30, 80.65and 81.5% respectively. These values agree with the reported values (Venketaraman and Chari, 1951; Mohan, 2004, Gopakumar et al, 1993). Fish muscle is a good source of protein. Most finfish muscle tissue contains about 18-22% protein (Sidwell, 1981). Mackerel meat had a crude protein content of 22%. The protein content in crustaceans ranges from 17-22% (Borgstrom, 1962). The crude protein contents of Shrimp and squid muscle were 17.5 and 15.0%. Gopakumar et al. (1993) reported crude protein content of 20.90 and 14.5 % for Indian white shrimp and squid obtained from west coast of India. Lipids forms one of the main constituents of fish muscle. It may either occur as triacyl glycerols, the

main form in which energy resources are stored or as mostly phospholipids and cholesterol that form the essential component of cellular and sub cellular structures (Love, 1997). The crude fat content of mackerel was 1.50 % whereas it was 1.55 and 1.12% for shrimp and squid. Many workers have reported on the lipid content of many species of Indian fish and shell fish (Gopakumar et al. 1993; Gopakumar and Nair, 1971, 1972 and 1975; Reena et al. 1996 and1999). The ash content of fish muscle is constituted by the minerals. Aquatic organisms absorb minerals from their diet and surrounding water and deposit them in skeletal tissue, muscle and different organs (Lall, 1989). The ash content of mackerel, shrimp and squid were 1.50, 0.90 and 0.75% respectively. Fin fishes usually have higher ash content than shell fish due to the presence of skeletal issues.

Table- 6. Proximate composition of raw materials

	Mackerel	**Shrimp**	**Squid**
Moisture	72.30±0.08	80.98±0.17	81.5±0.23
Crude protein	22.30±0.12	16.60±0.31	15.0±0.24
Crude fat	4.20±0.36	1.57±0.25	1.12±0.04
Ash	1.50±0.06	0.83±0.02	0.75±0.01

4.3.2. Quality Parameters

Fish is a highly perishable food item. Many of the problems concerning the canned fish quality can be related to the quality of the raw material. Taguchi (1980) reported that the quality of the canned fish product becomes poor as the freshness of the raw material is lowered. Thus, analyzing the quality of the raw material is of significant

importance in order to get an acceptable final product as the quality of an already spoiled cannot be enhanced by adopting any of the known methods of food processing. Although organoleptic analysis is the most common and fastest method to detect the freshness, issues like the subjective nature of this method and the need to obtain and train people who are able to carry out it with higher degree of accuracy indicates the need for chemical methods of analyzing freshness. Many attempts have been done world wide to establish a chemical index for decomposition or freshness. All these attempts centered on the detection of various compounds whose levels increase with decomposition or loss of freshness. The important parameters which were analysed to determine the freshness of the mackerel, shrimp and squid were K-value, volatile nitrogen compounds and lipid decomposition products, while biogenic amines and indole were determined exclusively in mackerel and shrimp respectively.

4.3.2.1. ATP- Break down products

ATP of fish muscle breaks down, either during the death struggle or subsequently. Various measurements of adenine nucleotides and their degradation products in fresh fish are used as chemical indices of freshness because the rates of change of these compounds in many species parallel rates of quality deterioration under usual handling (Jones et al., 1964; Dyer et al., 1966). Saito et al. (1959) were the first to estimate the freshness of muscles from the ratios of the sum of the inosine and Hx to the sum of all other ATP breakdown products. The K-value of mackerel, shrimp and squid are presented in Table-7. K-value of all the raw materials analysed were below 20%, indicating their freshness condition. Ehira (1976) reported K-value as one of the most important indicators of

freshness in fishes. Many authors have reported on the increase of K-value with storage of fishes in ice (Ochlencshlager, 1992; Mathew et al.1999).

4.3.2.2. Trimethyl Amine Nitrogen (TMA-N) and Total Volatile Base Nitrogen (TVB-N)

TMA and TVB-N are reported to be good indicators of freshness in case of fishes (Keay and Hardy, 1972; Gruger, 1972). These two parameters are reported to get increased with thermal treatment of fish muscle (Gallardo et al. 1990). Hence if the levels of TVB-N and TMA-N are high in the raw material, then the subsequent heat treatment can result in its levels much above the limits fixed. TVB-N and TMA-N contents of fresh mackerel, shrimp and squid are given in Table-7. The TVB-N and TMA-N contents of raw mackerel were 7.2 and 2.48 mg N/100 g respectively. This is in well agreement with the values reported for fresh mackerel by Surendran (1985) and Chand et al (2001). The TVB-N and TMA-N contents of Shrimp and squid were 9.98 and 2.12 mg N/100 g and 8.64 and 1.92 mg N/100 g respectively. Thus it can be seen that the levels of both these parameters in the raw materials fall well below the acceptability limit of 35-40 and 10-15 mg N/100 g for TVB-N and TMA-N respectively (Conell, 1995).

4.3.2.3. Thio Barbituric Acid (TBA) value

Fish fat is highly unsaturated and is easily oxidized, resulting in alteration in smell, taste, texture, colour and nutritional value. Oxidation starts immediately after the capture (Harris and Tall, 1989). The estimation of TBA value as a measure of the oxidative change remains the most widespread procedure for meat and meat products (Shahidi, 1994). The TBA values for raw mackerel, shrimp and squid were 0.68, 0.42 and

0.38 mg malonoldehyde/kg which is very well below the maximum limit of 2.0 mg malonoldehyde/kg, indicating their freshness (Table-7). TBA method actually measures the secondary oxidation products like aldehydes. Sinnhuber et al. (1958) and Tarladgis et al. (1960) reported the malonaldehyde as the likely compound in fats which condensed with 2-TBA to form the red chromogen, which can be determined spectrophotometrically.

4.3.2.4. Indole

Indole is a metabolite released from degradation of the amino acid Tryptophan by the bacterial enzyme tryptophanase. It has been suggested as a satisfactory chemical index of freshness of raw shrimp (Duggan and Strasburger, 1946). The raw shrimp used for the preparation of shrimp curry had an indole content of 0.88µg/100 g (Table-7). Since the presence of indole is closely associated with poor sensory quality and its amount is an index of the extent of putrefaction that has taken place, the lower level of indole content in the raw material used in the present study indicates its freshness. Moreover, the level of indole is much lower than the maximum limit of 25µg/100g fixed for class 1 shrimp by Chang et al. (1983); Finne (1992). The detection of indole is significant when sensory assessment is difficult and individual shrimp are very small (Ponder, 1978).

4.3.2.5. Biogenic amines

Biogenic amines formed by the bacterial decarboxylaton of amino acids due to their psychoactive or vasoactive nature are capable of causing problems in some individuals. Due to its heat resistant nature, biogenic amines can be present in sterilized

cans causing serious health problems to the consumers (Lopez–Sabater et al.1994) and hence its detection in raw materials used for canning is one of the necessary quality checks. Shalaby (1997) reported that the consumption of food containing biogenic amines is responsible for many pharmacological effects which lead to several types of food borne disease, including histamine poisoning (scomberoid poisoning) and tyramine toxicity (cheese reaction). Biogenic amines were determined only in case of raw mackerel as various reports have suggested its significance in case of scomberoid fishes (Taylor, 1986). The biogenic amine content of raw mackerel is given in Table-7. Six biogenic amines viz., putrescine, cadaverine, tryptamine, spermidine, spermine and histamine were detected in the raw mackerel meat. Among these six detected amines, histamine was present in the highest quantity (0.58 mg/100g) followed by cadaverine (0.54 mg/100g) and putersciene (0.48 mg/100g) respectively while spermine was the amine that was detected in the lowest quantity (0.08 mg/100g). The concentration of other amines was 0.16 and 0.20 mg/100g for spermidine and tryptamine respectively. Histamine formed from the de carboxylation of histidine, is the most potentially hazardous among all the biogenic amines and is the causative agent of scomberoid fish poisoning (Arnold and Brown, 1978). The level of histamine in the raw mackerel sample (0.58 mg/100g) agrees with the reports of many workers who measured histamine concentration of less than 1.0 ppm in many varieties of freshly caught scomberoid species (Frank et al, 1981; Thadhani et al, 2002). Moreover this value is very well below its toxicological level of >50 mg/100 g, capable of causing a health hazard (USFDA, 2001). The determination of other biogenic amines like cadaverine, purtescine, tyramine etc. is also equally important as they have been reported to potentiate the toxicity of histamine (Chu and Bjeldanes, 1981;

Taylor and Summer, 1986). The pharmacological effects of various biogenic amines are listed in detail by Shalaby (1997).

Since biogenic amines are found in very low amounts in fresh fish and their presence is related to bacterial spoilage, it can be used to estimate the freshness or degree of spoilage of fish (Fernandez –Salguero and Mackie, 1987) and many workers have reported it as a useful index of decomposition of fish (Meitz and Karmas, 1978; Yamanaka et al. 1989). Many quality related indices based on the levels of biogenic amines have been reported. Yamanaka et al.(1989) proposed the use of cadaverine. Meitz and Karmas (1977) proposed an index based on histamine, putresceine, cadaverine, spermine and spermidine contents while Veciana-Nogues et al.(1997) suggested the content of histamine, tyramine, cadaverine and putresceine.

4.3.2.6. Microbiological analysis

Landed fish harbors on its body large number of microorganisms. The most commonly used method for testing the raw material bacterial quality is the total viable count. Total aerobic bacterial counts had been used by many investigators to follow the deterioration of fish flesh and shellfish flesh (Griffiths and Stansby, 1934; Fitzgerald and Conway, 1937; Novak et al., 1956). The microbiological quality as indicated by the total plate count of the raw materials was within the range of 10^3 - 10^5 g^{-1} (Table-7.). Similar results for various species of landed fish and prawn were reported by many workers (Laxmanan et al. 1984; Karunasagar et al.1992; Surendran et al. 1985).

Table-7. Quality parameters of raw material

	Parameter	Mackerel	Shrimp	Squid
1.	K-value (%)	16	18	19
2.	TVB-N (mg N/100 g)	7.20±0.25	9.98±0.68	8.64±0.82
3.	TMA-N (mg N/100 g)	2.48±0.05	2.12±0.02	1.92±0.04
4.	TBA(mg malonoldehyde/kg)	0.68±0.02	0.42±0.02	0.38±0.01
5.	TPC (cfu/g)	3.84×10^4	3.42×10^4	3.36×10^4
6.	Indole (µg/100 g)	NA	0.88±0.01	NA
7.	Biogenic amines (mg/100g)		NA	NA
	a) Putrescine	0.48±0.04	„	„
	b) Cadaverine	0.54±0.02	„	„
	c) Tryptamine	0.20±0.01	„	„
	d) Spermidine	0.16±0.01	„	„
	e) Spermine	0.08±0.01	„	„
	f) Histamine	0.58±0.04	„	„

4.4. HEAT PENETRATION STUDIES

In thermal processing, the food that is packed inside the container is subjected to high temperature treatment to achieve commercial sterility. The most commonly employed temperature in case of low acid foods fall within the range of 115-150 ^{0}C (Jaiswal, 2002). Besides commercial sterility; the thermal process schedule delivered should yield a product with acceptable sensory attributes of colour, flavour and texture. The thermal process lethality is usually expressed in terms of F_0 value, which is the time in minutes the product has to be maintained at 121 ^{0}C to achieve a desired level of spore count reduction. Although a minimum F_0 value of 3 min can render the product commercially sterile, a much higher F_0 value is often preferred for the sensory attributes discussed earlier. The F_0 value recommended by Frott and Lewis (1994) for fish and fish products ranges from 5-20 min. The optimum F_0 value for a product of a specific fill weight and solid to liquid ratio is the one which renders a safe product with good sensory attributes. The standardization of process parameters involves heat processing a product to different F_0 values and selecting the optimum F_0 value based on the analysis of instrumental and sensory attributes.

4.4.1. Standardization of process parameters of ready to eat Squid masala

4.4.1.1. Heat penetration parameters

The heat penetration parameters of squid masala processed to F_0 7, 8 and 9 at 121 ^{0}C is given in Table-8. In all the cases, the filling weight was maintained at 160 g per can thereby maintaining a head space of 4 mm. Maintenance of uniform filling weight and

sufficient head space are factors which affects the heat penetration to the product and thus crucial in case of establishing the thermal processing schedule for a particular product (Jones et al. 1980; Berry et al. 1979). The come up time (CUT) which is the time in minutes taken by the retort to reach the processing temperature ranged from 5-6 min there by adhering to the range prescribed by NCA (1968). The lag factor of heating ($_j$h) for squid masala processed to F_0 7, 8 and 9 were 1.13,m1.43 and 1.51 respectively ($p<0.05$) while the lag factor of cooling ($_j$c) was 1.18 for squid masala processed to F_0 7 and 1.19 for samples processed to F_0 8 and 9 indicating that this parameter is independent of the sterilization value ($p>0.05$). fh value which represents the heating rate index did not show any significant difference with sterilization value ($p>0.05$). The g value which is the final temperature deficit decreased significantly ($p<0.05$) with the increase in F_0 value. A similar trend in g value was reported by Ali (2004) in case of tuna processed in brine to different F_0 values. The process time (B) taken to reach F_0 7, 8 and 9 were 32, 34 and 36 min ($p<0.05$). The total process time (TPT), which was found out by adding 58% of CUT to B varied significantly with change in targeted sterilization value and it was 35, 37 and 40 min for squid masala processed to F_0 7, 8 and 9. This indicates that both B and TPT increase with increase in sterilsation value. The cook value increased significantly ($p<0.05$) with F_0 value and was 82.6, 91.09 and 95.4 min, respectively. This increase in cook value with F_0 value is in agreement with the findings of Ali et al. (2005). Figures.7-9 represents the heat penetration characteristics of squid masala processed to F_0 7, 8 and 9.

Table-8. Heat penetration data of squid masala processed to F_0 7, 8 & 9 in indigenous polymer coated tin free steel cans.

Parameter	F_0 7	F_0 8	F_0 9
$_jh$	1.13 ± 0.12 [a]	1.43 ± 0.22 [b]	1.51 ± 0.19 [c]
$_jc$	1.18 ± 0.11 [a]	1.19 ± 0.15 [a]	1.19 ± 0.13 [a]
f_h (min)	23.5 ± 0.23 [a]	24.0 ± 0.35 [a]	25.0 ± 0.19 [a]
U	7.04 ± 0.16 [a]	8.16 ± 0.22 [b]	8.97 ± 0.24 [c]
f_h /u	3.43 ± 0.25 [a]	2.94 ± 0.36 [b]	2.79 ± 0.21 [c]
G	3.97 ± 0.12 [a]	3.38 ± 0.15 [b]	3.17 ± 0.10 [c]
CV (min)	82.63 ± 1.02 [a]	92.15 ± 1.15 [b]	96.7 ± 1.25 [c]
B (min)	32.0 ± 1.25 [a]	34.0 ± 1.35 [b]	36.0 ± 1.75 [c]
TPT (min)	35.20 ± 1.55 [a]	38.45 ± 1.25 [b]	41.35 ± 1.15 [c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

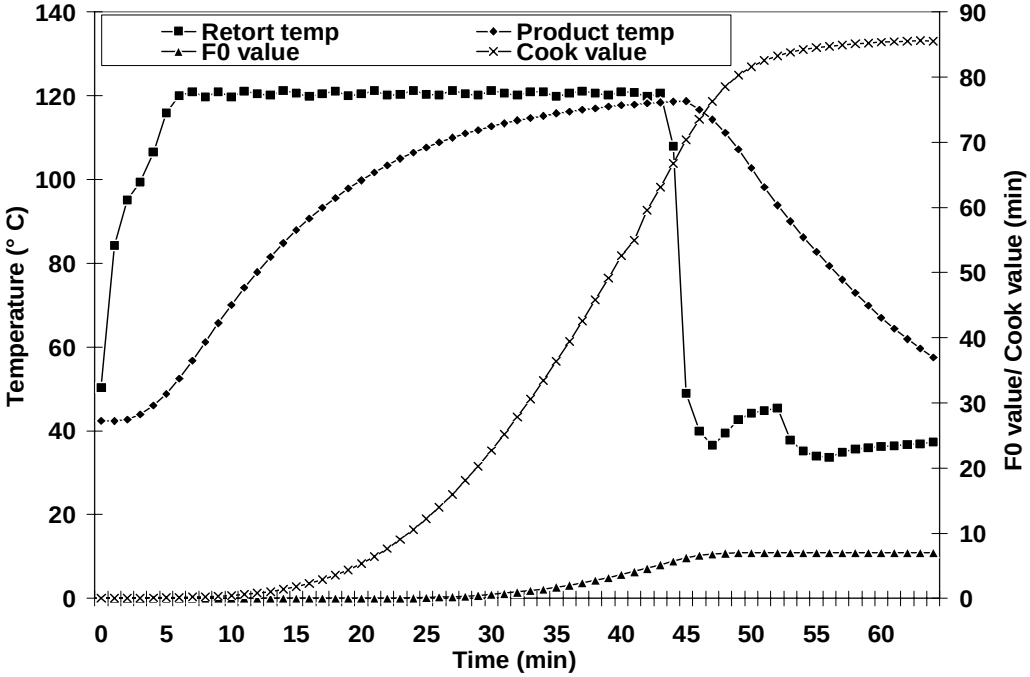

Fig-7. F_0 Value and cook value of squid masala processed to F_0 7

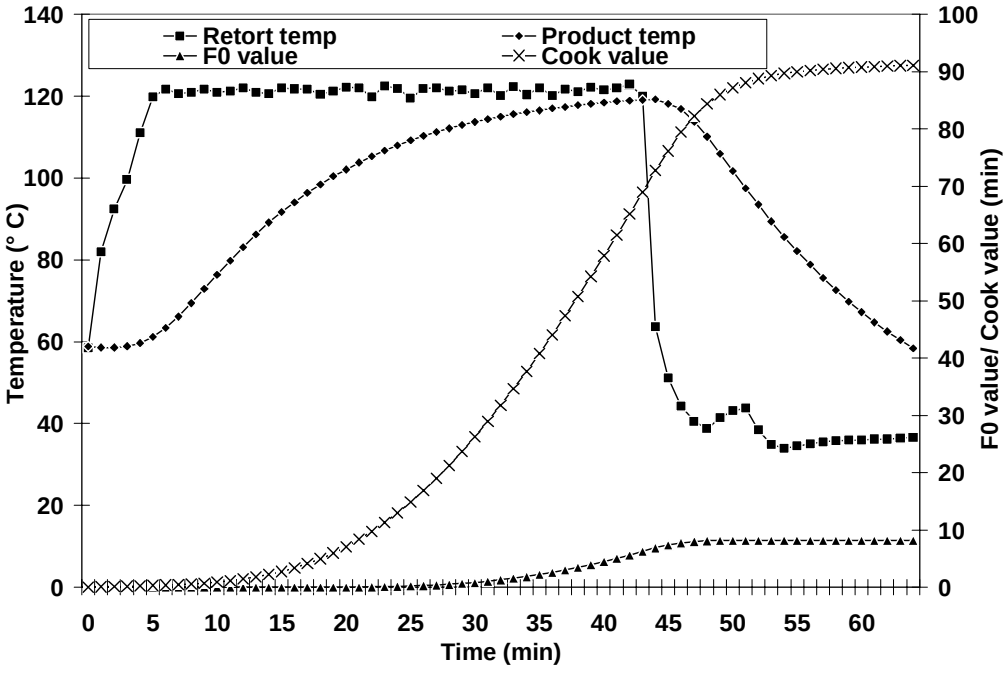

Fig-8. F_0 Value and cook value of squid masala processed to F_0 8

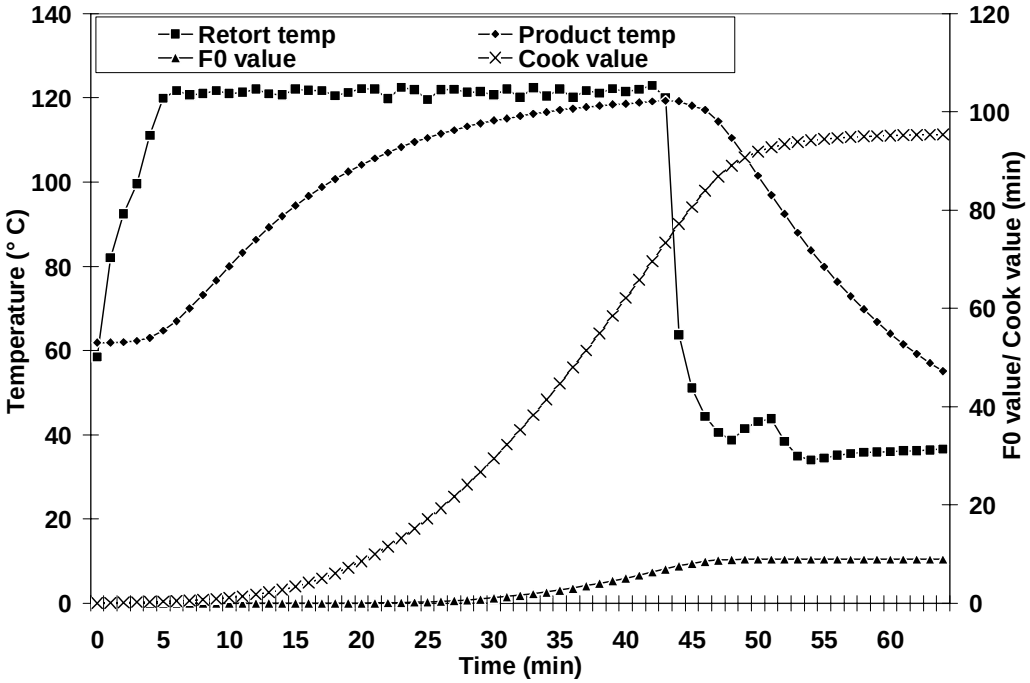

Fig-9. F_0 Value and cook value of squid masala processed to F_0 9

4.4.1.2. Sterility test

Squid masala processed to F_0 7, 8 and 9 were found to be commercially sterile as indicated by the absence of any turbidity in the thioglycollate tubes inoculated with samples processed at three F_0 values. This suggests that the heat treatment delivered to the product at all the three F_0 values was sufficient to make the products commercially sterile.

