HOKKAIDO UNIVERSITY

Title	STUDIES ON FREEZE-DRYING MECHANISM OF MARINE PRODUCTS
Author(s)	KOBAYASHI, Kiichirô
Citation	MEMOIRS OF THE FACULTY OF FISHERIES HOKKAIDO UNIVERSITY, 17(1-2), 1-70
Issue Date	1969-12
Doc URL	https://hdl.handle.net/2115/21849
Type	departmental bulletin paper
File Information	17(1_2)_P1-70.pdf

STUDIES ON FREEZE-DRYING MECHANISM OF MARINE PRODUCTS

Kiichirô KOBAYASHI

Faculty of Fisheries, Hokkaido University

Contents

I. Introduction

The technique of freeze-drying which had been successfully applied to the setting of biological specimens or to the preservation of medical articles, has been further developed indeed in America, England, Canada, Germany, Denmark, France and Japan since 1960 as one of the best preservation methods for many foodstuffs. It has nowadays reached the stage where it can yield acceptable products on vegetables, fruit juice, eggs, meats and their cookings (stew, hamburg, steak chop, etc.)[1] But only a few marine products have been dried in applying this method. Among those are sliced cod, boiled shrimp, boiled crab and so on.

In Japan, the original freeze-drying test was carried out in 1960 at the Agricultural Food Research Institution. A freeze-drying processing factory was established under its instructions and produced several kinds of cooked foods, such as shrimp calei, meat calei, Miso soup, Chawan-mushi, etc. What is more, other food factories and food research institutes have tried to test and produced several kinds of freeze-dried foos, but as yet did not succeed in putting them on the market except for a dried green tea powder.[2]

In order to solve many problems concerning the preservation of marine products,—unstable fish catch, excessive catch in a short fishing time, keeping

freshness of fish—the freeze-drying technique seems to be the ideal method. However, this technique is still at an initial stage in Japan in regards to its practical use because of the small number of people who consume freeze-dried fish as daily food.   As the Japanese generally take marine products fresh or briefly broiled rather than cooked along with vegetables and seasonings, they severely call for good taste, better appearance and nice smell of reconstructed food.

An analytical process for the freeze-drying technique was suggested by Kimura as shown in Table 1.   The author classified methodologically the method of study as follows;

1. Physical and mechanical field
    Theory and mechanism on freezing, drying and reconstruction
2. Histological field
    Bio-histological alternation by freeze-drying and reconstruction
3. Bio-chemical field
    Denaturation of the protein and the fat, examination of taste
4. Technical field
    Freeze-drying equipment, packaging
5. Economical field
    Production cost, marketing survey

Table 1.   Freeze-drying process

	Fresh raw material
Pre-treatment process	Washing
	Cutting and shaping
	Treatment to prevent quality change
	To flavour
Freeze-drying process	Refrigeration
	Vacuum dehydration
	Finishing
After treatment process...............	Selection and inspection
	Packaging
Reconstruction process	Rehydration

Therefore many researchers have been done by an all-out plan rather than by individual work.

The pilot researcher on freeze-drying was E.W. Flosdorf,[3] and his writing "Freeze-drying" issued in 1949 has become a motive force of research and development on freeze-drying.

In the second World War, the Danish Government has done great efforts to put this technique for foodstuffs into practice.   After the War this technique and equipment were transferred to Aberdeen in Scotland and a food research institute was established there in 1951.   The results done during 1955~1960 were issued in the

following book, "The Accerelated Freeze-drying Method of Food Preservation".[4]

Quartermaster Food and Container Institute in Canada has also issued "Freeze-dehydration of Food"[5] in 1962.

Many reports[6~7] and writings concerning this technique have been published and a number of meetings have been held in many countries. However, many problems[8~14] about this method have yet remained in suspension. For example, Decareau[15] said in his book that the development of freeze-dried food is now recognized to be so much remarkable but more additional researches are needed in the next three fields—processing, product and equipment.

As a subliming drying process of materials in vacuum chamber is only a simple physical phenomenon, its mechanism and theory look very unsophisticated, but biochemical and biohystological alternations with many complicated factors are often generated during freeze-drying process and precise measurements of physical quantities—temperature, pressure, weight, etc are so difficult that the analytical explanation of this processing is not yet accomplished nowadays.

In recent year, microscopic observation for the hystological fibers of dried foods has been developed. Dr. Nei[16~18] observed the drying process of several kinds of media through an electron-microscope.

Theory, mechanism and equipment concerning the freeze-drying process of ground products can be applied in the same manner for marine products, but special characteristics of marine products offered us a deal of interesting problems, —difficulty of application, merits of products, taste alternation, etc.