4.4.1.3. Instrumental colour

The high temperature treatment during thermal processing affects the colour of the product. Colour is one of the important attributes affecting the appearance and consumer appeal of foods. Thus the colour changes occurring to a product during thermal processing should be carefully monitored. The L*, a* and b* values of squid masala

processed to different F_0 values are given in Table-9. The L* value reduced significantly ($p<0.05$) with increase in the duration of exposure to heat processing and was 18.19, 16.85 and 15.47 for squid masala processed to F_0 7, 8 and 9. This decrease in L* with increase in heating time can be attributed to the Maillard's reaction (Haard, 1992). The redness value which is measured in terms of a* value also showed significant changes with increase in duration of exposure to heating and it increased from 8.13 in case of samples processed to F_0 7 to 8.28 at F_0 9. The increase in a* value with heating can be attributed to increase in the rate of browning with heating time (Van Boekel, 1998). b* value which was 19.67 for samples processed to F_0 7 showed significant decrease with increase in sterilization value and was 18.97 and 16.9 for samples processed at F_0 8 and 9 respectively.

Table- 9. Instrumental colour values of squid masala processed to F_0 7, 8 & 9.

	L*	**a***	**b***
F_0 7	18.19±0.16[a]	8.13 ±0.23 [a]	19.67±0.25 [a]
F_0 8	16.85±0.35[b]	8.20 ±0.45 [b]	18.97±0.54 [b]
F_0 9	15.47±0.46[c]	8.28 ±0.35 [c]	16.90±0.64 [c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

4.4.1.4. Analysis of texture

4.3.1.4.1. Texture profile analysis (TPA)

The results of texture profile analysis of squid muscle processed to different F_0 values is given in Figure.10. The various parameters analyzed were Hardness-1,

Hardness-2, Cohesiveness, Gumminess, Springiness and Chewiness. Hardness is probably the most critical texture attribute in meat or seafood products and can be defined as a property which depends on connective tissues consisting of mainly collagen and myofibrils, consisting of myosin and actin (Martens et al. 1982). Hardness-I and 2, the resistance at maximum compression during the 1^{st} and 2^{nd} compression respectively showed decreasing trend with increase of sterilization value. Hardness 1and 2 for squid muscle processed to F_0 7 were 2.18 and 1. 96 kgf, respectively. These two parameters decreased significantly to 1.61 and 1.36 kgf and 1.51 and 1.21 kgf when processed to F_0 8 and 9 respectively ($p<0.05$).Cohesiveness, the ratio of the positive force during the second compression to that during first was 0.20, 0.10 and 0.09 for squid muscle processed to F_0 7, 8 and 9 respectively. The gumminess which is the product of hardness 1 and cohesiveness also showed a decreasing trend with increase of processing time with squid muscle processed to F_0 values of 7, 8 and 9 recording 0.43, 0.16 and 0.13 kgf respectively. Springiness values for squid muscle thermally processed to F_0 values of 7, 8 and 9 were 0.47, 0.46 and 0.45 mm, respectively. Chewiness value which was 0.20 kgf/ mm for squid muscle thermally processed to F_0 value of 7 min, decreased to 0.19 and 0.06 kgf/ mm on processing to F_0 values of 8 and 9.

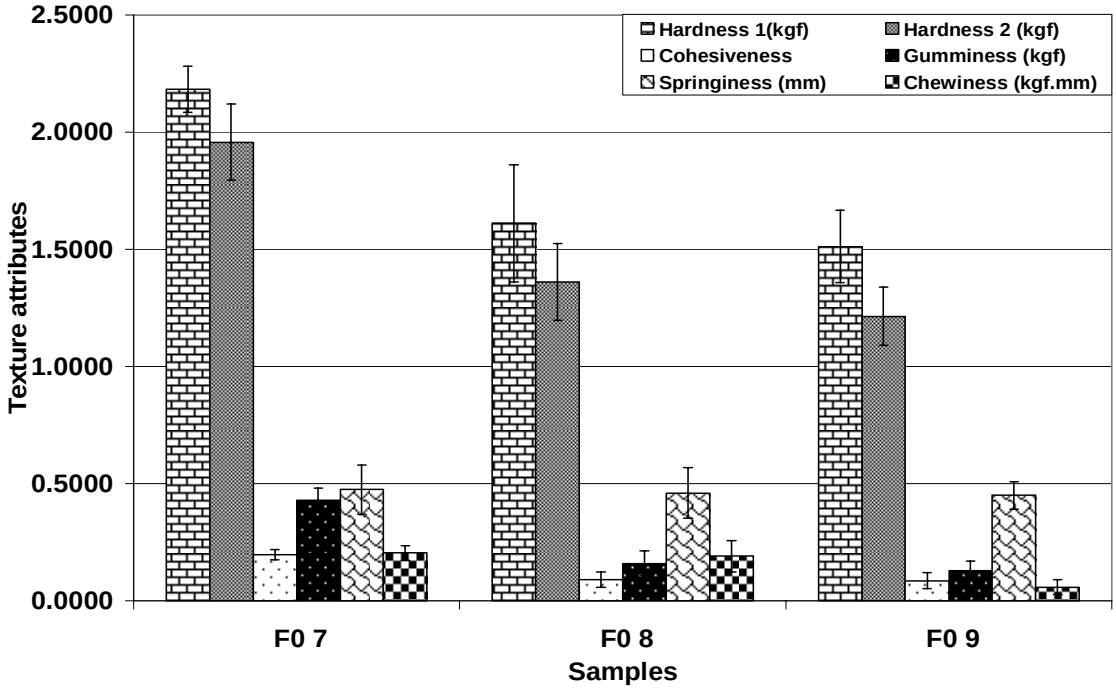

Fig-10. Texture profile attributes of squid muscle processed to F_0 7, 8 and 9

4.4.1.4.2. Warner–Bratzler shear force

The shear force processed squid muscle is given in Figure.11. The shear force of squid muscle, like TPA, showed a decreasing trend with cooking. It was 4.2, 3.9 and 3.4 N for squid muscles processed to F_0 values of 7, 8 and 9 ($p<0.05$). This is in agreement with the findings of Kolodzicjska et al. (1987) who reported that the toughness of squid mantle decreased gradually with increase in cooking time. The significant reduction occurred to the texture attributes of squid muscle with increase in the duration of exposure to heat treatment can be attributed to the gelatinization of muscle collagen and destruction of muscle cells leading to loss of muscle firmness and structure during cooking (Kugino and Kugino, 1994; Ando et al, 1999).

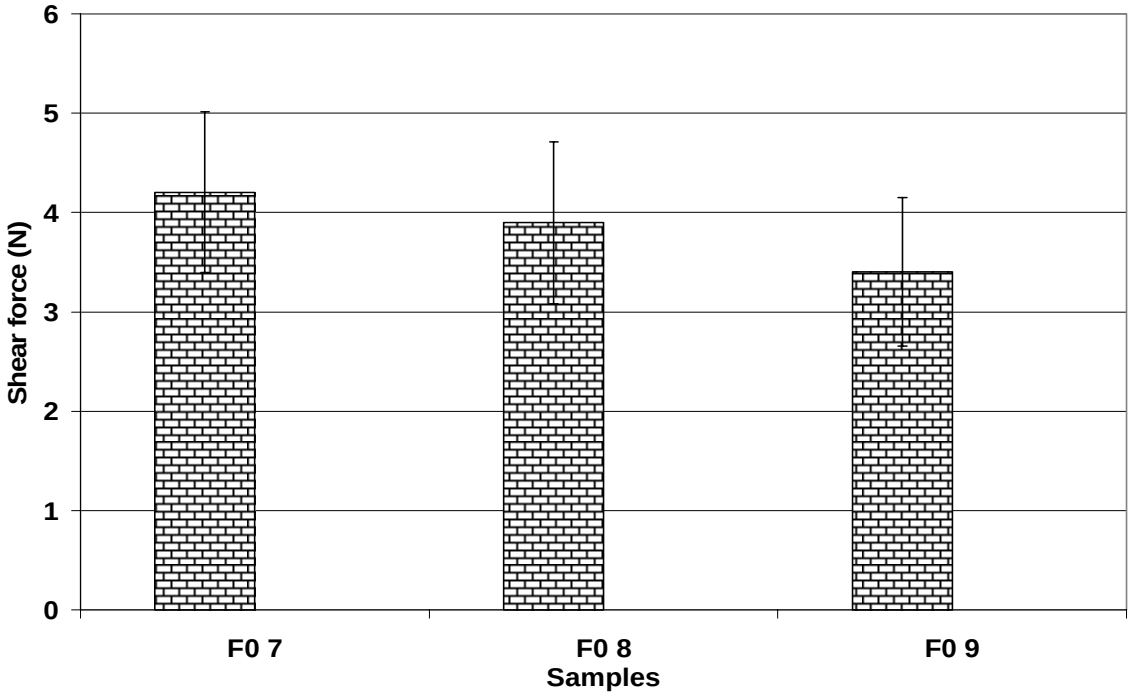

Fig-11. Shear force of squid muscle processed to F_0 7, 8 and 9

4.4.1.5. Sensory analysis

Sensory analysis of fish and fish products have always been a part of the production (Hanna, 1992; York and Sereda 1994). There is no single set of desired quality for all the fishery products since quality depends on regional preferences, consumer attitudes and method of preservation and consumption (Haard, 1992). The parameters covered under the sensory evaluation were colour, flavor texture and overall acceptability. Squid masala processed to three F_0 values was analyzed by a 10 member trained sensory panel. The results of the sensory analysis are presented in Table-10. It can be seen that all the sensory attributes examined except flavor, varied significantly ($p<0.05$) with F_0 value. The sensory scores given for the attribute of color by the panelists to the samples processed to F_0 7, 8 and 9 were 7.2, 8.5 and 6.5 respectively

($p<0.05$).Flavor of the product did not show any significant variation ($p>0.05$) with the sterilization value indicating that it is not dependent on the F_0 value. The attributes examined under the texture like chewiness, succulence, fibrosity and toughness showed significant variation with F_0 value ($p<0.05$). Squid masala processed to F_0 value 7 was harder in texture while those processed to F_0 9 were too softer in texture due to the longer duration of exposure to heat processing. The samples processed to F_0 8 on the other hand, were rated as ideal with respect to the texture. The overall acceptability score showed significant variation ($p<0.05$) with the F_0 value with squid masala processed to F_0 8 scoring the highest followed by those processed to F_0 7 and 9 respectively.

The analysis of instrumental color showed that the samples became darker with the increase in F_0 value. The sensory analysis revealed that the samples processed to F_0 8 min was ideal with respect to colour and was given the highest score for this attribute. Both TPA and shear force values decreased with increase in heating time. This well agrees with the sensory scores where the samples processed to F_0 9 were rated as softer than F_0 7 and 8. Samples processed to F_0 7 were found to be slightly harder in texture upon sensory analysis. Squid masala processed to F_0 8 with a cook value of 92 min was found to be ideal with respect to texture attributes by the sensory panelists. Based on the sensory analysis and the analysis of instrumental color and texture, an F_0 value of 8 min with a total process time of 38.5 min and cook value of 92 min was chosen as the optimum for squid masala in tin free steel cans.

Table-10. Sensory score of squid masala processed to F_0 7, 8 and 9

	Colour	Flavour	Texture				Overall Acceptability
			Chewiness	Succulence	Toughness	Fibrosity	
F_0 7	7.2±0.16 [a]	7.7±0.22 [a]	8.0±0.26 [a]	7.5±0.42 [a]	7.4±0.22 [a]	7.9±0.22 [a]	7.8±0.45 [a]
F_0 8	8.5±0.25 [b]	7.8±0.35 [a]	8.3±0.33 [b]	8.7±0.24 [b]	8.3±0.35 [b]	8.2±0.32 [b]	8.4±0.10 [b]
F_0 9	6.5±0.21 [c]	7.5±0.19 [a]	7.5±0.15 [c]	6.3±0.17 [c]	6.7±0.14 [c]	7.6±0.15 [c]	7.4±0.32 [c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

4.4.2. Standardization of process parameters of ready to eat shrimp curry

4.4.2.1. Heat penetration parameters

Shrimp curry packed in TFS cans was thermally processed at 121.1 ^{0}C to different F_0 values of 6, 7 and 8 min. The filling weight maintained in each can was 160 g and the head space provided was 4 mm. The heat penetration data of shrimp curry in indigenous polymer coated tin free steel cans processed to F_0 6, 7 and 8 are presented in Table-11. The come up time (CUT) varied between 5-6 min and is within the range specified by NCA (1968). The g value, which is the final temperature deficit decreased significantly ($p<0.05$) with the increase in F_0 value. The process time (B) taken to reach F_0 6, 7 and 8 showed significant difference ($p<0.05$) and were 38, 41 and 45 min respectively. The total process time which was found out by adding 58% of CUT to B was 41, 44 and 48 min for F_0 value 6, 7 and 8 respectively ($p<0.05$). Mohan et al. (2006) reported the standardisation of sterilization value for Shrimp kuruma in retort pouch and aluminium cans. The cook value is measure of heat treatment with respect to nutrient degradation

and textural changes that occur during processing. It can be seen that the cook value increased significantly ($p<0.05$) with increase in F_0 value and was 85.60, 91.09 and 95.4 min respectively. The heat penetration curves with respect to F_0 value and Cook value of shrimp curry processed to F_0 6, 7 and 8 are shown in Figures. 12-14.

Table-11. Heat penetration data of shrimp curry processed to F_0 6, 7 & 8 in indigenous polymer coated tin free steel cans

Parameter	$F_0$6	$F_0$7	$F_0$8
J_h	1.12 ± 0.12 [a]	1.41 ± 0.22 [b]	1.49 ± 0.19 [c]
J_c	1.18 ± 0.11 [a]	1.19 ± 0.15 [a]	1.19 ± 0.13 [a]
Fh (min)	24.0 ± 0.23 [a]	24.0 ± 0.35 [a]	25.0 ± 0.19 [a]
U	6.04 ± 0.16 [a]	7.04 ± 0.22 [b]	8.00 ± 0.24 [c]
f_h/u	3.97 ± 0.25 [a]	3.40 ± 0.36 [b]	3.13 ± 0.21 [c]
G	2.57 ± 0.12 [a]	2.23 ± 0.15 [b]	2.06 ± 0.10 [c]
CV (min)	85.6 ± 1.02 [a]	91.1 ± 1.15 [b]	95.4 ± 1.25 [c]
B (min)	38.0 ± 1.25 [a]	41.0 ± 1.35 [b]	45.0 ± 1.75 [c]
TPT (min)	41.0 ± 1.55 [a]	44.0 ± 1.25 [b]	48.0 ± 1.15 [c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

J_h-lag factor of heating, J_C-lag factor of cooling, fh-slope of heating curve, U-Number of minutes for sterilization at the retort temperature, g-Final temperature deficit, CV -Cook value, B-Ball's process time in minutes, TPT-Total process time.