A few reports mainly dealing with process improvement and quality denaturation and prevention can be had in foreign literatures.[19~20]

Nowadays, in Japan, many researchers—Kimura,[21~28], Ueoka,[29~33] Shibazaki,[34~37] Tamoto,[38] Takahashi,[39] Toyomizu,[40~42] Yamazaki,[43~45] etc.—have made studies on freeze-drying of fish, which could gradualy make the following points clear; relations between refrigeration and dehydration, drying conditions effects on dried fish quality, freeze-dried fish meat denaturation during reservation, etc. However, these reports are almost all concerned with qualitative rather than quantitive research.

The author has made some experimences on the freeze-drying of marine products since 1961 and reported much informations[46~50] on them. But unless the mechanism of freeze-drying—relations among drying temperature, vacuum material temperature, water content, drying rate, etc.—become quantitatively clear, many experinces on freeze-drying may be carried out in groping about in the dark. Of cource, several theoretical reports based on the heat transmission theory or the gas molecular theory have been issued, but they have not always given us satisfactory solutions, for it seems to be difficult to apply these thories to the practical food processing.

The author has tried to get a simple equation of freeze-drying by simplifying many complex conditions as much as possible. Relations between many factors concering the subliming drying process can be understood by this equation.

Then the author has made many experiences on the freeze-drying of marine products under similar condition, and got quatitativey the drying characteristics of them.

Microscopic photographs were also added to investigate the aspect of tissue fibers.

II.　Theory and Mechanism of Freeze-Drying

When a pre-frozen fresh material is placed in a vacuum cabinet, sublimation will begin from the surface of the material by an enthalpy holding in itself, and will continue during the time when small heat quantity transferred from the cabinet wall or the other thing is becoming in equilibrium to the subliming latent heat quantity. If the heat transfer were comletely shut out, sublimation would cease at a certain low tempertature. Then, in order to continue sublimation, the heat quantity just suitable to sublimation should be supplied to the material from outside.

How does this heat supply act upon the subliming-rate and subliming inter-face temperature, and what influences do the drying-temperature, vacuum degree, shape and size, organization and construction give to them ? Answers to these questions belong to the physical and mechanical research field on freeze-drying process, and is just the object of the author's experiment. It may be the best way to get a theoretical equation including whole factors having connections with this process. However, the equation would be of no purpose unless the solution should easily be obtained.

The author has tried to make clear the freeze-drying mechanism by improving

a comparatively simplified theoretical equation.   Therefore, the following assumptive conditions become necessary;

(1).   A flat material has a large area in comparison with its thickness.   Sublimation is done only in the direction of a normal line at the surface.

(2).   As sublimation advances, the subliming surface intrudes parallel to the surface into the material, and after that a porous dried layer is formed.

(3).   The upper surface temperature of a material is kept at constant level and heat transfers only in a normal line direction from the surface to the bottom.

(4).   As a porous dried layer has by far a smaller heat capacity than a frozen part, the transferred heat quatitity is consumed only to the interface sublimation. Then the temperature rise of a material is considered to be negligibly small.

(5).   A subliming vapour grown up at an interface passes through a porous dried layer and emits out from an upper surface.

(6).   A porous dried layer consisted of many unsystematic small pores with blind alleys, branches and curves, but now is assumed to consist of many capillary tubes.

With these assumption, as Fig. 1 shows, supposing that a flat material with thickness (L) be putting freeze-drying into practice, after some times (t), a dried
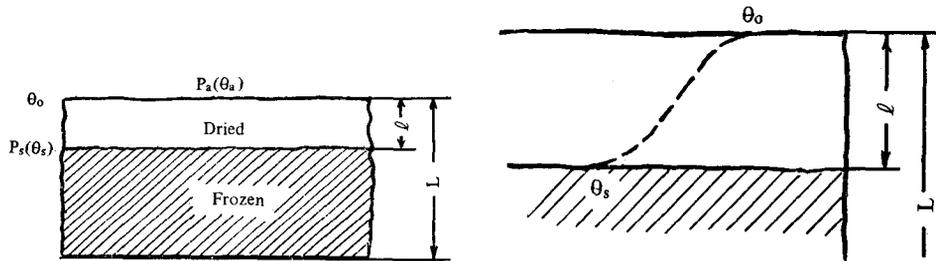

Fig. 1(a)   Fig. 1(b)

Fig. 1 (a).   Sectional view of material during freeze-drying
Fig. 1 (b).   Temperature gradient at the dried layer with thickness (l)

layer with thickness (l) be formed at the upper part of it, the transferred heat quantity will be

$$Q = - K \cdot d\theta/dl$$

Where

Q=transferred heat quantity in cal/cm^2.min
$d\theta/dl$=temperature gradient in the normal line direction at the surface
K=heat conductivity of a dried layer in cal/cm.min.°C
When both (K) and $(d\theta/dl)$ ae constant, then

$$Q = K \cdot (\theta_o - \theta_s)/l \qquad\qquad (1)$$

Where

θ_o=surface temperature in °C

θ_s=subliming interface temperature in°C

Here, (K) and $(d\theta/dl)$ should be discussed.