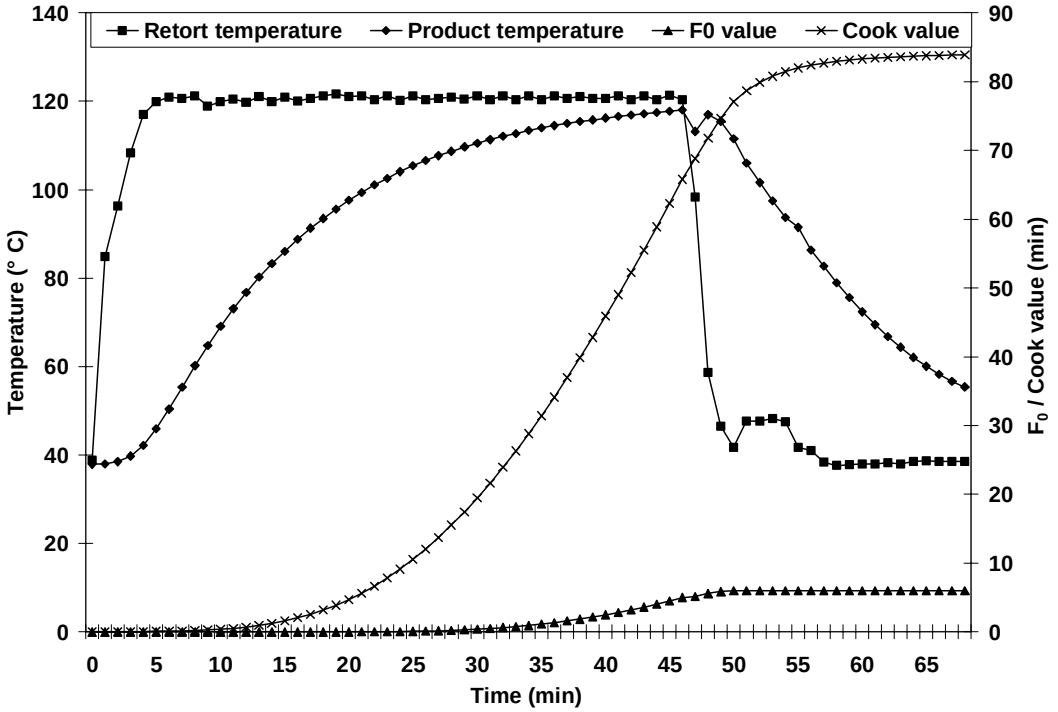

Fig-12. F_0 Value and cook value of shrimp curry processed to F_0 6

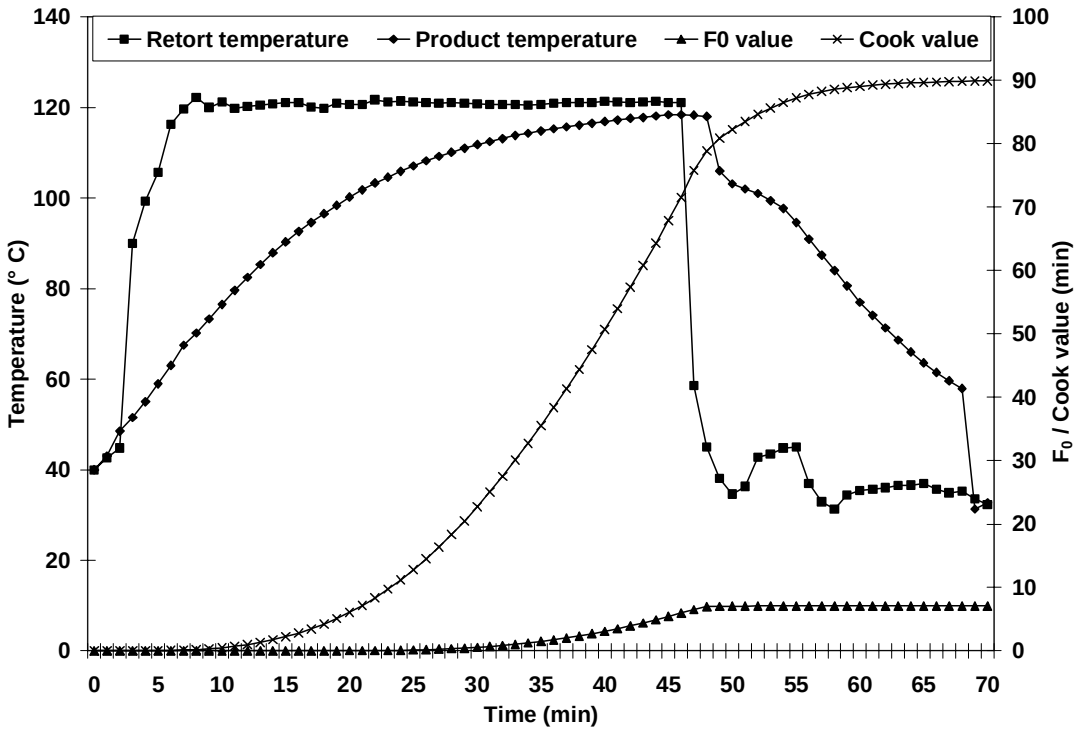

Fig-13. F_0 Value and cook value of shrimp curry processed to F_0 7

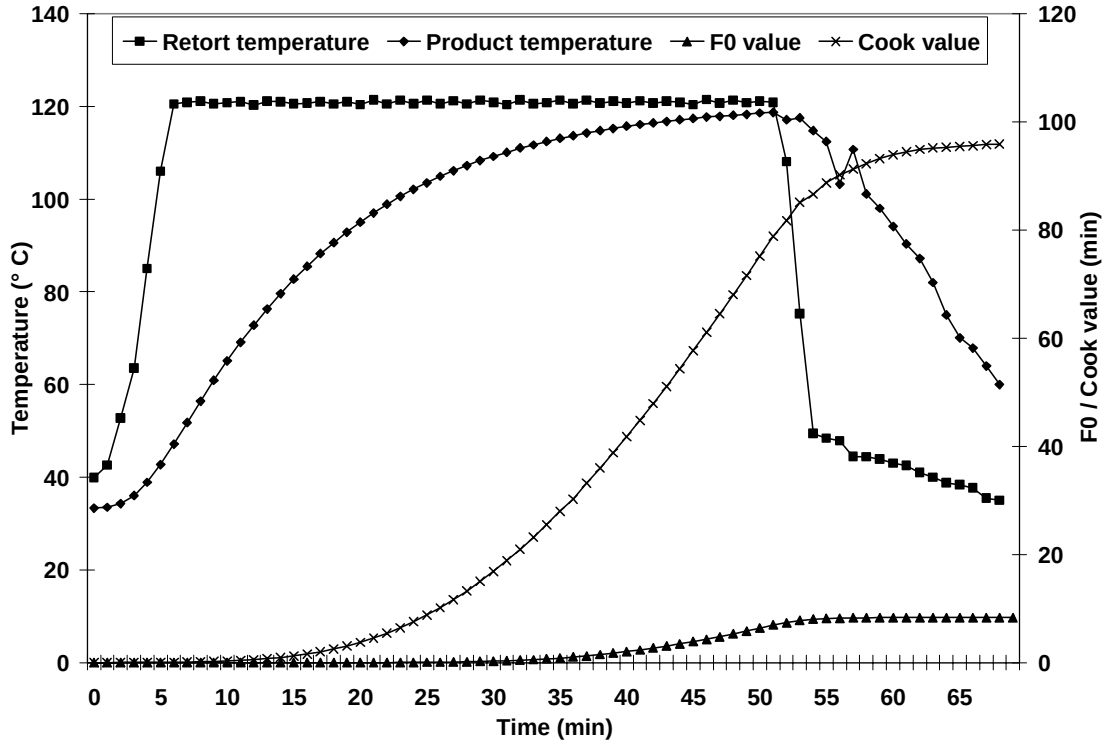

Fig-14. F_0 Value and cook value of shrimp curry processed to F_0 8

4.4.2.2. Sterility test

Sterility test is done to assist in determining the efficacy of a heat process and is the assessment of the soundness of the container (Evancho et al. 1973). Shrimp curry processed to F_0 6, 7 and 8 were found to be commercially sterile thereby indicting the adequacy of heat treatment delivered.

4.4.2.3. Instrumental colour

The instrumental colour values expressed in terms of L*, a* and b* values of shrimp curry processed to different F_0 values is depicted in Table-12. The L* value of shrimp curry processed to F_0 6 was 17.39 which reduced significantly ($p<0.05$) with increase in the duration of exposure to heat processing and was 16.85 and 16.07 for

samples processed to F_0 7 and 8. This decrease in L* with increase in heating time can be attributed to the Maillard's reaction (Haard, 1992). a* value which is the measure of the redness also showed significant changes with increase in duration of exposure to heating. The samples processed at F_0 8 had significantly higher a* value of 8.60 as compared to 8.36 and 8.03 for shrimp curry processed to F_0 7 and 6. The increase in a* value with heating can be attributed to increase in the rate of browning with heating time (Van Boekel, 1998). b* value which was 16.67 for samples processed to F_0 6 showed significant decrease with increase in sterilization value and was 15.87 and 14.90 for samples processed at F_0 7 and 8 respectively.

Table-12. Instrumental colour values of shrimp curry processed to F_0 6, 7 & 8.

	L*	**a***	**b***
F_0 6	17.39 ± 0.16^{a}	8.03 ± 0.23^{a}	16.67 ± 0.25^{a}
F_0 7	16.85 ± 0.35^{b}	8.36 ± 0.45^{b}	15.87 ± 0.54^{b}
F_0 8	16.07 ± 0.46^{c}	8.60 ± 0.35^{c}	14.90 ± 0.64^{c}

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

4.4.2.4. Analysis of texture

Texture is the most important factor regarding shrimp sensory quality as it exhibits dramatic changes during extended thermal processing (Ma et al. 1983). The texture of shrimp muscle was determined by TPA and Warner Bratzler shear force methods.

4.4.2.4.1. Texture Profile Analysis

The result of texture profile analysis of shrimp muscle is summarized in Figure.15. Hardness-I and 2 are the resistance at maximum compression during the 1st and 2nd compression respectively. Among the thermally processed samples, the hardness-1and 2 were found to decrease with increase in processing time (F_0 value) and were 2.45 and 1.91, 2.17 and 1.79 and 1.76 and 1.54 kgf for shrimp processed to F_0 6, 7 and 8 ($p<0.05$). Cohesiveness, the ratio of positive force area during the 2nd compression to that during 1st compression of thermally processed samples did not show any significant change with F_0 value. The Cohesiveness values for shrimp processed to F_0 6, 7 and 8 were 0.34, 0.32 and 0.30 respectively ($p>0.05$). Gumminess which is the product of hardness-1 and cohesiveness on heat processing decreased to 0.83, 0.69 and 0.53 kgf for F_0 6, 7 and 8 ($p<0.05$) indicating that it is dependent on the processing time. Springiness which refers to the height that the food recovers during the time that elapses between the end of 1st compression and the start of 2nd compression was 0.89, 0.79 and 0.61 mm for shrimp processed to F_0 6.7 and 8 ($p<0.05$). Chewiness values shows significant decrease with processing time and was 0.79, 0.55 and 0.33 kgf/mm respectively for shrimp processed to F_0 6.7 and 8 min. Mizuta et al (1999) reported that changes in muscle collagen have important functions in the textural changes of shrimp meat during heat processing. The lowering of various texture attributes with heating time can be attributed to the softening of muscle arising out of the conversion of collagen to gelatin and the dissociation of muscle proteins (Bouton and Harris 1972; Ma et al. 1983). Mohan et al. (2007) reported that shrimp muscle processed in retortable pouches had significantly better texture parameters expressed in terms of hardness 1and2, springiness and

chewiness as compared to the products in cans and they have attributed this to the higher heating time taken by canned products compared to pouch products to attain the same sterilization value.

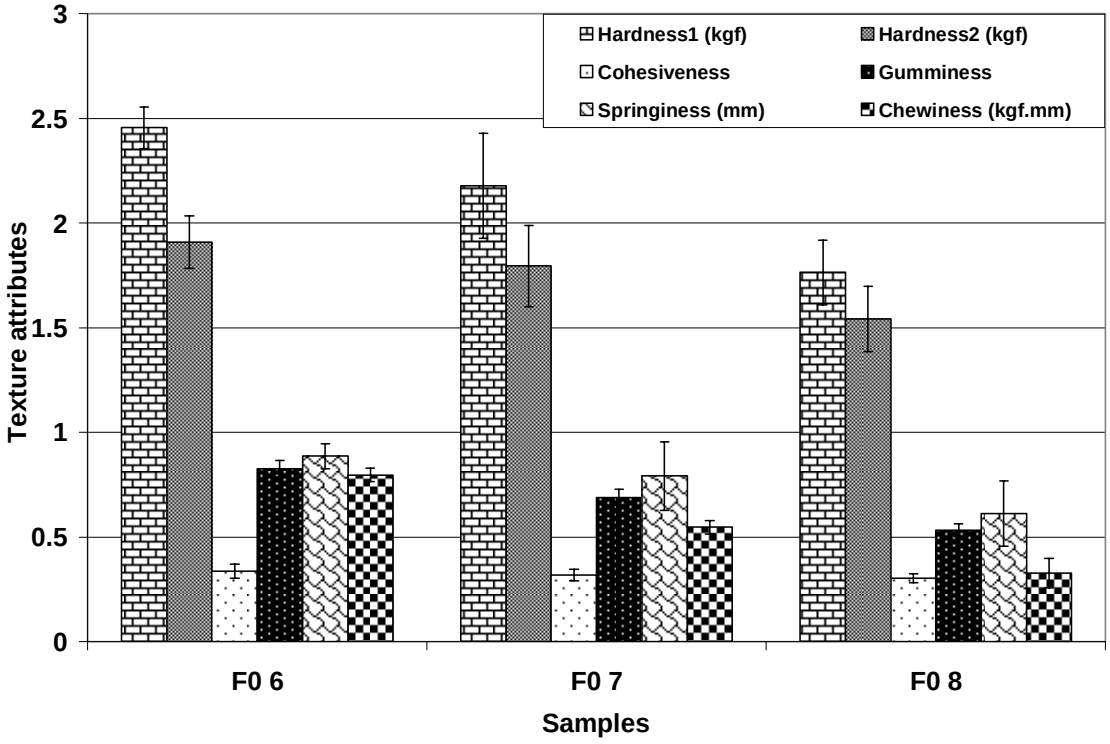

Fig-15. Texture profile attributes of shrimp muscle processed to F_0 6, 7and 8

4.4.2.4.2. Warner Bratzler shear force

The shear force of the shrimp pieces was determined at the centre of 2nd segment as described by Erdogdu and Balaban (2000).The shear force for thermally processed shrimp meat is given in Figure. 16. The shear values for shrimp muscles processed to F_0 6, 7 and 8 were 6.3, 5.86 and 5.46 N respectively ($p< 0.05$). This clearly indicates that the shear force of shrimp muscle is significantly affected by the heating time. Another notable finding is that shear force also follows the same trend of texture profile. This finding is well supported by the reports of several workers who have related the shear force with hardness and chewiness (Ahmed et al. 1972; Webb et al. 1975).

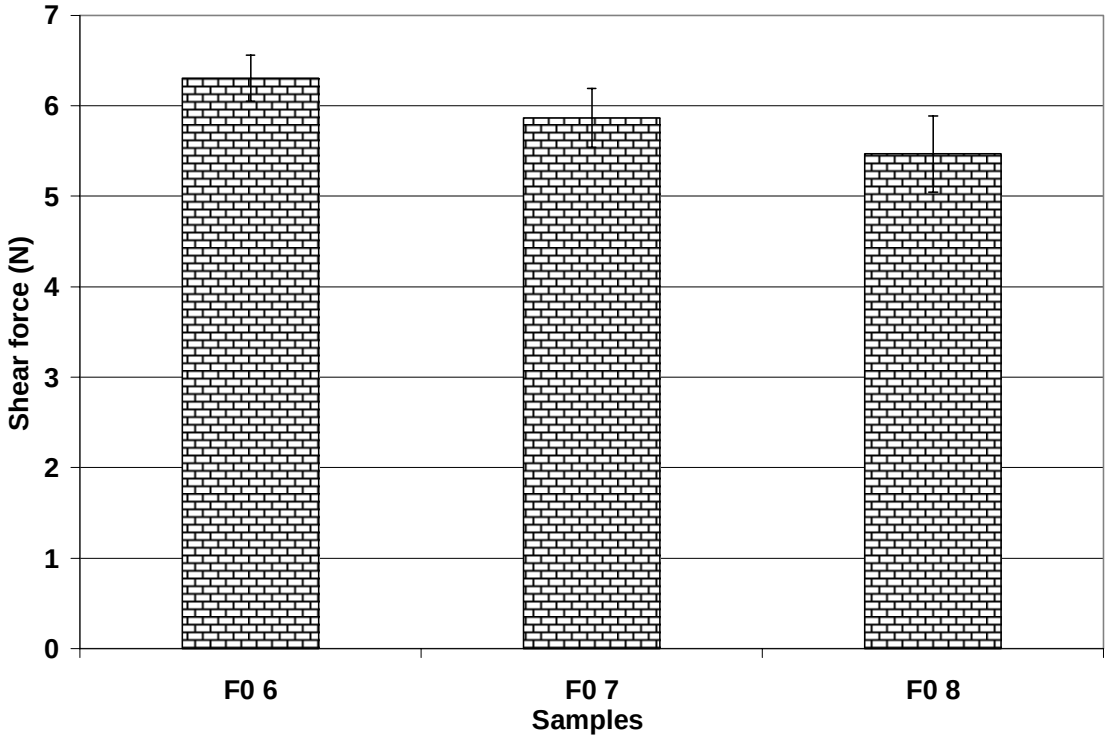

Fig-16. Shear force values of shrimp processed to F_0 6, 7and 8

4.4.2.5. Sensory Analysis

Shahidi and Botta (1994) described sensory quality of shrimp as a complex set of characteristics including appearance, aroma, taste and texture. The sensory scores given by the panelists for shrimp curry processed to different F_0 values are given in Table-13. Significant effects of processing time on the colour of the shrimp curry could be noticed upon sensory evaluation in that curry processed to F_0 8 was rated as darker and was thus given the least score by the panelists. Samples processed to F_0 7 were rated as having ideal colour. Flavor of the shrimp curry processed at different F_0 values did not exhibit any significant change with sterilization value. This agrees well with the findings of Ma et al. (1983) who reported that the characteristic canned shrimp flavor is developed

relatively early in a process and it does not change substantially after prolonged heating. Among the various sensory attributes, texture is the most important one as it is the parameter more likely to undergo changes with heating. The various parameters analysed under texture were chewiness, succulence, toughness and fibrosity. Shrimp pieces of samples processed to F_0 6 were felt to the panelists as harder in texture and those processed to F_0 8 were too soft while those processed to F_0 7 were rated as having significantly acceptable texture as compared to other two batches ($p<0.05$). Shrimp curry processed to F_0 7 was given the highest overall acceptability score among the three batches.

Table-13. Sensory score of shrimp curry processed to F_0 6, 7 & 8

	Colour	Flavour	Texture				Overall Acceptability
			Chewiness	Suculence	Toughness	Fibrosity	
F_0 6	8.0±0.16[a]	7.27±0.22[a]	8.0±0.26[a]	7.5±0.42[a]	7.42±0.22[a]	7.51±0.22[a]	7.8±0.45[a]
F_0 7	8.5±0.25[b]	7.30±0.35[a]	8.3±0.33[b]	8.7±0.24[b]	8.39±0.35[b]	8.72±0.32[b]	8.4±0.10[b]
F_0 8	7.6±0.21[c]	7.20±0.19[a]	7.5±0.15[c]	6.3±0.17[c]	6.71±0.14[c]	6.38±0.15[c]	7.4±0.32[c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

Based on the analysis of instrumental colour, texture, shear force and sensory scores, shrimp curry processed to F_0 7 min with a total process time of 44.0 min and cook value of 91.1 min was found to be ideal and was selected for storage study

4.5. STORAGE STUDY

Canned foods are one of the stable foods. Hayakawa et al. (1978) reported that quality of canned products gradually deteriorates during storage, especially when it is stored at relatively higher temperatures. Since canned foods are stored for variable time periods before being consumed, it would be interesting to know the storage life of these products in orders to establish its expiry date. Ready to eat squid masala and shrimp curry were prepared and processed in large scale according to the chosen F_0 values and kept for storage studies at room temperature (30±2 ^{0}C) during which samples were taken on monthly basis and were analyzed for instrumental color, TPA, shear force, TBA, pH and sensory characteristics for a period of one year. Since ready to eat products are consumed without any further preparation, parameters like colour and appearance play vital role in the acceptance of the product.

4.5.1. Changes in pH of ready to eat fish products during storage

Hydrogen ion concentration is of relevance in case of muscle foods as it affects its texture. In case of heated fish muscle, an exceptionally high effect of pH on the toughness was reported at the range 5.7-6.7 by Dunajski (1979). The pH of squid masala and shrimp curry during storage is summarized in Figure. 17. It can be seen that the initial pH of squid masala and shrimp curry are 5.5 and 6.0 respectively indicating that it is towards the acidic side. The acidic nature of the product can be attributed to the acidity contributed by the curry ingredients like tomato. During storage, the pH of the products was found to exhibit a decreasing trend. On the 6th month of storage, the pH of squid masala and shrimp curry was found to be 5.2 and 5.7 respectively which are significantly lower as compared to initial values. On the 12th month of storage, the pH of squid masala

and shrimp curry was 5.1 and 5.6 respectively. The results of present study agrees with the findings of Mallick et al.(2006) who reported a decreasing trend in pH in case of north Indian style rohu curry stored in cans after 6 months of storage at room temperature and at 37±2 ^{0}C . Mohan (2004) reported a slight reduction in the pH of shrimp kuruma upon storage in both retort pouch and aluminium cans.