1). (K) value depends on a vacuum degree in extra high vacuum,[53] but in practical use of ordinary freeze-drying process, it may be safely said that (K) value is nearly constant.

2). (K) value also depends on a moisture content of a dried layer.[51] As the moisture content gradually decreases as the drying goes on, (K) value also changes, but a measurement of moisture content during drying is so difficult that (K) value is considered to indicate the mean value of it throughout the drying. Namely, here (K) is regarded to be constant for one material.

Nei has measured the moisture content change by weighing the dried layer of samples at every stage of drying.

Henceforth, the author wishes to put forward his argument as (K) and $(d\theta/dl)$ are in this case constant.

Now, vapour sublimated at the frozen interface should escape out from the surface passing through the porous dried layer. The driving force to emit out this vapour is directly in proportion to the pressure gradient along the vapour stream in vacuum (Darcy's law).[54] Then the subliming vapour quantity emitted out through the dried layer per area unit is presented as follows in time unit;

$$q = -\varphi \cdot dp/dl$$

Where

q=subliming vapour quantity per area unit, time unit g/cm².min

dp/dl=pressure gradient in a normal line diretion at the upper surface

φ=vapour transfer coefficeint[55] of a porous dried layer g/cm.min.mmHg

Conductivity means the vapour quantity passing through a porous dried layer per time unit when 1 mmHg of pressure difference exists between both end of a small pore 1 mm in length. Putting (d) as a diameter of a small pore, (φ) is said to be in proportion to (d^4) in a viscous stream,[71] and (d^3) in a molecular stream. (φ) is also depends on vapour temperatur and pressure.

As a dried layer includes in itself many kinds of small pores of irregular shapes and arranged at random, (φ) is not a constant value at any thickness of a dried layer. But, here, the outhor has dealt with (φ) as a mean value of heat transfer coefficeint of each pore.

Then the author wishes to put forward his argument as (φ) and (dp/dl) being constant, likewise (K) and $(d\theta/dl)$.

Here, he gets

$$q = \varphi \cdot (p_s - p_a)/l \qquad (2)$$

Where

p_s=satulated vapour pressure at the subliming interface

p_a=atmosphere saturated vapour pressure near the condenser

The equation (1) means a heat transfer phenomenon and (2), mass transfer phenomenon.   Hitherto, many researchers have treated either (1) or (2) separately,[56~60] but the author has treated to combine (1) and (2) as one phenomenon by the point of heat balance theory.

Assuming that the whole conducted heat quantity is consumed only to the sublimation of ice, he gets the following equation;

$$K \cdot (\theta_o - \theta_s)/l = \lambda \cdot \varphi \cdot (p_s - p_a)/l \qquad (3)$$

Where

λ=latent heat of ice cal/g

Clausies-Claperon's theory says;

$$\log p_s = a + b/(273 + \theta_s)$$

Where

(a) and (b)=constant

This equation says that (p_s) has a linear connection with θ_s.

Then he can put;

$$p_s = a \cdot \theta_s \qquad (4)$$

Where

a=convention coefficeint

(p_a) is closely resembling a partial vapour pressure round the condenser.

Then he can put;

$$p_a = \beta \cdot \theta_a \qquad (5)$$

Where

β=convention coefficient

Putting (4) and (5) into (3), he gets;

$$\theta_s = (K \cdot \theta_0 + a \cdot \varphi \cdot \beta \cdot \theta_a)/(K + \lambda \cdot \varphi \cdot a) \qquad (6)$$

The equation (6) shows that when (φ) and (K) values are regarded to be constant, the subliming interface temperature (θ_s) is decided as a linear function of (θ_0) and (θ_a).

The author has tried to make numerous calculations in the following two cases;

1. K=0.005 cal/cm,min.°C

λ=675 cal/g

θ_a=-44°C $(p_a$=0.06 mmHg)