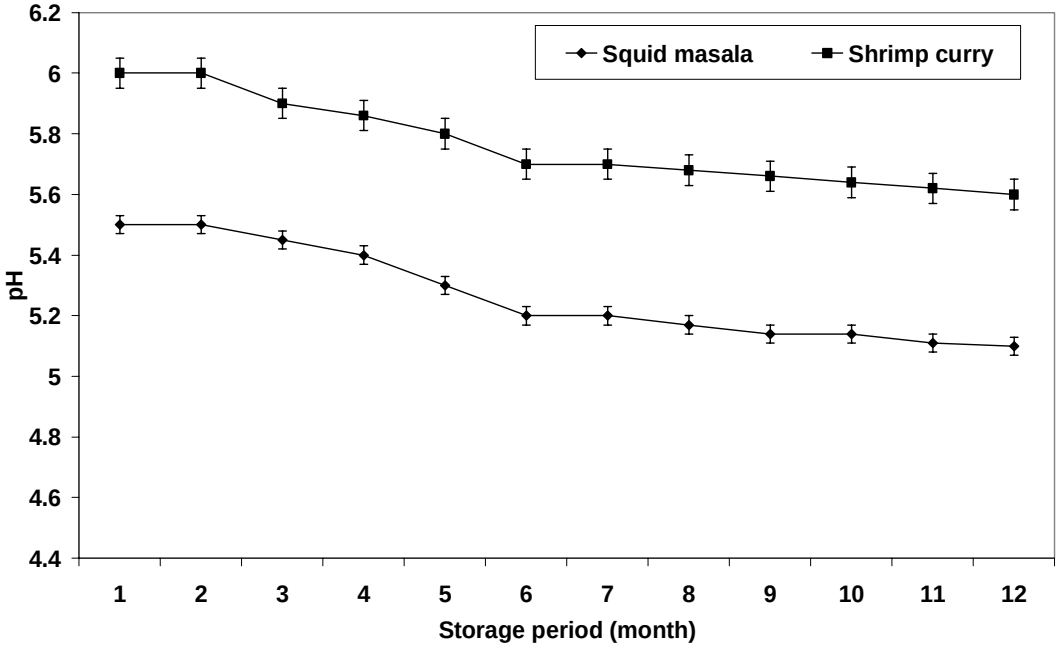

Fig-17. Change in the pH of squid masala and shrimp curry during storage at room temperature

4.5.2. Change in the instrumental color values of ready to eat fish products during storage

The instrumental colour values of squid masala and shrimp curry during storage at room temperature is given in Figures 18 & 19. Both the samples had initial L* value f 16.85. This low lightness value is due to the addition of curry ingredients. With storage the L* value exhibited significant reduction in case of both the samples. The L* value of squid masala and shrimp curry at the end of storage study was 14.85 and 15.6 respectively. The

initial a* value of squid masala and shrimp curry 8.2 and 8.36 respectively. The higher a* value san be attributed to the addition of tomato and red chilly as curry ingredients. He a* value was found to increase slightly with storage and was 9.39 ands 8.85 at the end of storage study. The b* value of squid masala and shrimp curry on the first month of storage was 18.97 and 15.87 respectively which n storage did not change appreciably. The b* value at the end of 12 month storage study was 19.18 and 15.92 for squid masala and shrimp curry respectively.

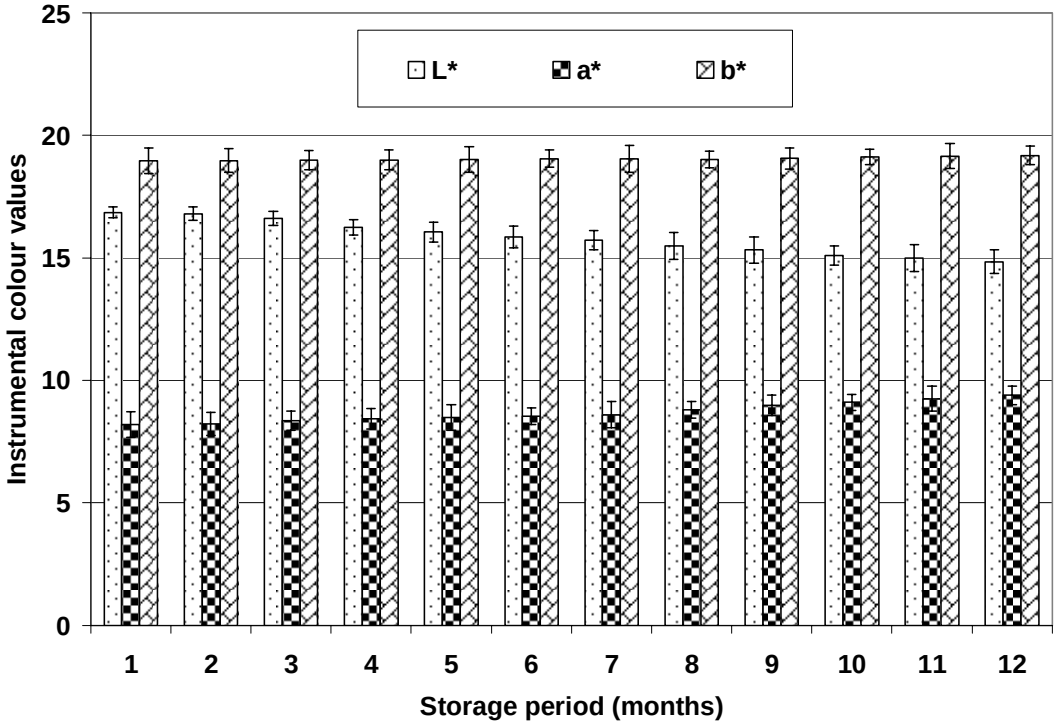

Fig-18. Change in the instrumental color values of ready to eat squid masala during storage at room temperature

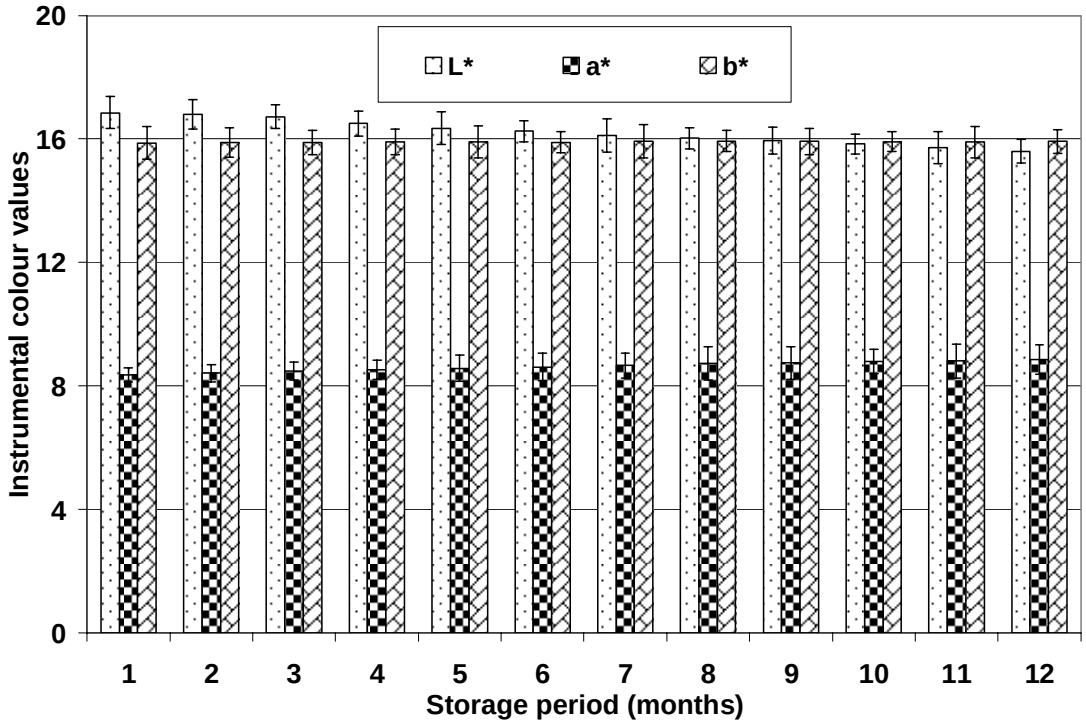

Fig-19. Change in the instrumental color values of ready to eat shrimp curry during storage at room temperature

4.5.3. Changes in the texture profile attributes of ready to eat fish products during storage

Texture is one of the important quality attribute affecting the consumer acceptability of a food product. The analysis of texture becomes even more important in case of canned products which are intended for long periods of storage as storage period is one of the determinants in texture (Ahmed et al. 1972).

The texture profile attributes of squid and shrimp muscle during the storage period of 12 months at room temperature is given in Figures.20-24.

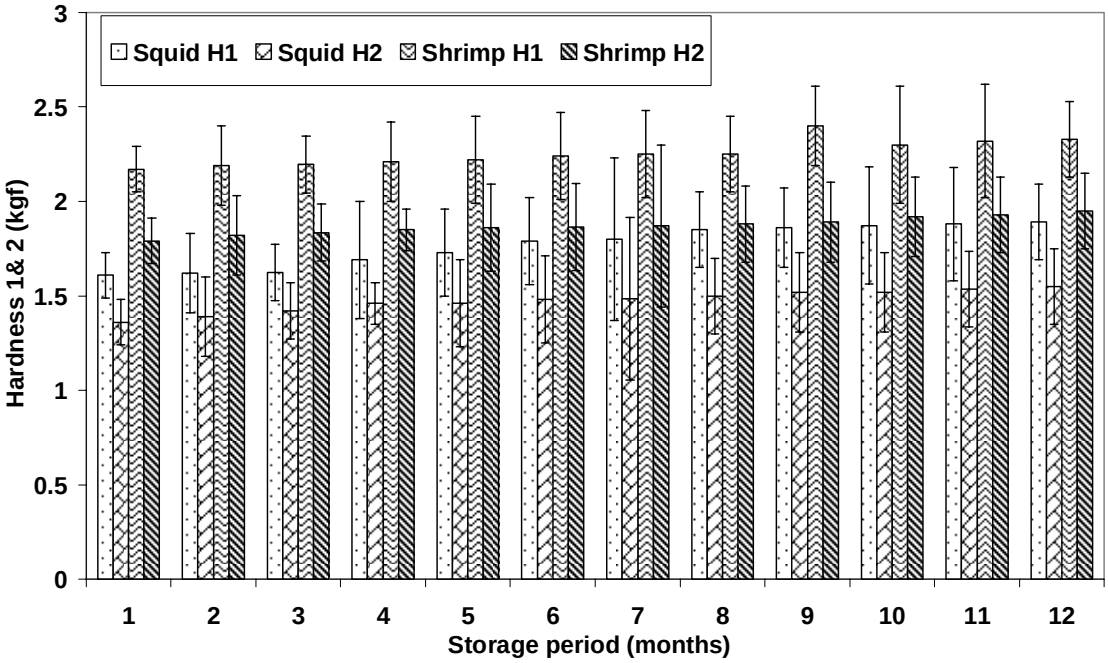

Fig-20. Change in the Hardness-1 & 2 values of ready to eat squid and shrimp muscle during storage at room temperature

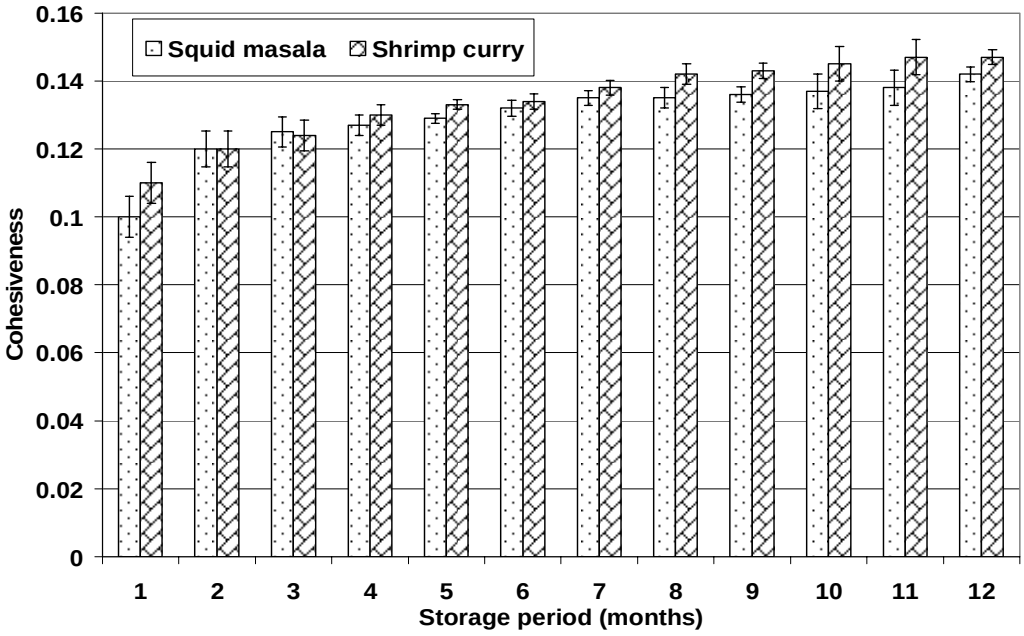

Fig-21. Change in the cohesiveness of ready to eat squid and shrimp muscle during storage at room temperature

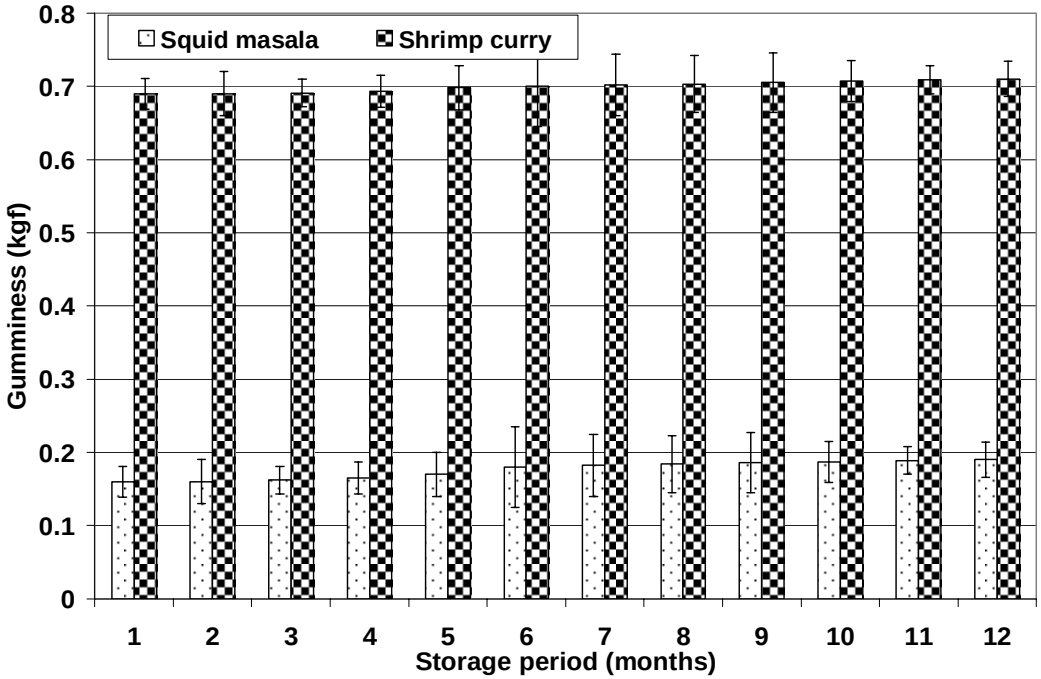

Fig-22. Change in the gumminess of ready to eat squid and shrimp muscle during storage at room temperature

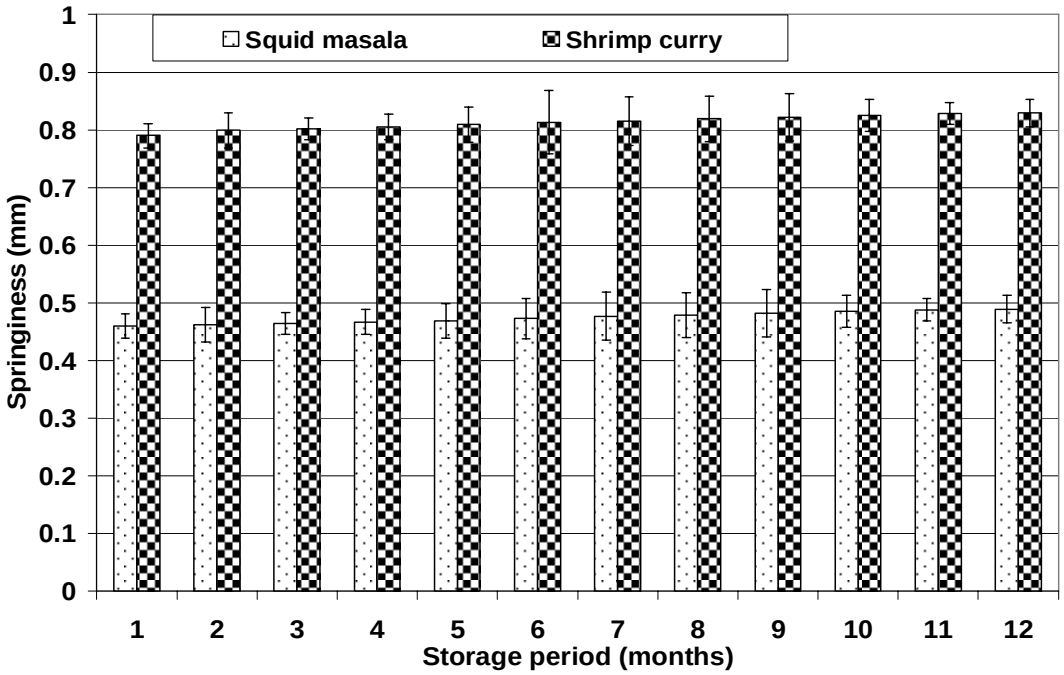

Fig-23. Change in the springiness of ready to eat squid and shrimp muscle during storage at room temperature

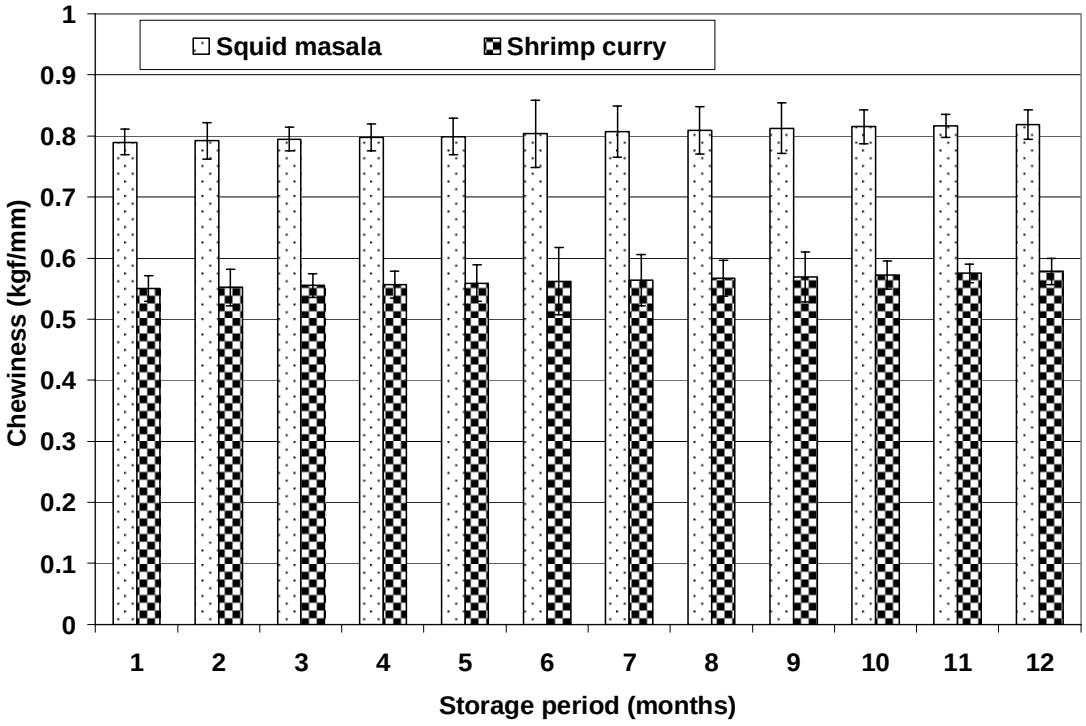

Fig-24. Change in the chewiness of ready to eat squid and shrimp muscle during storage at room temperature

Hardness 1 & 2 for squid and shrimp muscle on the first month of storage were 1.61 & 1.36 and 2.17 & 1.79 kgf, respectively. The hardness values did not show much variation during the initial months of storage for both the products. In case of squid masala, the hardness values showed slight increase on the 6th month of storage. On the 8th month of storage, both hardness 1& 2 showed significant increase ($p<0.05$) and were 1.85 and 1.5 kgf respectively. Thereafter the increase in hardness 1 & 2 were not so significant ($p>0.05$). The hardness 1 &2 of squid pieces on the 12th month of storage were 1.89 & 1.55 kgf respectively. The hardness 1 & 2 of shrimp pieces showed almost the same trend of squid muscle during the initial months of storage and it did not show any significant changes during the first five months of storage. On the 7th month, both these parameters increased significantly ($p<0.05$) to 2.25 and 1.87 respectively. Hardness 1 & 2 on the 10th

month of storage were 2.30 & 1.92 respectively and these two parameters slightly increased to 2.33 & 1.95 respectively ($p>0.05$) on the 12th month of storage. Increase in the toughness with storage was reported by Gangal and Magar (1967) in case of crab meat canned in different types of media. Mallick et al. (2006) reported that the hardness 1 & 2 of rohu canned in curry medium showed slight increase on the 6th month pf storage at room temperature and at 37 0C. As described by Howgate (1977), the increase in the hardness 1 & 2 with storage can be attributed to the lowering of pH with storage.

Cohesiveness which refers to the internal bonding of the muscles did not show any significant change with storage at room temperature in case of both squid and shrimp muscle. The cohesiveness of squid and shrimp muscle on the first and sixth months of storage was 0.10 & 0.32 and 0.11 & 0.34 respectively. No significant change could be noted even at the 12th month of storage study which indicates that this parameter is independent of storage period.

The gumminess value of squid and shrimp muscle on the 1st month of storage was 0.16 & 0.69 respectively which on the 6th and 12th months of storage reached 0.18 & 0.70 and 0.19 & 0.71 respectively. The springiness and chewiness values also did not show any significant change with storage at room temperature.

4.5.4. Changes in the shear force value of ready to eat fish products during storage

The change in the shear force value of squid and shrimp muscle with storage at room temperature is given in Figure. 25. From the figure, it can be seen that the shear force of both squid and shrimp meat increased significantly with storage period. The shear force value of squid and shrimp meat which was 3.9 & 5.86 N on the 1st month of storage increased significantly to 4.35 & 6.0 N respectively on the 6th month of storage

($p<0.05$).The shear force value again showed significant increase and reached 4.51 & 6.18 N on the 12th month of storage at room temperature ($p<0.05$).

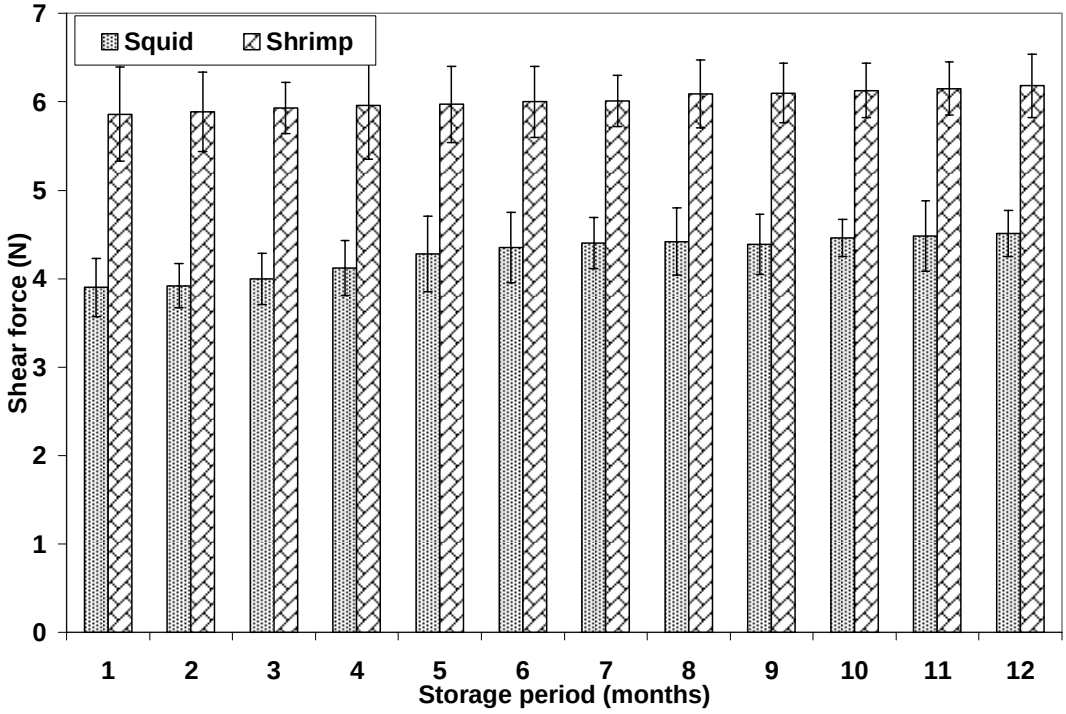

Fig-25. Change in the shear force value of ready to eat squid and shrimp muscle during storage at room temperature

4.5.5. Changes in TBA value of ready to eat fish products during storage

Lipid oxidation appears to be the primary mechanism of quality loss in heat sterilised foods subjected to extended storage (Kanner, 1992). It affects appearance, texture, flavour and nutritive value. Thus determination of TBA, which is an indicator of secondary oxidation, is of prime importance. Chia et al. (1983) reported that heating of fish muscle results in fall in TBA value. The changes in TBA value of squid masala and shrimp curry during storage is given in Figure. 26. The TBA value of both the products showed a gradual increase with time upto 8 months of storage at room temperature. The TBA values for squid masala and shrimp curry which were 0.340 & 0.386 mg

malonaldehyde/ kg of meat on the first month of storage increased to 0.352 & 0.398 mg malonaldehyde/ kg of meat on the 6th month of storage ($p<0.05$) and on the 8th month of storage it increased to 0.360 & 0.428 in case of squid masala and shrimp curry respectively. Afterwards TBA value showed a decreasing trend. The TBA value of squid masala and shrimp curry on 12 month of storage was 0.32 & 0.40 mg malonaldehyde/ kg respectively. Several authors reported a similar trend for TBA during the storage of various canned products (Aubourg et al. 1997; Manju et al. 2004). According to Pokorny (1981); Aubourg et al. (1995) this decrease in TBA value might be due to two reasons, the first one of which is due to the loss of the secondary oxidation products from the muscle into the curry medium and second one being the fact TBA can react with other reactive compounds like amino groups, resulting in its reduction.

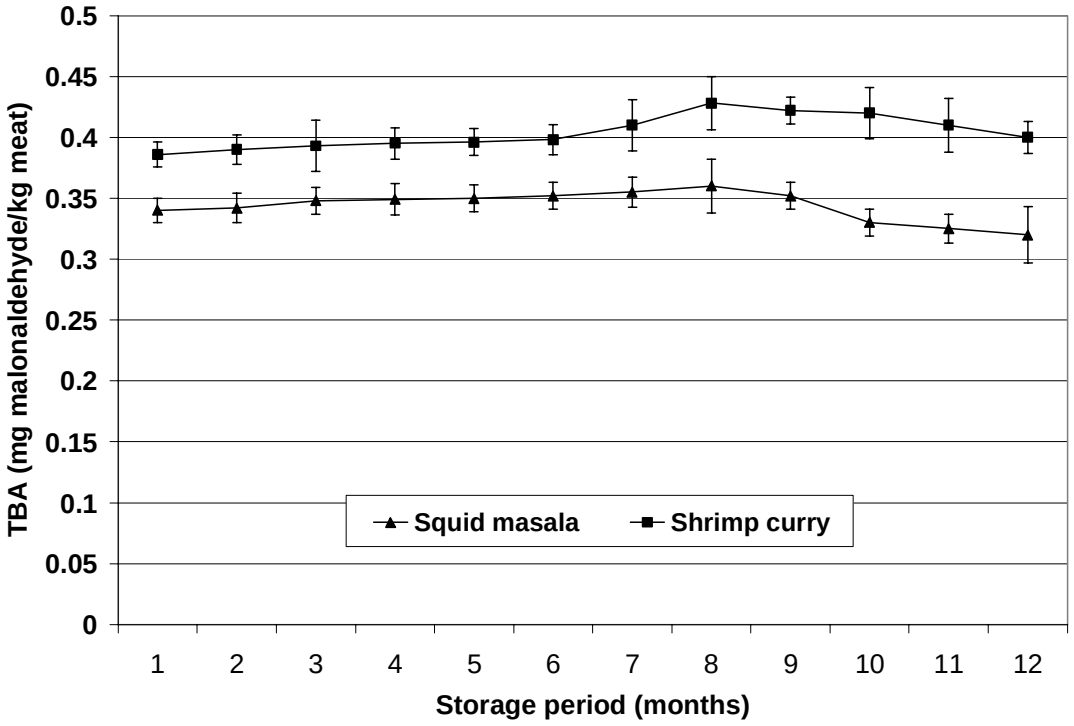

Fig-26. Change in the TBA value of ready to eat squid masala and shrimp curry during storage at room temperature

4.6. CANNING OF MACKEREL IN BRINE AT DIFFERENT RETORT TEMPERATURES

Thermal processing is done by heating the food in a pressurized steam or water retort at a prescribed time-temperature combination which can bring about sufficient bacterial reduction. In case of low acid foods, the organism of public health concern is *C. botulinum* due to its spore forming nature that makes it highly heat resistant The most commonly employed temperature in case of low acid foods fall within the range of 115-150 ^{0}C (Jaiswal, 2002). Some of the parameters influencing the temperature of processing involve type of food, temperature dependence of the most heat labile component in the food, heating medium employed, type of container and number of batches to be processed. Lund (1977) reported that the temperature dependence of bacterial destruction is markedly higher than for the deterioration of the quality parameters. This difference in temperature dependence suggests that it is better to process at high temperature for short period in order to reduce the changes in the sensory and nutritional qualities during thermal processing. If a product is sterilized at different temperatures but to the same bacteriological inactivation level, the negative effects of heat treatment will be pronounced on the product that is sterilized at lower temperature due to the increased time taken to attain the required lethality (Ohlsson, 1980a). These facts form the basic principle of high temperature short time (HTST) processing. In order to determine the effects of different retort temperatures on the heat penetration characters, sensory and biochemical aspects, mackerel was processed in brine at three retort temperatures of 115, 121 and 130 °C to a common F_0 value of 8 min.

4.6.1. Effect of different retort temperatures on Heat penetration characteristics

Mackerel in Brine (MIB) was processed at three processing temperatures to a common lethality factor (F_0 value) of 8min. The heat penetration curves with respect to F_0 value and Cook value of mackerel in brine processed at 115, 121 and 130 °C are shown in Figures. 27-29. The heat penetration parameters of MIB processed at 115, 121 and130 °C are given in Table 16. The come up time (CUT) ranged from 6.35 to 7.15 min. The lag factor of heating, j_h shows a decreasing trend with increase of temperature and was 1.16, 0.92 and 0.81 at 115, 121.1 and 130 °C, respectively ($p < 0.05$). This is in agreement with the findings of Ramaswamy and Grabowski (1999). They have also reported that the j_h value is highly influenced by the processing temperature and container shape. The lag factor of cooling (j_c) shows a contrasting trend with j_h factor and increased with increase of processing temperature. This is because core temperature of product processed at higher temperature will be higher at the time of cooling and will take comparatively more time to get reduced to the desired level. The heating rate index (f_h) decreased significantly ($p < 0.05$) with the increase of processing temperature and was 18.5, 16 and 13min for mackerel processed at 115, 121.1 and 130 °C, respectively. This is in agreement with the findings of Ma et al. (1983). When the processing temperature increases, the heat penetration to the product core occurs at a faster rate and this in turn reduces the time taken by the straight line portion of heating curve to travel one log cycle. Ball's process time (B) decreased with increase of processing temperature ($p < 0.05$) and was 56, 29 and 10 min for MIB processed at 115, 121.1 and 130 °C, respectively. The total process time, which was found out by adding 58% of CUT to B also showed significant reduction ($p < 0.05$) with increase of retort temperature. The total process time

for MIB processed at 115, 121.1 and 130 °C was 60, 33 and 15min, respectively. Thus thermal processing mackerel in brine at 121.1 °C reduced the total process time by 45% as compared to processing at 115 °C whereas at 130 °C the reduction was 75%.

Cook value is used for the theoretical evaluation of the sensory and nutritional changes of the product during thermal processing. The z-value for cook value can be experimentally determined for different sensory parameters and for different foods (Ohlsson, 1980b).The z-value for the calculation of cook value with respect to different sensory and nutritional parameters are given by Leonard et al. (1964); Ohlsson (1980b). The cook value was found to exhibit an inverse relationship with processing temperature ($p < 0.05$) and was maximum at 115 °C and minimum at 130 °C. A reduction of 36% and 55% in cook value could be attained by thermal processing mackerel in brine at 121.1 and 130°C, respectively, as compared to that at 115 °C. Cook value is the measure of heat treatment with respect to nutrient degradation and textural changes that occur during processing. An important indicator for identifying the conditions that promote better quality retention is Cook value to F_0 value ratio (C_0 / F_0 ratio) Ramaswamy and Grabowski (1999). Ohlsson (1980b) reported that the objective of any process should be to minimize the cook value at any given level of lethality. A low cook value means lower levels of heat induced changes to the sensory and nutritional quality of the food. C_0 / F_0 ratio of mackerel processed at 115, 121.1 and 130 °C is given in Table-14. Processing at 130°C helped to reduce it by half as compared to at 115 °C. The highest Cook value to F_0 value ratio is associated with mackerel processed at 115 °C followed by those processed at 121.1 °C, whereas mackerel processed at 130 °C recorded the lowest ratio ($p < 0.05$). These observations imply that the temperature of processing influences the C_0 / F_0 ratio.

Mansfield (1962) reported that sterilization rates are slower than cooking rates at low processing temperatures and higher than cooking rates at higher temperatures of processing. The extent of C_0 / F_0 ratio is found to influence instrumental texture, color and the sensory parameters. Mackerel processed at 130 °C owing to the lowest ratio, retained better texture and color and scored the highest in sensory evaluation as compared to those processed at 115, 121.1 °C.

Table-14. Heat penetration characteristics of Mackerel processed in brine at 115, 121.1 & 130 °C

Parameter	115 °C	121.1 °C	130 °C
Come up time(min)	6.35 ± 0.25 [a]	6.00 ± 0.29 [a]	7.17 ± 0.31 [b]
j_h	1.16 ± 0.12 [a]	0.92 ± 0.09 [b]	0.81 ± 0.08 [c]
j_c	1.03 ± 0.11 [a]	1.05 ± 0.14 [a]	1.09 ± 0.19 [b]
f_h	18.5 ± 0.23 [a]	16.0 ± 0.19 [b]	13.0 ± 0.17 [c]
U	32.6 ± 1.6 [a]	8.00 ± 0.32 [b]	1.03 ± 0.13 [c]
fh/u	0.57 ± 0.002 [a]	2.00 ± 0.012 [b]	12.6 ± 0.15 [c]
g	0.09 ± 0.002 [a]	1.25 ± 0.06 [b]	10.2 ± 0.34 [c]
B (min)	56.0 ± 1.21 [a]	29.0 ± 1.13 [b]	10.0 ± 1.05 [c]
TPT (min)	60.0 ±1.53 [a]	32.7 ±1.36 [b]	15.0 ± 1.45 [c]
CV (min)	122.30 ± 0.97 [a]	78.0 ± 1.49 [b]	54.5 ± 1.56 [c]
CV/ F_0 Ratio	15.3 ± 0.49 [a]	9.75 ± 0.65 [b]	6.88 ± 0.29 [c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

J_h-Lag factor of heating; j_c-Lag factor of cooling; f_h-Slope of heating curve; U-Time in min for sterilization at retort temperature; g-Final temperature deficit; B-Ball's process time; TPT-Total Process Time; CV-Cook value, CV/ F_0 Ratio- Cook value to F_0 value ratio.