θ_o=15, 40, 60, 100°C

2. K=0.005

λ=675

$\theta_a = -60°\text{C}$ $(p_a = 0.008 \text{ mmHg})$

$-39°\text{C}$ $(p_a = 0.1 \text{ mmHg})$

$\theta_o = 40°\text{C}$

Several lines plotted on a semi-logarithmic paper in Fig. 2 show the relations between (θ_s) and $(\log \varphi)$ in the cases of 1 and 2.
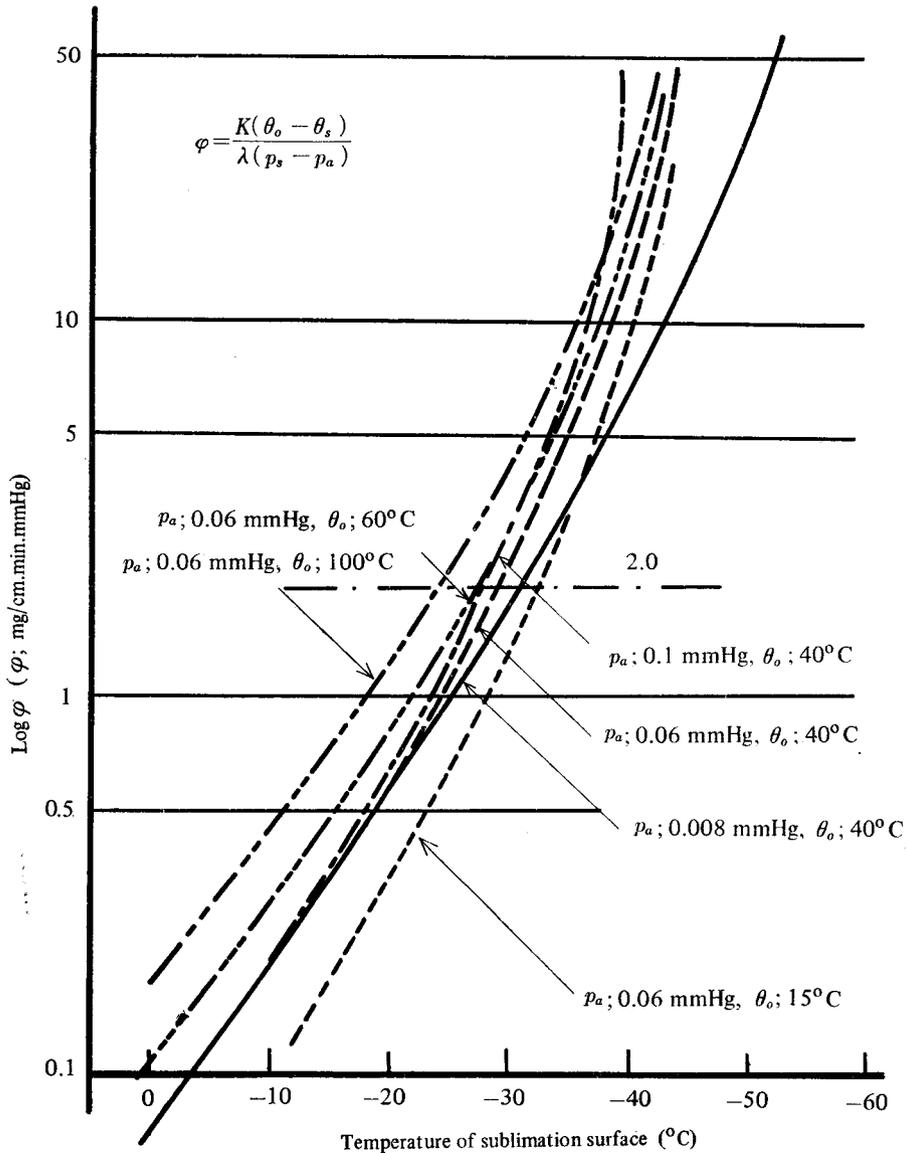
$$\varphi = \frac{K(\theta_o - \theta_s)}{\lambda(p_s - p_a)}$$

p_a; 0.06 mmHg, θ_o; 60° C

p_a; 0.06 mmHg, θ_o; 100° C

2.0

p_a; 0.1 mmHg, θ_o; 40° C

p_a; 0.06 mmHg, θ_o; 40° C

p_a; 0.008 mmHg, θ_o; 40° C

p_a; 0.06 mmHg, θ_o; 15° C

Log φ (φ; mg/cm.min.mmHg)

Temperature of sublimation surface (°C)

Fig. 2. Relations between temperature of sublimation surface and vapour transfer coefficient of dried layer

Here, the author will explain the direction for the use of this graph.   At a certain time, the drying conditions is supposed to be the same as in the case 1, that is;

$K=0.005$

$\theta_a=-44°C$

$\theta_o=40°C$

$\lambda=675$

Let's obtain the subliming interface temperature (θ_s), whn $(\varphi)=2.0$.   From one line in Fig. 2, he gets;

$\theta_s=-29°C.$

A saturated vaour pressure (p_s) fitting for $\theta_s=-29°C$ is 0.31 mmHg

Then a driving force $p_s-p_a=0.31-0.06=0.25$ mmHg

Subliming vapour quantity at $l=0.2$ cm is calculated by this formula(2),

$q=2.0·0.25/0.2=0.0025$ g/cm^2.min$=2.5$ mg/cm^2.min

If an atmospheric pressure (p_a) were risen up by a condenser capacity drop, namely $p_a=0.1$ mmHg

Then $p_s-p_\alpha=0.31-0.1=0.21$ mmHg

The emissive vapour quantity would become;

$q=2.1$ mg/cm^2.min

In order to fill up this decrease $(2.5-2.1=0.4$ mg/cm$_2$.min), (θ_s) rises up to increase the suturated vapour pressure at the subliming interface, and the conductive heat quantity deceases by reducing the temperature difference between the upper surface temperature and the subliming interface temperature.

This action may be considered as a kind of self control system.   Namely, in proportion as (θ_s) rises over or falls down, this self-control action works in the opposite direction, and finally, attending with a damping oscillation,[62~63] (θ_s) reaches a certain settled temperature $-27°C$.   But it is so difficult practically to measure a subliming interface temperature and this oscillating phenomenon.

Regarding the former, it is due to a subliming interface movement, and the latter is due to the uncertainty of a small temperature change measure by the thermometer time lag, and a large heat capacity of a frozen part which causes insensible temperature change measurements.   Nei[62] also reported that the drying-rate oscillation was detected in an unstable first stage of sublimation.

Now, the author will discuss the effects of drying temperature.

A drying temperature means that of a material during the drying process, but as it depends on time and place, a tray temperature in contact with a material was considered as a drying temperature.   As before mentioned, it corresponds to (θ_o).   If (θ_o) is risen up, inferring by the equation (6), (θ_s) and $(\theta_o-\theta_s)$, it must also have a certain increase.   This temperature rise causes successively a conductive heat quantity increase, a drying-rate increase, a drying time reduction.

The higher the drying temperature becomes, the shorter the drying time becomes. But too high temperature makes a material turn out bad, so a drying temperature shoud be kept under a certain optimum temperature, lest a dried material should detect any quality denaturation.

Ueoka[30] reported that no protein denaturation was got under 70°C of a tray temperature, and much denaturation was distinctly noticed above 80°C, and there were remarkable differences of rehydrating-rate and meat tissue reconstruction between fresh fish meat and dried fish meat, even if it was dried at 54–56°C.

Fish meat is dried at low temperature, and, after being reconstructed, it resembles fresh meat. Accordingly, an optimum drying temperature should be kept at the highest limit 35°C.

Secondarily, the author will discuss the effects of a vacuum. A vacuum degree depends on a trap temperature which is difficult to keep practically under –50°C —corresponding saturated vapour pressure is 0.03 mmHg. Calculating a vacuum degree effect on a drying-rate by the equation (6), a drying-rate increase will not be anything so large as to be expected, even if a material is dried in a lower vacuum. For instance, when $\varphi = 2.0$, $\theta_o = 40°C$ and (p_a) is fallen down from 0.06 mmHg ($\theta_a = -44°C$) to 0.0185 mmHg ($\theta_a = -70°C$), a drying-rate increase is at most 2.08%. Contrarily, when $\varphi = 2.0$, $p_a = 0.06$ mmHg, (θ_a) is risen up from 40°C to 60°C, a drying-rate increase can reach 26.3% above.

Now, going back to the equation (2), it will not come into being when l=0.

In this case, it should be discussed as a free surface evaporation in a vacuum.

A subliming vapour quantity at the frozen free surface in vacuum is shown by Langmuir's formula[64] as follows;

$$q = \frac{p_s}{\sqrt{2\pi R}} \cdot \sqrt{\frac{M}{T}} \quad g/cm^2 \cdot min$$

Where

   p_s = saturated vapour pressure of ice under an absolute temperature

   R = gas constant

   M = molecular weight of water

   T = absolute temperature of ice

Calculating drying-rate at a surface temperature –30°C by this formula,

   $T = 273 + (-30) = 243°C$

   $M = 18$ g

   $p_s = 0.03$ mmHg

Then a subliming vapour quantity (q) in an absolute vacuum is 0.282 g/cm².min.

But a practical subliming vapour quantity is so much smaller than this calculated value, because, it prevents the evaporation that vapour molecules come into collision with residual air molecule in vacuum.

Then the author puts a coefficient (γ) in Langmuir's formula,

$$q = \gamma \cdot \frac{p_s}{\sqrt{2\pi R}} \cdot \sqrt{\frac{M}{T}}$$

Where

$$1 > \gamma > 0$$

It means a constant value which depends on a frozen surface condition and a vacuum degree.

The term looked upon as a constant surface sublimation, said to be "The stage of the constant rate of drying". At the end of this stage, the drying-rate suddenly falls, which is due to the occurrance of a resistance of heat and vapour transfer by the growth of a dried layer.

This stage is said to be "The first stage of the decreasing rate of drying".

Next, after the whole ice was sublimed and no ice remained in a material, undrozen water is still existing, which is said to be a bound water.[65~67] It needs great energy and a long time to remove this water. This term is said to be "The second stage of the decreasing rate of drying" and drying-rate remarkably falls down at this stage. These three stages are seen both in an ordinary drying process and the freeze-drying process. Chiba[68] has certified the presence of these three stages by experiments on rat serum.