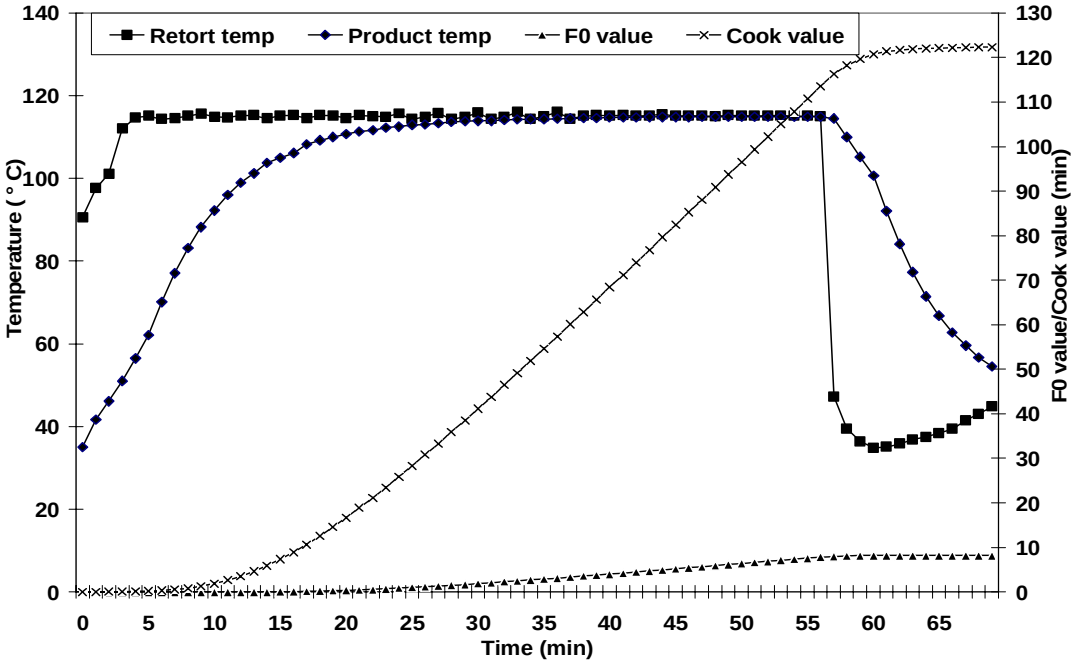

Fig-27. F_0 Value and cook value of mackerel in brine processes at 115 ^{0} C

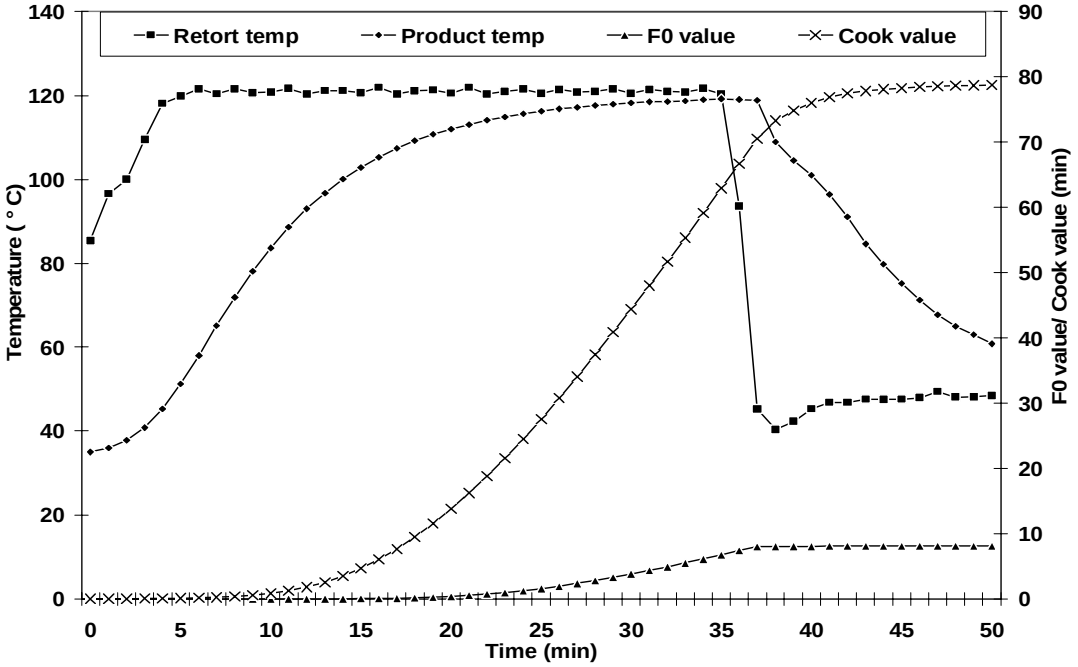

Fig-28. F_0 Value and cook value of mackerel in brine processes at 121 ^{0} C

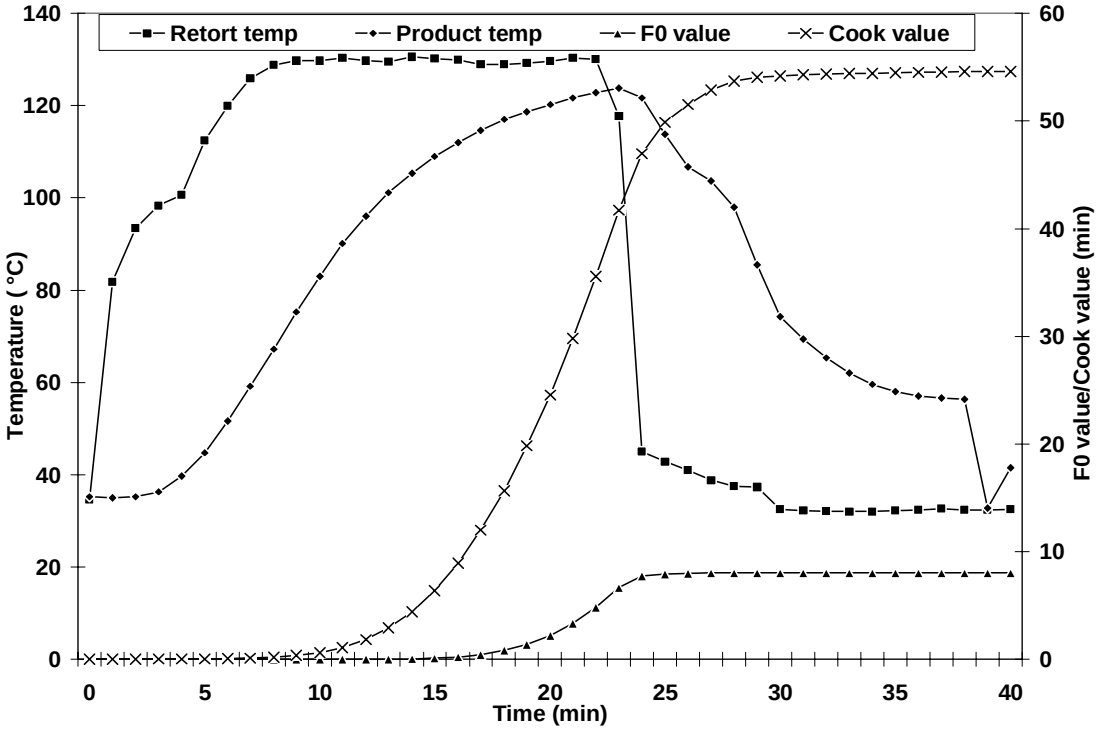

Fig-29. F_0 Value and cook value of mackerel in brine processes at 130 ^{0} C

4.6.2. Effect of different retort temperatures on the instrumental color values

The L*a* b* color values of raw, precooked and processed mackerel are given in Table-15. The raw mackerel meat had L* value of 38.9 which on precooking, increased significantly ($p < 0.05$) to 63.1. This may be due to the leaching out of muscle pigments along with the precook exudates during precooking. This is in agreement with the findings of Haard (1992). Many workers have reported that the increase in L* value during cooking of fish muscle may be due to the leaching of white connective tissue containing collagen located between the segments of muscles (Dunajski,1979; Sikorski et al. 1984; Kimura et al. 1988). Among the thermally processed samples, the L* value decreased significantly ($p < 0.05$) with the increase in processing time or reduction in processing temperature and was 65.2, 62.3 and 59.7 for mackerel processed at 130, 121.1 and 115 °C, respectively. This can be attributed to the Maillard reaction occurred during the heat processing of fish muscle and the dependence of the reaction on the duration of heating (Van Boekel, 1998). Mackerel processed at 115 °C, owing to the comparatively lower processing temperature, took 27 min and 45 min more than those processed at 121.1 °C and 130 °C, respectively to attain the targeted lethality value of 8 min, whereas mackerel processed at 121.1 °C had to be heat processed for 18 min more as compared to those at 130 °C. This clearly indicates that the L* value of mackerel meat is affected by the duration of exposure to heat processing. Raw mackerel meat had a higher a* value of 3.45 due to the presence of the muscle pigments which decreased significantly ($p < 0.05$) to 0.893 upon precooking. This may be due to the heat induced denaturation of myoglobin and oxidation of carotenoid pigments (Haard, 1992). On thermal processing, a* value increased significantly as compared to precooked sample. Among the thermally

processed samples, a* value significantly increased with increase of processing time or decrease in processing temperature and was 0.96, 1.22 and 1.38 at 130, 121 and 115 °C, respectively. As reported by Bhattacharya et al. (1994) and Kong et al. (2007), the increase in a* value at lower retort temperatures can be attributed to the increase in the rate of browning with the increase in duration of exposure to heat treatment. The b* values which was 6.62 for raw mackerel increased significantly ($p < 0.05$) to 11.1 on pre cooking. Kong et al. (2007) reported that the heating up of fish muscle resulted in the increase of b* value due to the heat induced denaturation of myoglobin and oxidation of carotenoid pigments. Significant reduction in b* value could be noticed between precooked and thermally processed samples. Thermal processing at higher temperatures resulted in higher b* values ($p < 0.05$). The b* value of mackerel processed at 115, 121 and 130 °C were 10.04, 10.1 and 11.3, respectively. Bhattacharya et al. (1994) reported that increasing the processing temperature or time increased the visual lightness, but reduced both the redness and the yellowness of salmon muscle.

Table-15. Instrumental color values of raw, precooked and mackerel processed in brine at different retort temperatures

	Raw	**Pre cooked**	**115 °C**	**121.1°C**	**130 °C**
L*	38.9 ± 0.23^{a}	63.1 ± 0.36^{b}	59.7 ± 0.31^{c}	62.3 ± 0.29^{d}	65.2 ± 0.38^{e}
a*	3.45 ± 0.25^{a}	0.89 ± 0.19^{b}	1.38 ± 0.28^{c}	1.22 ± 0.34^{d}	0.96 ± 0.36^{e}
b*	6.62 ± 0.21^{a}	11.1 ± 0.28^{b}	10.04 ± 0.34^{c}	10.1 ± 0.27^{d}	11.3 ± 0.32^{e}

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

4.6.3. Effect of different retort temperatures on the Texture Profile attributes and Warner Bratzler (WB) shear force

The results of texture profile analysis are given in Figure. 30. The various parameters analyzed were hardness 1, hardness 2, cohesiveness, gumminess, springiness and chewiness. Hardness 1 and 2 are the resistance at maximum compression during the 1st and 2nd compression, respectively. The hardness 1 and 2 values for raw mackerel were 4.03 kgf and 3.51 kgf, respectively. On precooking these values decreased to 2.88 kgf and 2.27 kgf, respectively ($p<0.05$). The hardness 1 and 2 values of mackerel processed at three retort temperatures were significantly lower than the precooked samples. Among the thermally processed samples, the hardness 1 and 2 were found to decrease significantly ($p<0.05$) with decrease in processing temperature and were 2.67 and 1.94, 1.93 and 1.31 and 1.80 and 1.21 kgf for mackerel processed at 130, 121.1 and 115 °C, respectively. In all the cases, the hardness-1 values were higher than hardness-2 values. This is because a non compressed sample has a firm texture as compared to already compressed one. The texture of fishes and crustaceans is highly influenced by the collagen content of the meat. The relationship between total collagen content and raw meat firmness has been reported by Sato et al. (1986). They have also reported that the texture of cooked fish meat is affected by the gelatin derived from the muscle collagen. During precooking, the core temperature of mackerel was found to attain 92 °C. Dunajski (1979) reported that the heating up of fish muscle upto 60 °C results in the denaturation

of collagen to gelatin. The lowering of hardness 1 and 2 on precooking and thermal processing of mackerel is due to the effect of temperature on the collagen and the resultant softening of the muscle. Tanaka et al. (1985) reported that thermal processing of mackerel at higher temperature produce firmer muscle. Cohesiveness, the ratio of positive force area during the 2nd compression to that during 1st compression of raw mackerel was 0.23 which decreased to 0.17 on precooking ($p<0.05$) and on thermal processing at 130, 121.1 and 115 °C got further reduced to 0.12, 0.08 and 0.07, respectively. Precooked samples had higher cohesiveness values as compared to thermally processed samples ($p<0.05$). No significant change with respect to cohesiveness could be noted between mackerel processed at 115 and 121.1 °C ($p>0.05$). Dunajski (1979) reported that the collagen fibers of fish muscle loose their original structure and become solubilised when the muscle temperature reaches about 60 °C. During precooking and thermal processing, the core temperature of the muscle is maintained at a temperature above 60 °C. This thermal denaturation of collagen results in a total loss of binding properties of connective tissues. Thus the decreasing trend in cohesiveness exhibited by mackerel meat on precooking and thermal processing can be attributed to the loss of binding properties of connective tissues. Gumminess which is the amount of energy required to disintegrate a semisolid food product to a state ready for swallowing decreased significantly from 0.68 kgf incase of raw mackerel to 0.49 kgf on precooking ($p<0.05$). Thermally processed samples recorded lower value for gumminess as compared to precooked samples. Although samples processed at 130 °C had significantly higher gumminess value as compared to the other two batches, no significant difference could be seen between mackerel processed at 115 and 121 °C.

Springiness which refers to the deformation that the food recovers during the time that elapses between the end of 1st compression and the start of 2nd compression was 1.30 mm and 1.22 mm for raw and pre cooked mackerel. Among the thermally processed samples, mackerel processed at 115 °C had significantly low gumminess value as compared to those at 121and 130 °C whereas no significant variation could be seen between samples processed at 130 and 121°C. Chewiness values for raw, precooked and mackerel thermally processed at 130, 121.1 and 115 °C were 0.89, 0.60, 0.35, 0.16 and 0.13 kgf.mm respectively. Loss of other textural parameters like springiness, gumminess and chewiness also occurs as a result of heat induced changes in muscle.

The WB shear force for raw, pre cooked and thermally processed mackerel is given in Figure.31. It can be seen that shear force also followed the same trend of texture profile. It was found that the raw mackerel muscle was tougher than the precooked one in that the shear force which was 8.19 N for raw mackerel decreased significantly to 6.81 N upon precooking in steam ($p<0.05$). Thermally processed samples had lower shear values as compared to precooked samples ($p<0.05$). The temperature of processing was found to be a significant factor affecting the shear force value of mackerel muscle. Mackerel processed at higher temperature recorded higher shear force values than those at lower temperature due to the reduced time of exposure to thermal processing. The shear values for mackerel processed at 130°C which was 6.30 N, reduced significantly to 5.86 N and 5.46 N upon processing at 121.1 and 115 °C, respectively. Skrede and Storebakken (1986); Bhattacharya et al. (1993) reported that Shear force of fish muscle increased as temperature of processing increased.

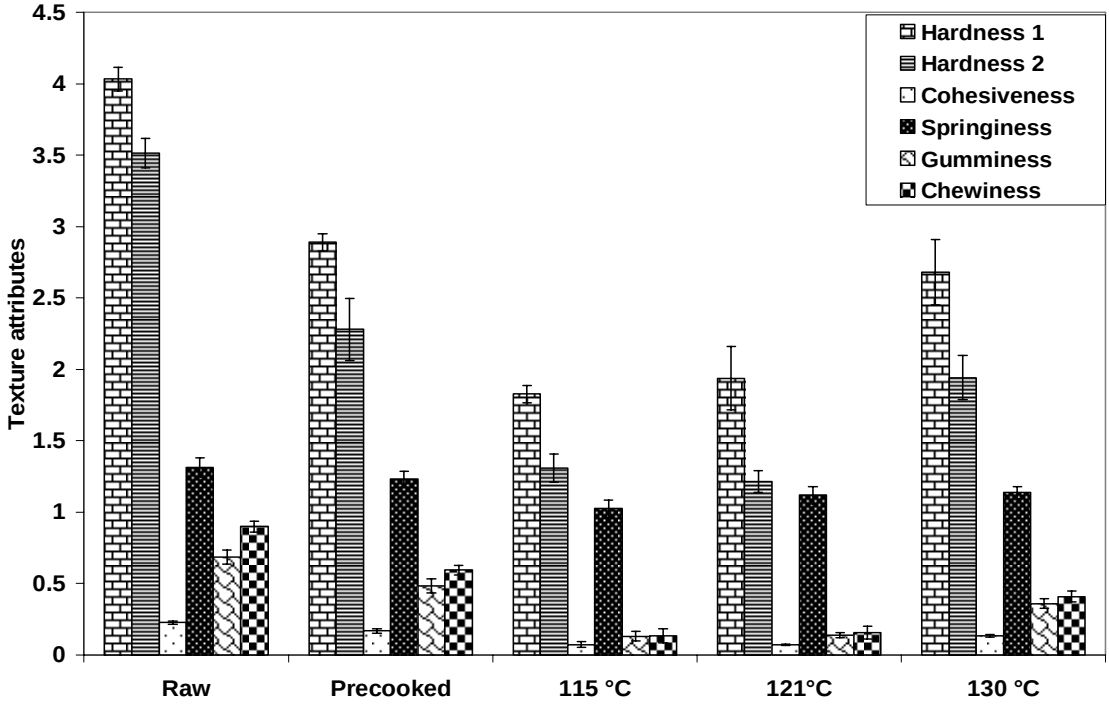

Fig.30. Texture profile attributes of mackerel meat

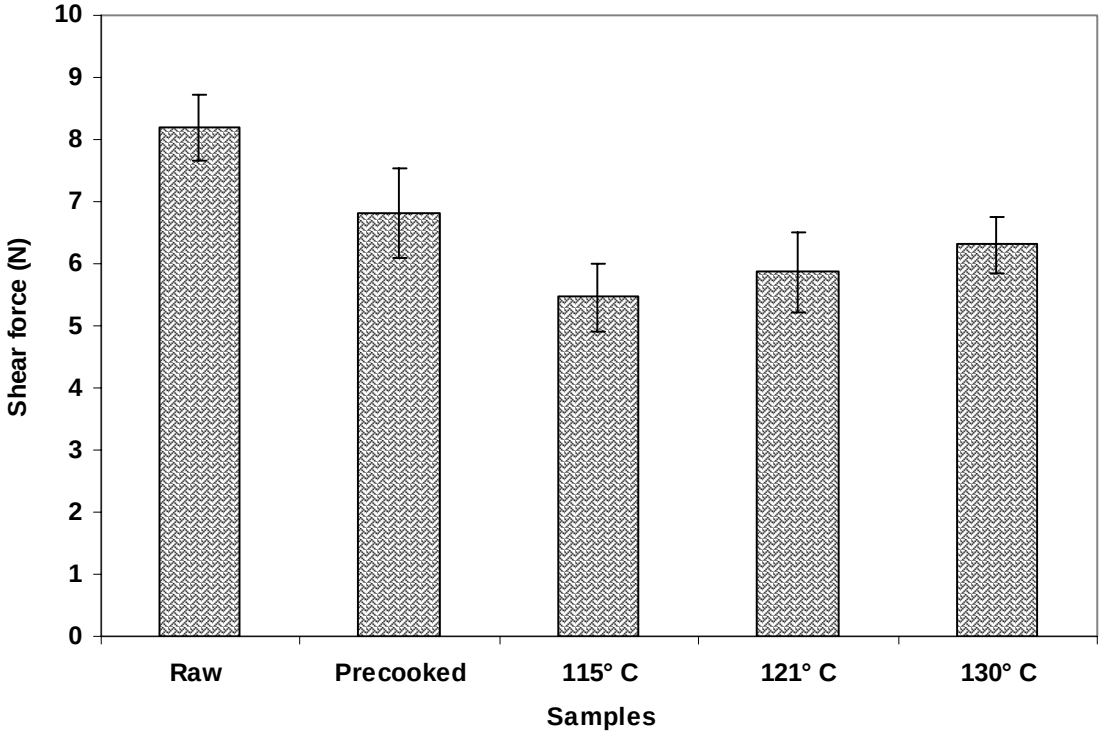

Fig.31 . Shear force values of mackerel meat

4.6.4. Effect of thermal processing on the sensory score of canned mackerel

The sensory score given by the judges is given in Table-16. Mackerel processed at 115 °C was found to be the darkest among the three batches and was given the least score by the panelists whereas the panelists gave mackerel processed at 130 °C maximum score in terms of color. There was significant difference in terms of this sensory attribute between the 3 batches ($p<0.05$). This is in agreement with the findings of instrumental color values. The flavour was not found to be influenced by the temperature of processing ($p>0.05$). The texture parameters of chewiness, succulence, toughness and fibrosity were found to be influenced significantly ($p<0.05$) by the temperature of processing, with the mackerel processed at 130°C recording highest values followed by those processed at 121 and 115 °C. This may be due to the shorter duration of exposure to heat processing given in case of samples processed at 130 °C as compared to those at 121 and at 115 °C. Mackerel processed at 130 °C was given the highest overall acceptability score followed by those processed at 121.1 °C and least score was given to mackerel processed at 115 °C ($p<0.05$).

Table-16. Sensory score of mackerel processed in brine processed at different retort temperatures

	Color	Flavor	Texture				Overall Acceptance
			Chewiness	Succulence	Toughness	Fibrosity	
115 °C	6.87 ± 0.08[a]	7.21 ± 0.08[a]	6.72 ± 0.02[a]	6.87 ± 0.08 [a]	6.35 ± 0.03 [a]	7.82 ± 0.07[a]	7.17 ± 0.05 [a]
121 °C	7.53 ± 0.06[b]	7.24 ± 0.09[a]	7.37 ± 0.05[b]	7.53 ± 0.06 b	7.53 ± 0.02 b	8.04 ± 0.07b	7.64 ± 0.02 b
130 °C	8.28 ± 0.07c	7.33 ± 0.00a	8.38 ± 0.03c	8.28 ± 0.07 c	8.74 ± 0.04 c	8.28 ± 0.09c	8.46 ± 0.01 c

Results are presented as mean (standard deviation (SD) of 10 replications

Values that have different superscript letters (a, b, c) differ significantly with each other ($P<0.05$; Duncan's multiple range test)

4.6.5. Effect of thermal processing at different temperatures on the biochemical parameters of mackerel.

4.6.5.1. Proximate Composition

The proximate composition of raw, precooked and thermally processed mackerel is given in Table-17. The chemical composition of fish muscle varies greatly from one species to another **(**FAO**,** 2002**;** Love**,** 1988**)** and one individual to another depending on age, sex, feed intake, swimming and sexual changes in connection with spawning environment and season (Balogun and Talabi, 1985; FAO, 2002). Processors have a direct interest in the chemical composition of fish, needing to know the nature of the raw material before the techniques of chilling, freezing, smoking or canning can be correctly applied (FAO, 2002).