Now, in order to plot these three stages on a graphic paper, the following method is generally used, that is, to put a residual water content on the abscissa, and drying-rate on the ordinate. Here, the drying-rate can be obtained by means of the following four operations;

a. measurings of the decreasing weight and drying time of a material
b. plotting these measured values on a graphic paper
c. differenciating the above curve graphically by time
d. dividing the obtained differencial values by an effective subliming area of a material

The residual moisture content is obtained by the next operation; a freeze-dried material is crushed into pieces and heated by an ultrared rays lamp within the limits of not being burned. The initial weight of a material (W_o) minus the remained material weight (w_d) is an initial water content. Putting a notation (W) on a measuring weight of a material at every time interval of a drying process, the residual moisture content is shown in the following formula;[69]

$$\frac{W - w_d}{W_o - w_d} \cdot 100\%$$

Besides, there is another way to put a drying-rate on the ordinate and a drying time on the abscissa. Naito and Sahara[63] have explained the drying process in

this way and got the following empirical formula;

$$q = q_o \cdot e^{-\delta t}$$

Where

    q=drying-rate

    q_o=constant drying-rate

    t=drying time

    δ=Naito's coefficient

This formula is very convnient to indicate a rough characteristic of a freeze-dried material druing drying process, but the author has preferred to adopt the former method. If perculiar values of a heat conductivity and vapour transfer coefficient under a certain condition were obtained by its drying-rate—residual moisture content curve, the drying-rate and drying time under the other condition could be calculated by the equation (1), (2), and (6).

At the end of a drying process, the drying-rate falls noticeably and drying time is lengthened. This stage is due to a very small and slow evaporation of a part of non-frozen bound water in a material. This drying time elongation has great influence upon the cost of a freeze-drying process, but to what extent should a minimum water content be needed for drying food is still awaiting further information. This lowest point of such determination depends upon a certain species of dried food and a preservation method. In this research, the final moisture content after the secondary stage of a drying method remained just a small percent, but some reports[70] said that it needed less than 1% for preservation.

Many arguments on a final moisture content after freeze-drying have been presented, but sufficient results could not be obtained because of the difficulties in measuring a residual moisture content during the process, or the lack of accuracy of measuring apparatuses. The author will outline a few of these arguments.

(a). The time when the temperature of the last dried point in a material is close to the drying temperature (tray temperature), is regarded to be the end of a freeze-drying process.

(b). The time when the decrease of a weight druing drying reaches nearly zero, is regarded to be the end of a freeze-drying process.

(c). The time when the increase of a vapour pressure around a drying material reaches nearly zero, is regarded to be the end of a freeze-dying process.

III. Experimental Apparatus

The experimental apparatus which has been used in this research was basically designed by the author, and was made with the co-operation of Nippon Shinku Hoso Co. and Misaki Reiki Co. It was completed in Nov. 1962, and three years later, a

hot water heating system was improved into an ultrared rays heating system.   The
reason is that it was not easy to measure a weight decrease by a hot water heating
system directly contacting with a material surface, but it is convenient when
using an ultrared heating system which could radiate apart from a material.   Fig.
3 shows the diagrammatic sketch of the freeze-drying apparatus, and Table 2 shows
the parts of this apparatus.   For the purpose of measuring the material tem-
perature, several thermocouples made by Chino Manuf. Co. were used.   The
electro automatic balancing recorder was used also.   Several thermisters made by
Shibaura Manuf. Co. were used for measuring the inner cabinet temperature and
trap temperatures.

VC; Drying cabinet	LV; Leak valve	T; Thermister
RC; Refrigeration coil	V; Pneumatic valve	EV; Expansion valve
VJ; Vacuum joint	BC; Bellows coupling	PV; Packless valve
RT; Refrigeration cabinet	WP; Water pump	VP; Vacuum pump
RP; Refrigeration piping	GT; Geissler tube	R; Refrigerator
UR; Ultrared heater	PB; Pilani gauge	S; Volt-stat
CV; Controle valve		

――――――― Evacuation piping

━━ ━━ ━ Cold water circulation with cooler working

━━━━━ Freon circulation with refrigerator working

〰〰〰 Ultrared heater control wiring

Fig. 3.   Schematic arrangement of freeze-drying unit

Table 2. Technical data of freeze-drying unit

Over-all dimensions
              height   2200 mm
              width   2500 mm
              depth   1650 mm

Preliminary freezing cabinent construction

	outside	inside
height	760 mm	400 mm
width	945 mm	550 mm
depth	885 mm	500 mm

        stainless steel rectangular cabinet, sharp freezing, foam polystyrene thermal insulator, freezing capacity 800 Cal/hr

Trays
        size 350×450×13 mm, 4 plates in one batch, max. loading ca. 6 kg of marine raw materials

Refrigerator
        2.2 kw electric motor drive, capacity 800 Cal/hr, refrigerant Freon R-22, sharp freezing

Vacuum drying cabinet construction
        mild steel cylindrical vessel, internal surface is protected by stainless steel plates.

                diameter   650 mm
                length   650 mm
                inside volume   212 litre

        ultrared heating (200 v, 300 w×4), volt-stat control

Evacuating system
        1 ps rotary pump

Condenser
        mechanical refrigerated condenser, size 400 mm dia., 500 mm length, inside volume 58 litre, capacity 800 Cal/hr, temperature as low as −50°C