4.6.5.1.1. Moisture

Water is the principle component in fish and shellfish meat, which varies from 28 to 90% by weight (Stansby, 1962). Moisture content of raw mackerel was 72.3 % which is in agreement with the findings of Chand et al (2001). On Precooking in steam, which is an open process, significant reduction in the moisture content could be observed. As reported by Broek (1965) the precooking of fish flesh leads to the release of a fair amount of water from proteins. The amount varies depending upon the species and quality of fish, for example about 17.5% in case of tuna and 19-34% in case of sardines. Most water in

meat is located within the myofibrils, in the narrow channels between thick and thin filaments; therefore water lost during cooking is a result of protein denaturation and coagulation (Offer, 1984; Bertola et al., 1994). In the present study, moisture content was reduced to 65.2% from 72.3% ($p<0.05$) upon precooking. The reduction in moisture content with precooking is reported by many workers (Joshi and Saralaya, 1982; Mustafa and Medeiros, 1985; Catrillion et al, 1996). In fact one of the main purposes of precooking and draining is to reduce the moisture content of fish muscle and to prevent the large amount of liquor being cooked out of the fish in the can during sterilization. The problems associated with the release of moisture during the thermal processing on the quality of the final product are discussed by Balachandran (2003). Foegeding et al. (1996) reported that the loss of water during cooking occurs as a result of changes in both Myofibrillar and collagen muscle proteins. Understanding the dynamics of moisture loss during cooking is important for process control of final product yield and quality in meat processing industries. No significant difference in the moisture content could be noted between the precooked and thermally processed samples. This present observation is in corroboration with the studies carried out by Perez (1990), which showed that sterilization being a process done with the cans already closed, limits the water loss from the fish muscle. It is very much important to note that among the thermally processed samples, the processing temperature did not have any significant influence on the moisture content while significant difference with respect to this parameter was observed between raw and precooked mackerel meat. The moisture content of mackerel in brine processed at 115, 121 and 130 °C were 63.8, 63.9 and 63.2% respectively.

4.6.5.1.2. Crude protein

The value of fish for human consumption is due to its relatively high protein content, good digestibility and the high biological value of its protein (Seet and Brown, 1983). Sidwell (1981) reported that most finfish muscle tissue contains about 18- 22% protein The crude protein content of raw mackerel was 22.3% which is slightly higher than the reports of Iwasaki and Harada (1985) in case of Pacific mackerel and Gopakumar (1997) in case of Indian mackerel. On precooking under steam, the crude protein content significantly increased to 25.6%. This increase in crude protein level can be attributed to the decrease in moisture content (Castrillion et al, 1996; Gracia et al, 2004). Thermal processing at different temperatures did not bring about any changes in the crude protein level compared to precooked samples. The crude protein content of mackerel processed at 115, 121 and 130 °C were 24.9, 25.15 and 25.5%. This indicates that the crude protein content is independent of processing temperature. Similar trend in the crude protein content of tuna was reported by Castrillion et al. (1996).

4.6.5.1.3. Crude fat

Lipid is the most concentrated form of energy stored in the fish (Love, 1997). Fish lipid is rich in PUFA which makes it an important component in human diet. Many workers have reported that consumption of fish reduce the risk of cardio vascular diseases, promote neural development in infants, cure cancer (Conner, 1997; Kinsella, 1986). Aubourg et al (1990) reported that the quality of canned fish product has close relationship with lipid content and composition. The crude fat content of raw mackerel was 4.2%.This value is similar to the reports of Chand et al.(2001) but significantly lower than the values reported by Gopakumar (1997). The lipid and moisture content of fishes

usually exhibits an inverse relationship. Upon precooking, the fat content increased to 6.30% ($p<0.05$). This significant increase in fat content of fish muscle with precooking is the result of the reduction in moisture content occurred during the precooking stage. Similar trend in the contents of moisture and crude fat contents of fish muscle was reported by Castrillon et al. (1996) in case of precooked tuna. Thermal processing at different temperatures did not bring about any significant changes in the crude fat content of the fish muscle. The crude fat content of mackerel processed at 115, 121 and 130 °C were 6.50, 6.42 and 6.53% respectively ($p>0.05$).

4.6.5.1.4. Ash

Raw mackerel muscle had ash content of 1.50%. This closely agrees the reported values (Chand et al. 2001; Gopakumar, 1997). Upon precooking, the ash content increased from 1.50% to 3.40% ($p<0.05$). This is contrary to the reported trends in the ash content. Many workers reported a reduction in the ash content with precooking and attributed this to the loss of minerals along with the moisture lost during steam cooking. But in the present study, the mackerel meat was given a cold blanching for 30 min in 6% brine solution prior to precooking during which sufficient amount of salt must have penetrated the muscle. Thus, the increase in ash content is contributed by the increased salt content of fish muscle upon cold blanching. Thermally processed samples recorded higher ash content than precooked samples. The ash content of mackerel processed at 115, 121 and 130 °C were 4.50, 4.20 and 3.85 % respectively. This can be attributed to the effect of the packing media. Mackerel pieces were canned in 2% brine. Thus the salt pick up from the packing medium is responsible for the higher ash content of thermally processed samples. Among the thermally processed samples, mackerel processed at 115

°C was found to have higher ash content followed by samples processed at 121 °C. As reported by Pirazoli et al.(1980), this may be due to the higher rate of salt absorption occurred as a result of longer duration of heating in case of samples processed at 115 and 121 °C compared to those at 130 °C.

Table-17. Proximate composition of raw, pre cooked and thermally processed mackerel

	Raw mackerel	**Precooked**	**115 °C**	**121 °C**	**130 °C**
Moisture (%)	72.30±1.88 [a]	65.20±1.64 [b]	63.80±0.40 [b]	63.90±0.34 [b]	63.20±0.26 [b]
Crude protein	22.30±0.46 [a]	25.26±0.42 [b]	24.90±0.62 [b]	25.15±1.20 [b]	25.50±1.42 [b]
Crude fat	4.20±0.54 [a]	6.30±0.62 [b]	6.50±0.44 [b]	6.42±0.84 [b]	6.53±0.72 [b]
Ash	1.50±0.02 [a]	3.40±0.08 [b]	4.50±0.12 [c]	4.20±0.22 [c]	3.85±0.02 [d]

Results are presented as mean ± standard deviation (SD) of 3 replications

Values that have different superscript letters (a, b, c , d, e) differ significantly with each other (P<0.05; Duncan's multiple range test)

4.6.5.2. Volatile Compounds

TMA and TVB-N are reported to be good indicators of freshness in case of fishes. The source of volatile bases in fish muscle is TMAO. The origin, distribution and the role of TMAO in fishes is well documented (Gibb and Hatton, 2004; Seibel and Walsh, 2002). Hughes (1959) experimentally proved that cooking of fish muscle sealed in glass tubes results in breakdown of TMAO into TMA-N, ammonia and mono methylamine. Testing the changes in the low molecular weight nitrogen compounds during thermal processing is reported as an objective method of testing canned products (Faber and Ferro, 1956., Slabyj and True, 1978). The TVB-N and TMA-N content of Raw, precooked and thermally processed mackerel meat are given in Table-18. The TVB-N

and TMA-N content of raw mackerel were 7.2 and 2.48 mg N/100 g respectively. The TVB-N and TMA-N content of fresh mackerel as reported by Surendran and Gopakumar (1985) and Chand et al (2001) were 7.90 and 2.52 and 7.40 and 1.2 mg N/100 g respectively. Thus it can be seen that the levels of TVB-N and TMA-N content of the mackerel samples fall within the reported range, indicating the freshness of the samples. On precooking, both the TVB-N and TMA-N content increased significantly. The TVB-N and TMA-N content of precooked samples were 13.8 and 4.24 mg N/100 g respectively ($p<0.05$) which are 48 and 42% higher than the contents of the respective component in raw fish muscle. Among the thermally processed samples, the levels of both TVB-N and TMA-N were found to increase significantly with the increase in the duration of heating. The levels of TVB-N in case of MIB processed at 115, 121 and 130 °C were 26.40, 21.24 and 17.64 mg N/100 g respectively ($p<0.05$) whereas, the levels of TMA-N were 10.40, 7.80 and 6.12 for MIB processed at 115, 121 and 130 °C respectively ($p<0.05$). The % increase in TVB-N and TMA-N content of thermally processed samples compared to raw samples are 73 and 76, 66 and 68 and 59 and 59 % for MIB processed at 115, 121 and 130 °C respectively. The reason for the higher levels of both TVB-N and TMA-N with reduction in retort temperature or increase in the duration of heating can be assumed from the heat penetration data. From the heat penetration data (Table-16), it can be seen that MIB processed at 115 °C, took 27 and 45 min more than samples processed at 121and 130 °C whereas MIB processed at 121°C took 18 min more than samples processed at 130 °C to attain the targeted sterilization value of 8 min. Many workers have reported the effect of heating time on the extent of formation of both TVB-N and TMA-N. Chia et al. (1983) in a comparative study on the

effect of different containers on the quality attributes of various fishery products heat processed to a common sterilization value found that the levels of both TVB-N and TMA-N were higher in case of retort pouch products than canned products owing to the longer processing time taken by the latter to attain the targeted sterilization value. Gallardo et al. (1990) reported that the increase in TVB-N content of fish muscle with heating can be attributed to the heat induced breakdown of TMAO and some amino acids. Another noteworthy finding is that although heat processing of fish muscle resulted in the increase of both TVB-N and TMA-N, their levels in all the samples analyzed were within the acceptability limit of 35-40 and 10-15 mg N/100 g for TVB-N and TMA-N respectively (Conell, 1995). As reported by Gallardo et al. (1990), if a good quality raw material is employed and an appropriate sterilization treatment is carried out, canned samples will have levels of volatile base nitrogen compounds within a satisfactory and acceptable limit

4.6.5.3. Sulfhydryl group

Sulfhydryl (thiol) and disulfide bonds play an important role in maintaining the structural and functional properties of native proteins. During thermal processing, disulfide cross-linking of protein molecules due to oxidation of sulfhydryl groups may occur. This has been demonstrated in a variety of muscle foods by many workers (Opstverdt et al. 1984; Hamm and Hoffmann, 1965). Maloney et al. (1966) have shown that the antioxidant nature of -SH compounds inhibits the rate of rancidity in lipids. Cooked meat becomes rancid more quickly than unheated meat, which could be attributed to the heat induced reduction in -SH Compounds in cooked meats (Hofmann and Hamm,1978). The changes happening to sulphydryl and disulfide groups and

formation of hydrogen sulfide are of particular interest in case of canned foods as it has significant impacts on the taste and texture of these foods (Hamm and Hoffmann, 1965). The changes in the -SH group during the various stages of thermal processing is given in Table-18. From the Table, it can be seen that the -SH group content of raw mackerel is 72.10 μmol -SH g^{-1} DM. Precooking for 30 min resulted in significant reduction in the -SH group content of fish meat and it reduced to 60.12 μmol SH g^{-1} DM ($p<0.05$) thereby resulting a 17 % reduction as compared to raw samples. Hamm and Hoffmann (1965) reported that at temperature more than 70 °C, the -SH group decreases, because of its oxidation to disulphide bonds. During the precooking process, the core temperature of the muscles was found to attain a range of 75-80 °C. Upon thermal processing, the -SH group content of the mackerel sample was found to reduce significantly and among the thermally processed samples, and the rate of reduction increased with the increase in the duration of exposure to heating. The -SH group content of MIB processed at 115, 121 and 130 °C were 34.46, 46.2 and 52.2 μmol SH g^{-1} DM respectively ($p<0.05$). A percentage wise analysis of the reduction in -SH group contents at various retorting temperature in comparison with the raw samples shows that processing at higher temperature retains more -SH group components. Processing at 130 and 121 °C helped in attaining 73 and 64% retention of -SH group components whereas at 115 °C, retention of only 48% could be attained in comparison with the raw samples. This clearly indicates that the higher processing time taken by samples processed at 115 °C resulted in more than 50% loss of -SH group components as compared to raw samples. Synoweicki and Shahidi (1991) reported approximately 50% reduction in -SH groups in seal meat after heating for 40 min at 80 °C. If we compare the effect of increasing the retort temperature

from 115 to 130 °C on the retention of -SH group components, it can be seen that the -SH group content of samples processed at 130 °C is 11.73 and 34.16 % higher than the samples processed at 121and 115 °C respectively whereas, samples processed at 121 °C has 25.41% more content of -SH group as compared to samples processed at 115 °C. Many workers have reported on the effect of heating time on the extent of degradation of -SH group. Opstverdt et al. (1984) found a linear decrease in the content of SH group when the ground meat of two species of fish was heated for a period of 20 min at temperature intervals ranging from 40-115 °C. Thippeswamy (2000) in a comparative study on the effect of various processing methods on the -SH group compounds of milk fish, reported a higher degree of retention of -SH group in samples subjected to deep frying (170 °C) than retorted samples (115 °C). The author concluded that although the temperature of retorting is much lower than the deep frying, the higher loss of -SH compounds must have occurred as a result of increased duration of exposure to heat treatment in case of retorted samples.

Table-18. TVB-N, TMA, Sulphydryl group contents of raw, pre cooked and thermally processed mackerel

	Raw mackerel	**Precooked**	**115 °C**	**121 °C**	**130 °C**
TVB-N (mg N/100 g)	7.20±0.05[a]	13.80±0.02[b]	26.40±0.06[c]	21.24±0.10[d]	17.64±.08[e]
TMA (mg N/100 g)	2.48±0.01[a]	4.24±0.04[b]	10.40±0.11[c]	7.80±0.05[d]	6.12±0.03[e]
-SH group (μ mol SH g^{-1} DM)	72.10±0.22 [a]	60.12±0.35 [b]	34.46±0.20 [c]	46.20±0.15 [d]	52.34±0.36[e]

Results are presented as mean ± standard deviation (SD) of 3 replications

Values that have different superscript letters (a, b, c , d, e) differ significantly with each other (p<0.05; Duncan's multiple range test)

4.6.5.4. Amino acid profile

An important aspect of protein from its nutritional perspective is its amino acid composition. Fish muscle is an excellent source of amino acids. Tarr (1999) reported that fish is a high quality protein food as it contains all the essential amino acids in sufficient amounts. Balachandran (2001) reported that fish protein can be utilized for supplementing the vegetable proteins so as to provide a nutritionally balanced protein source due to its abundance of many essential amino acids. The nutritional value of food protein depends upon the distribution of the amino acids that can be absorbed in the bio available form. This bioavailability may be modified during processing and storage. Most phenomena involved in the improvement in or loss of both nutritional and physiological properties of food proteins result from the protein denaturation and chemical modification of amino acids (Finot, 1997). Thus the amino acid profiling of mackerel muscle subjected to thermal processing at various retort temperatures will help to reveal the changes occurring to the various amino acid fractions during various steps of commercial canning and at different retort temperatures. The amino acid composition of raw, precooked and processed mackerel meat is given in Table-19.

Table-19. Amino acid composition of raw, pre cooked and thermally processed mackerel (g/16g N2)

	Raw	**Precooked**	**115 °C**	**121 °C**	**130 °C**
Asp	10.74±0.12	11.00±0.22	11.43±0.33	11.71±0.36	12.35±0.69
Thr	3.82±0.03	3.77±0.03	3.65±0.01	3.41±0.02	3.42±0.19
Ser	4.75±0.06	4.76±0.04	4.89±0.07	4.91±0.11	4.93±0.16
Glu	18.92±0.21	18.51±0.32	18.58±0.25	18.13±0.36	18.44±0.65
Pro	3.92±0.05	3.83±0.02	3.52±0.06	3.73±0.01	3.81±0.03

Gly	4.97±0.04	5.16±0.05	5.16±0.15	5.18±0.22	5.11±0.33
Ala	9.30±0.23	10.30±0.42	10.17±0.31	10.21±0.35	10.25±0.51
Cys	1.59±0.001	1.35±0.002	0.56±0.01	0.88±0.001	1.02±0.11
Val	5.59±0.04	5.85±0.03	6.36±0.19	6.79±0.18	6.54±0.27
Meth	2.79±0.01	2.60±0.01	1.25±0.02	1.57±0.02	1.74±0.06
Iso	3.97±0.04	4.48±0.02	4.52±0.11	4.50±0.23	4.42±0.16
Leu	8.64±0.22	8.86±0.18	8.69±0.24	8.43±0.34	9.21±0.45
Tyr	3.16±0.03	2.81±0.06	2.08±0.03	2.01±0.01	2.06±0.03
Phe	5.63±0.02	5.39±0.05	5.20±0.13	5.90±0.11	5.43±0.15
His	5.85±0.04	4.95±0.02	3.98±0.02	3.64±0.04	3.85±.11
Lys	2.81±0.01	2.69±0.01	2.15±0.03	2.27±0.02	2.39±0.04
Arg	2.14±0.02	2.10±0.03	2.17±0.01	2.36±0.01	2.29±0.05
Try	1.21±0.01	1.20±0.03	1.19±0.01	1.23±0.01	1.20±0.02

Results are presented as mean ± standard deviation (SD) of 3 replications

Values that have different superscript letters (a, b, c , d, e) differ significantly with each other ($P<0.05$; Duncan's multiple range test)

It can be seen that the most predominant amino acid in raw mackerel muscle is glutamic acid followed by aspartic acid and alanine. The predominance of gluatamic acid and aspartic acid in the muscle of Atlantic mackerel was reported by Iwasaki and Harada (1985). In the present study, the first three dominant amino acids constituted about 39.50% of the total amino acid content of raw mackerel meat. Cysteine and argenine were the two limiting amino acids. The ratio of Essential amino acids (EAA) to Non essential amino acids (NEAA) of mackerel was 0.74. Pre cooking resulted in some modifications in the contents of some amino acids although glutamic acid, aspartic acid and alanine remained as the three major amino acids quantitatively. They contributed 40.60% of the total amino acids in pre cooked mackerel meat. The amino acids that

recorded increase upon precooking were aspartic acid, glycine, alanine, valine, isoleucine and leucine. The amino acids that recorded reduction in its content with precooking were threonine, glutamic acid, proline, cysteine, methionine, tyrosine, phenylalanine, histidine, lysine and argenine. Among these, Cystein, methionine and lysine recorded significant reduction upon pre cooking ($P<0.05$). The % retention of Cysteine, methionine and lysine of precooked mackerel as compared to raw samples were 85, 83 and 95.7% respectively. A similar trend in the contents of theses three amino acids with pre cooking was reported by Seet and Brown (1983). However the one noteworthy finding regarding the lysine is that its retention value during precooking is better than the reported values in other fishes. Analysis of the thermally processed samples shows that, irrespective of the temperature of processing glutamic acid, aspartic acid and alanine forms the first three major amino acids quantitatively. Except sulphur containing amino acids and lysine, thermal processing at different temperature did not bring about any noticeable changes in the amino acid composition of the mackerel muscle. The % retention of cysteine in case of mackerel processed at 130, 121 and 115 °C in comparison with raw samples was 64, 50 and 35% respectively. A comparison of the effect of different retort temperatures on the cystein retention shows that samples processed at 130 °C retained 14and 45% more cystein than those processed at 121 and 115 °C while processing at 121 °C resulted in 36% more retention of cystein as compared to processing at 115 °C. The loss of cysteine can be well related to the reduction in SH group upon heat processing. In comparison to raw samples, mackerel meat processed at 115, 121 and 130 °C had 45, 56and 62% retention of methionine. Among the thermally processed samples, at 130 °C methionine retention of 10and 28% could be attained in comparison to those at 121and 115 °C.