Instruments
        temperature; thermocouples and thermisters
        vacuum;   3 Pilani gauges and 1 Geissler tube
        weight;   remote controle balance

The author found out that it was very difficult to measure the correct temperature of a material or the inside of a cabinet, because of the difficulties of setting closely the thermocouples in the appointed places, or of keeping the material away from the heat transmission along the thermometer lead wires. For the purpose of measuring the vacuum degree at three inside points, Pilani gauges were used, which were made by Shimazu Manuf. Co. and in order to measure the weight change, the Kett moisture content meter was used, and its lever balance was reconstructed to the chain loading type remotedly controlled by a small motor. By reading the change of the chain length through the peep window, the author could get the weight change of a material at any drying times. Fig. 4 shows this apparatus and Fig. 5 shows the relation between the chain length and the material weight change.
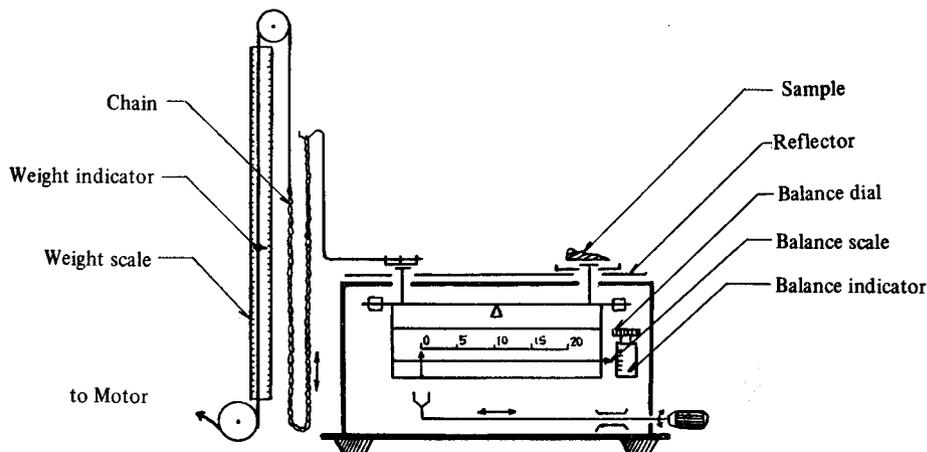
Fig. 4. Schematic figure of chain balance
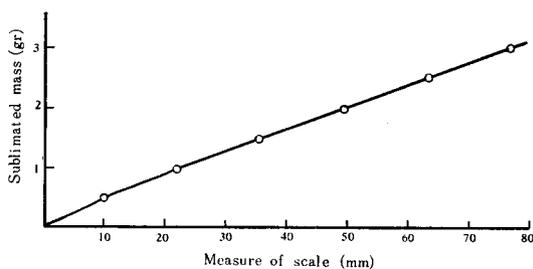
Fig. 5. Calibration curve of balance

This apparatus can help perceive a minimum visible reading of the chain
length of 0.5 mm and 25 mg material weight change.

IV. Choice of Raw Materials

Materials used in the preliminary experiments;
Potato: *Solanum tuberosum* L.
Whale meat: *Balaneoptera borealis* Lessgn
Salmon meat: *Oncorhynchus masow* Brevoort
Prawn: *Pandalus hypsinotus* Brandt
    Materials used in the freeze-drying experiments;
Potato: *Solanum tuberosum* L.
Atka mackerel meat: *Pleurogrammus azonus* Jordan et Metz
Tuna meat: *Thunnus thynnus* (Linne)
Halibut meat: *Paralichthys orivaceus* Temminck et Schlegel

Squid meat: *Ommasirphes sloam pacificus* Steenstrup
Octopus: *Ocutopus vulgaris* Cuvier
Abalone: *Nordotis discus hannai* (Ino)
Scallop adductor muscle: *Patinopecten (Mizuhopecten) yessoensis* (Jay)
Short necked clam: *Tapes (Amygdala) Philippinarum* A. Adams et Reeve
Clam (Ezo-Bakagai):   *Mactra sulcataria* Reeve
Prawn: *Pandalus hypsinotus* Brandt
Matured eggs of sea urchin: *Strongylocentrotus nudus* (A. Agassiz)
Kelp (Makonbu):   *Laminaria japonica* Areschoug

V. Experiments on Pre-Freezing

(1) Mechanical freezing

A freeze-drying technique consists of two main successive processes, the first is pre-freezing and the second, vacuum drying. Many reports[71~77] concerning the influences of pre-freezing conditions upon the subsequent drying and the qualities after reconstruction, have been presented.

As it is evident that a drying process can not improve the qualities of a dried material, freezing conditions should be such as to offer minimum damages on the quality of a material and to make the drying process cost as little as possible.