Between 121and 115 °C, methionine retention of 20% could be attained. Donoso et al. (1962) reported that processing conditions have effect on the amount of amino acids especially sulfur containing which are not stable under heat processing. The decrease in the contents of sulphur containing amino acids with heat treatment can be attributed to their heat sensitive nature (Nielsen, et al. 1985) As cystein is heat sensitive, careful preservation may be of importance not only for nutritive value but also for the protection against several classses of diseases. Hamm and Hoffman (1968) reported that a deficiency of total cytine (sum of cysteine and cystine) in nutrition increases the requirements of one of the essential amino acids, methionine which can be metabolized to cysteine. Lysine retention in thermally processed samples as compared to raw samples was 85, 81 and 76 % for mackerel processed at 130, 121 and 115 °C. The level of lysine retention in the present study closely resembles the reported values. Seet and Brown (1983) reported retention of 80-85% for lysine in case of canned tuna. This indicates that better lysine retention is accompanied with higher retort temperature or shorter duration of heating. Hodge (1953) reported that a major cause of heat induced reduction in nutritive value of protein is the non enzymatic browning in which the Є amino group of lysine is the most reactive one. Analysis of L*, a* and b* values of mackerel processed at different temperatures clearly indicates the occurrence of non enzymatic browning, resulting in the decrease of L* value and increase of b* value with duration in he heating time. Lysine has been reported as a limiting factor in protein quality as food (Tanaka et al.1980) and thus thermal processing which decreases lysine content can result in the decreased nutritional value of the protein. A comparison of the lysine retention among the heat processed samples shows that samples processed at the shortest time (130 °C) had

better retention than those at lower temperatures. Lysine retention of 5and 10 % could be attained at 130 °C, as against samples processed at 121 and 115 °C while samples processed at 121°C had 5.3% more retention of lysine than those at 115 °C. Over processing was reported to reduce the lysine content in canned tuna (Castrillion et al., 1996). Amino acid analysis of raw, pre cooked and thermally processed mackerel reveals that except sulphur containing amino acids and lysine, the contents of various amino acids fractions remained more or less the same. This well agrees with the reports of Seet and Brown (1983) who reported that the amino acid profile of tuna canned at different temperatures remained without any noticeable changes.

4.6.5.5. Mineral composition

Aquatic organisms absorb minerals from their diet and surrounding water and deposit them in skeletal tissue, muscle and different organs (Lall, 1989). As reported by Haard (1992), minerals are significant because of their nutritive value, safety considerations and their influence on taste and flavor. The mineral content of raw, precooked and thermally processed mackerel meat is given in Table-20.

Table-20. Mineral composition of raw, precooked and thermally processed mackerel

	Na (mg/100g)	**K (mg/100g)**	**Ca (mg/100g)**	**Mg (mg/100g)**	**Zn (mg/100g)**	**Fe (mg/100g)**
Raw mackerel	85.0± 1.25[a]	365.6±2.36[a]	52.0±0.88[a]	39.2±0.68[a]	0.72±0.04[a]	6.24±0.28[a]
Precooked	87.4± 1.02[b]	352.4±1.98[b]	49.2±1.08[b]	32.6±0.42[b]	0.65±0.02[b]	5.74±0.42[b]
115^{0}C	88.8± 0.98[c]	345.8±1.22[c]	46.7±1.18[c]	30.8±0.38[c]	0.64±0.03[b]	4.65±0.36[c]
121^{0}C	88.4± 1.44[c]	343.8±2.82[c]	47.3±1.06[c]	31.6±0.86[c]	0.64±0.01[b]	4.78±0.26[c]
130^{0}C	88.1± 1.18[c]	346.1±3.45[c]	47.5±0.78[c]	31.2±0.22[c]	0.63±0.02[b]	4.82±0.18[c]

Results are presented as mean ± standard deviation (SD) of 3 replications. Values that have different superscript letters (a, b, c) differ significantly with each other ($p<0.05$; Duncan's multiple range test)

4.6.5.5.1. Sodium (Na)

Raw mackerel meat had Na content of 85.0 mg/100g. This level falls within the range of 30.0- 90.0 mg/100g prescribed by Nettleton (1985) for fresh fish fillets. Dudek et al (1989) reported Na content of 80.0 mg/100g in case of raw mackerel. Although the fish muscle has undergone considerable loss of moisture during the pre cooking stage and a significant reduction in Na content was expected along with the precook exudate, the precooked samples had significantly higher levels of Na as compared to raw samples ($p<0.05$). On pre-cooking, the Na content of meat increased to 87.4 mg/100g. This increase in the levels of Na can be attributed to the uptake of Na by the fish muscle during cold blanching in brine. Lall (1995) reported that processed fishery products have higher Na content due to the addition of salt or Na containing compounds during processing. The Na content of mackerel processed at 115, 121 and 130 ^{0}C was 88.8, 88.4 and 88.1 mg/100g respectively indicating that the change in the retort temperature has no significant effect on the Na content of the meat ($p>0.05$). But thermally processed samples had significantly higher levels of Na as compared to precooked samples ($p<0.05$). This may be due to the diffusion of Na from 2% Na Cl solution which was added to the cans as packing medium prior to sealing. Dudek et al (1989) reported that canned shrimp blanched in brine prior to sterilisation process had significantly higher levels of Na content than raw meat. Sodium is important in osmoregulation, acid-base

balance and membrane potential of cells, as well as in the active transport across cells membranes (Lall, 1995).

4.6.5.5.2. Potassium (K)

It is the most abundant mineral in fish muscle tissue (Lall, 1995). The K content of raw mackerel is 365.6 mg/100g which is higher than the range of 250.0- 320.0 mg/100g reported by Kinsella (1988). On precooking, the K content significantly decreased to 352.4 mg/100g ($p<0.05$). This can be attributed to the leaching of this mineral along with the precook exudate. Thermal processing resulted in further decrease in the K content of the fish. This is due to the diffusion of this element into the packing medium during sterilisation process (Seet and Brown, 1983). Slabyj and Carpenter (1977) reported significant reduction in the K content of blue mussel meat after canning. Dudek et al.(1982) in a comparative study of the mineral retention in fishery products subjected to various methods of processing, reported that canned products have low retention of K. Thermal processing at different temperatures did not have any effect on the K content of mackerel meat. Potassium serves as the monovalent cation to balance intercellular anions and participate in neuromuscular functions (Lall, 1995).

4.6.5.5.3. Calcium (Ca)

Seafood is one of the useful sources of Calcium. In fishes Ca is mainly concentrated in the bones. Raw mackerel meat had a Ca content of 52.0 mg/100g. Generally, the Ca content of fin fishes is lower than crustaceans as the latter require Ca for shell formation. Pre cooking resulted in significant reduction in the Ca content of the mackerel meat which again can be attributed to the leaching effect. The calcium content

of precooked mackerel was 49.2 mg/100g ($p<0.05$). Slabyj and Carpenter (1977) reported significant losses in Ca content with steaming in case of blue mussel meat. Although thermal processing resulted in reduction in the Ca content as compared to pre cooked meat, its content was independent of retort temperature. Seet and Brown (1983) also reported a significant loss of Ca in canned tuna as compared to precooked and raw samples. The Ca content of mackerel processed at 115, 121 and 130 ^{0}C was 46.7, 47.3 and 47.5 mg/100g respectively ($p>0.05$). Nettleton (1985) reported that seafood can be a useful source of Ca and their Ca contents vary significantly from 6-120 mg/100g depending on the species and the processing method. An advantage of fish canning is that the sterilisation process makes the bones soft textured and thus edible providing an important source of Ca (March (1982).Calcium is required for growing children and for women especially during reproductive years to minimize subsequent osteoporosis (NIH, 1984).

4.6.5.5.4. Magnesium (Mg)

In fish muscle, the distribution of Magnesium is similar to that of Calcium and phosphorus with the major proportion being located in the bones (Lall, 1995). Fishery products like many other animal products are poor sources of Mg. The Mg content of raw mackerel meat was 39.2 mg/100g. Lall (1995) reported that the average Mg content of the edible portions of most fin fishes and shell fishes range between 21.0 and 45.0 mg/100g. Precooking of mackerel in steam resulted in significant reduction of Mg content. The Mg content of precooked mackerel meat was 32.6 mg/100g ($p<0.05$). The Mg content of fish was reported to be decreased significantly ($p<0.05$) after frying, grilling, baking and boiling (Gokoglu et al. 2004). Castrillion et al. (1986) reported a

significant reduction in the Mg content of tuna followed by steaming. Thermal processing of mackerel in brine did not bring about any further significant reduction in Mg content and among the thermally processed samples, the processing temperature was not found to have any significant effect on the Mg levels. Schroeder et al. (1969) reported significant loss of Mg in canned haddock. Mg is a prosthetic ion in enzymes that hydrolyse and transfer phosphate groups. Hence it is essential for energy requiring biological functions such as membrane transport, generation and transmission of nerve impulse, contraction of muscles and oxidative phosphorylation. It is also essential for the maintenance of ribosomal structure and thus protein synthesis.

4.6.5.5.5. Zinc (Zn)

Zinc is an essential element for growth, reproduction, wound healing and normal functioning of the immune system and other physiological processes. The essential function of Zn is based on its role as an integral part of a number of metalloenzymes and as a catylist for regulating the activity of the specific Zn dependent enzymes. In general, fish have low Zn contents when compared to mollusk and crustaceans. The average Zn content of marine and freshwater fish is approximately 0.80 mg/100g. The mackerel meat used in the present study had a Zn content of 0.72 mg/100g. This agrees with the reports of Dudek et al. (1989). Precooking in steam followed by thermal processing at different temperatures did not result in any significant reduction in Zn content. The Zn content of precooked and mackerel processed at 115, 121 and 130 ^{0}C were 0.65, 0.64, 0.64 and 0.63 mg/100g respectively. Many workers have reported increased levels of Zn after canning in metallic cans (Schroeder et al, 1967; Dudek et al, 1989).

Fish and fishery products are normally packed in cans coated with oleoresinous C enamel containing zinc oxide to prevent the black discolouration due to formation of iron sulphide. As reported by Schroeder et al. (1967) the increased levels of zinc in canned products is due to the Zn dissolution from the enamel coating. Zn levels in canned products contradictory to the reported levels attained in the present study can be attributed to the use of polymer coated tin free steel cans that are devoid of zinc containing enamel coating.

4.6.5.5.6. Iron (Fe)

The levels of iron found in sea foods can range from 0.3-7.0 mg/100g (Nettleton, 1985). Kinsella (1988) reported that shellfish and dark fleshed fish like mackerel, sardines etc. are reasonably good sources of Fe, supplying 1.0-2.0 mg/100g muscle. Fe plays vital role in several biochemical reactions. The Fe content of raw mackerel was 6.24 mg/100g. This is significantly higher than the values reported in Indian mackerel by Gopakumar (1993). Fischer and Deng (1977) reported that dark muscle contains more Fe than light muscle. Precooked samples had Fe content lower than that of raw meat, due to the leaching of this element along with the precook exudates. The Fe content of precooked mackerel was 5.74 mg/100g ($p<0.05$). Thermal processing at different temperatures still lowered the content of Fe in the sample. The Fe content of mackerel processed at 115, 121 and 130 ^{0}C was 4.65, 4.78 and 4.82 mg/100g respectively ($p<0.05$). This clearly indicates that the Fe content of thermally processed mackerel meat is independent of the variation in processing temperature. The reduction in Fe content of thermally processed samples observed in the present study is in contrary to the reports of Dudek et al (1989). Increased levels of Fe in samples thermally processed in metallic

cans have been reported by these authors and they have attributed this to the leaching of this element from the base metal of the can through the imperfections on the tin and lacquer layer. Lall (1995) reported that the Fe content of processed fish and fishery products may be influenced by the widespread possibilities of contamination from ferrous metals during cooking and processing. However, the polymer coating of TFS cans that substitutes the lacquer coating of conventional cans acts as an efficient barrier thereby preventing any possible food metal interaction and the subsequent leaching of iron from can body to the food.

Although the Fe content of processed meat suffered leaching during precooking and subsequent thermal processing, its level is either equal to or superior to the reported values for iron in canned products by Tuzen and Soylak (2007) and Ikem and Egiebor, (2005) Although considered a trace mineral, diets lacking in iron can contribute to the deficiency condition known as anemia (Tuzen and Soylak , 2007). As a component of haem in haemoglobin, myoglobin, cytochromes and other proteins, Fe plays an essential role in the transport, storage and utilization of oxygen. It is also a cofactor or a number of enzymes.

The mineral content of raw, precooked and mackerel processed at different temperatures reveals the effect of various stages of canning process on the contents of Na, K, Mg, Ca, Zn and Fe. The levels of these elements in raw meat agree the reported values (Gopakumar, 1993). Among the 6 minerals analysed, K is the most abundant element while Zn is the least abundant one. Except sodium all the other 5 elements suffered significant reduction on precooking in steam. This agrees with the reports of mineral loss followed by precooking in tuna by Castrillion et al (1986). Precooked

mackerel meat had significantly higher sodium content than raw meat. This is due to the absorption of Na occurred during the cold blanching done in 10 % brine. Thermal processing resulted in significant reduction in the levels of minerals except sodium. Leaching of minerals into the liquid portions could be responsible for the low retention of minerals other than sodium in canned meat (Seet and Brown, 1983). The significantly higher levels of sodium noticed in thermally processed samples is due to the diffusion of this element from the packing media (2% brine) during heat processing in addition to the salt uptake occurred during the cold blanching process. Lall (1985) reported that unlike vitamins and lipids, the nutritive value of minerals are not affected during the processing but there may be a net gain or loss of some elements. The losses of inorganic elements during processing are mainly physical, due to liquid discarded from fishery products. Comparison of the mineral composition of mackerel meat processed at 115, 121 and 130 ^{0}C reveals that the temperature of processing has no significant effect on the elemental composition of fish meat.

5. SUMMARY AND CONCLUSIONS

In the present work, Indigenous polymer coated Tin Free Steel cans were analyzed for their suitability for thermal processing and storage of fish and fish products following standard methods. These cans were having water holding capacity of 180 ml and were found to withstand internal air pressure of 30 psi for about 15 seconds without undergoing any bulging or leakage through the double seam area. The cut out analysis of polymer coated tin free steel cans showed that the base plate and end plate have thickness of 0.19 mm (0.15 mm of base steel + 20 μ PET coating on either side) and 0.28 mm (including PET coating on either side), respectively. The percentage overlap of polymer coated tin free steel cans is 63 % which is higher than the required value of 45%. The results of analysis for double seam parameters done using manual method was compared with that of the results of analysis using the semi automatic double seam analyzer SEAMetal 9000M and good agreement could be achieved between the two methods. Testing for lacquer coating integrity of polymer coated TFS cans using LCB detector indicated that 97% of the tested cans had polymer coating free from any defects. The cans were found to be resistant to sulphide blackening which indicates the perfection of the polymer coating. Dealmination test using different solvents showed that the PET coating is resistant to delamination by solvents except chloroform and carbon tetra chloride. The values of water soluble, chloroform soluble and n-heptane soluble extractives of polymer coated TFS cans were 6.9, 0.64 and 25.0 mg/liter respectively.

The indigenous polymer coated TFS cans were compared with other commercially available containers like tin and aluminium cans for its suitability for thermal processing and storage of fish and fish products. All the three types of containers were found to have percentage overlap which is much higher than the prescribed limit. Upon testing for pressure holding capacity, both tin and TFS cans were found to withstand an internal air pressure up to 30 psi without showing any bulging for the prescribed period of 15 seconds while the aluminium cans bulged at 27 psi**.** Test for lacquer coating integrity using LCB detector

indicated that the polymer coating of TFS cans are superior to the lacquer coating of tin and aluminum cans. About 85 % of the tin and 77 % of aluminium cans failed the test, indicating the poor coating integrity of these cans. In some cases, the imperfections on the coating were even visible to naked eye in the form of scratches. On the contrary, about 97 % of the TFS cans tested were found to pass the LCB test indicating the perfection of the polymer coating. The extractive value for tin, aluminium and TFS cans using distilled water as simulant was 16.4, 12.2 and 6.9 ppm, respectively whereas the chloroform soluble extractives for the same were 0.80, 0.72 and 0.64 ppm respectively. The overall migration values of tin, aluminium and TFS cans using n-Heptane were 48.2, 34.5 and 25.6 ppm respectively. The suitability of tin, aluminium and TFS cans for storage of fish products showed that tin cans developed rusting on external surface even at the sixth month of storage while TFS cans were free from any signs of rusting even at the end of 18 months storage study. Aluminium cans lost its characteristic appearance on storage due to the formation of its oxide. TFS cans exhibited excellent content releasing property while fish pieces were found attached to the walls of tin and aluminium cans. Development of black dicolouration could be noted on the inner surface of tin cans while TFS cans were free from any sulphide stains on storage. Analysis for various metallic contaminants indicated that the levels of tin, lead and iron contents of products packed in tin cans and aluminium content of products packed in aluminium cans increased with storage while no significant increase in the level of chromium and iron could be found in samples stored in polymer coated TFS cans.

The raw materials used for the development of ready to eat thermally processed fish products were found to be of fresh condition. The values for various biochemical and microbiological parameters of the raw materials were well within the limits.

Based on the analysis of commercial sterility, instrumental colour, texture, WB-shear force and sensory parameters, squid masala processed to F_0 value of 8 min with a total process time of 38.5 min and cook value of 92 min was chosen as the optimum for squid

masala in tin free steel cans while shrimp curry processed to F_0 7 min with total process time of 44.0 min and cook value of 91.1 min was found to be ideal and was selected for storage study.

Squid masala and shrimp curry thermally processed in indigenous polymer coated TFS cans were found to be acceptable even after one year of storage at room temperature based on the analysis of various sensory and biochemical parameters.

Mackerel in brine was processed at different retort temperatures of 115, 121 and 130°C to a common F_0 value of 8 min. The study indicated the suitability of indigenous polymer coated TFS cans for processing at high temperature and pressure. The analysis of heat penetration parameters indicated that lag factor of heating (j_h) and heating rate index (f_h) decreases while the lag factor of cooling (j_c) increases with increase of processing temperature. Ball's process time (B) decreased with increase of processing temperature ($p < 0.05$) and was 56, 29 and 10 min for MIB processed at 115, 121.1 and 130 °C, respectively. The total process time, which was found out by adding 58% of CUT to B also showed significant reduction ($p < 0.05$) with increase of retort temperature and was 60, 33 and 15 min for MIB processed to 115, 121.1 and 130 °C respectively. The cook value was found to exhibit an inverse relationship with processing temperature ($p < 0.05$) and was maximum at 115 °C and minimum at 130 °C. The temperature of processing was found to influence the C_0 / F_0 ratio and the highest and lowest Cook value to F_0 value ratio was associated with mackerel processed at 115 °C and 130 °C respectively. Analysis of instrumental colour values showed that both L* and b* values decreased significantly while a* value significantly increased with the increase in processing time or reduction in processing temperature. Instrumental analysis of texture showed that hardness-1 & 2 decreased with reduction in retort temperature while cohesiveness value did not show any appreciable change with decrease in temperature of processing. Other texture profile parameters like gumminess, springiness and chewiness decreased significantly with increase of processing time. W-B

shear force values of mackerel meat processed at 130 °C were significantly higher than those processed at 121.1 and 115 °C. Mackerel processed at 130 °C were given the highest rating for various sensory parameters by the panelists upon sensory analysis. Processing at different retort temperatures did not bring about any significant changes in the proximate composition of mackerel meat. The levels of TMA and TVBN were found to increase with the increase in duration of heating. A similar trend was exhibited by –SH group. Amino acid profiling of mackerel processed at different retort temperature showed that except sulphur containing amino acids and lysine, thermal processing at different temperature did not bring about any noticeable changes. Tehrma;l processing at different temperatures did not bring about ay significant change in the mineral content of mackerel meat.

- The study indicated that the indigenous polymer coated TFS cans are suitable for thermal processing and storage of various fish and fish products.
- Indigenous polymer coated TFS cans were found to be superior to the conventional tin and aluminium cans
- Ready to eat squid masala and shrimp curry processed in TFS cans could be stored at room temperature with acceptable qualities for more than one year.
- HTST processing of mackerel in brine helped in reducing the process time and improving the quality.
- The study also indicated that indigenous polymer coated TFS cans with easy open ends can be a viable alternative to the conventional tin and aluminium cans. The industry can utilize these cans for processing ready to eat fish and shell fish products for both domestic and export markets. This will help in reviving the canning industry in India.

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