In cold preservation of foods, it is well-known that quick freezing and low temperature are very effective to prevent quality denaturation. But in the case of freeze-drying of food, some people[33] say that it is not always necessary to refrigerate in low temperature which is apt to worsen the quality. Others say that higher freezing temperature rather shortens the drying time and rehydration is easy.

What is more, foodstuffs have to be produced in large quantities, so a higher expensive refrigerating method should be avoided.

In a recent mechanical freezing method, –55°C may be a limit when a Freon–22[79] is used, and –20°C may be the practical cold stock temperature. Liquid Nitrogen with ultra low temperature –196°C may be allowable only in the laboratory as refrigerant because of its high cost and of the difficulty in manipulating it.

In a freezing process, large ice crystals are formed because of the lapse of time through "the zone of maximum ice crystal formation"[77~78] which is found between –2~–5°C. Rapid freezing is defined to pass through the zone within 35 minutes and, when it takes more than 35 minutes, it is slow freezing. But, as the freezing-rate is affected by inner or outer material conditions, it needs to make clear the size of the material used and how it is refrigerated. One of the answers is to find the freezing curve of the material. The author also adopted this method.

The results of pre-freezing experiments by sharp freezing are shown in Tables 3~6 and Figs. 6~12.   The author has deduced from these results the following items;

(a)   Salmon and whale fresh meat and salmon boiled meat made up as a plate type with 10 mm in thickness are considered to be slowly freezing at –20°C.   But a cylindrical type prawn is considered to be rapidly freezing at –22°C because of

Table 3.   Freezing condition of Potato (sharp freezing)

Object of test	effect of sample thickness
Shape	cube
Size	A; $10 \times 10 \times 10$mm, B; $20 \times 20 \times 20$mm
Treatment	fresh
Air temperature	–22°C, –40°C, –50°C
Specific gravity	1.17 gr/cm^3
Water content	80%

Table 4.   Freezing condition of Whale meat (sharp freezing)

Object of test	effect of pre-treatment
Shape	flatwize
Size	$40 \times 40 \times 20$ mm
Treatment	A; fresh B; boiled
Air temperature	–22°C, –40°C, –50°C
Specific gravity	A; 0.96gr/cm^3, B; 1.00gr/cm^3
Water content	A; 72.6%, B; 42.2%

Table 5.   Freezing condition of Salmon meat (sharp freezing)

Object of test	effect of pre-treatment
Shape	flatwise
Size	A; $20 \times 20 \times 10$mm, B; $15 \times 15 \times 10$mm
Treatment	A; fresh B; boiled
Air temperature	–20°C, –40°C, –50°C
Specific graivty	A; 1.13gr/cm^3, B; 1.36gr/cm^3
Water content	A; 76.5%, B; 71.8%

Table 6.   Freezing condition of Prawn (sharp freezing)

Object of test	freezing of cylindrical meat
Sample	Toyama-ebi
Shape	cylindrical meat
Size	max. dia. 11mm
	length 29mm
Treatment	A; fresh (stripped) B; boiled (stripped)
Air temperature	–22°C, –35°C, –55°C
Specific gravity	A; 0.98gr/cm^3, B; 1.35gr/cm^3
Water content	A; 81%, B; 72.7%
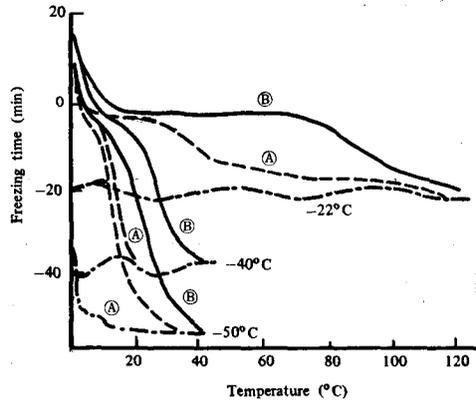
Fig. 6. Freezing curve of Potato
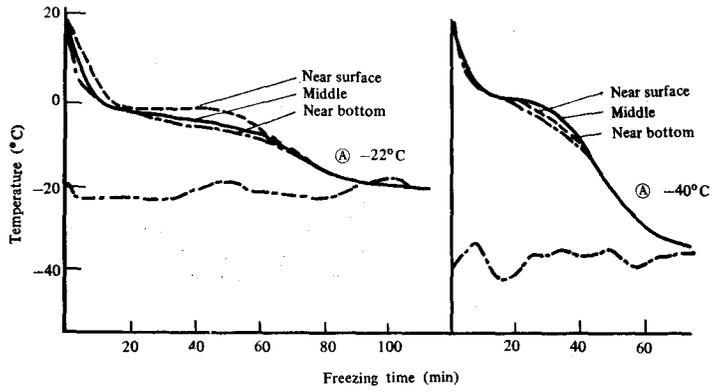
Fig. 7. Freezing curve of Whale meat
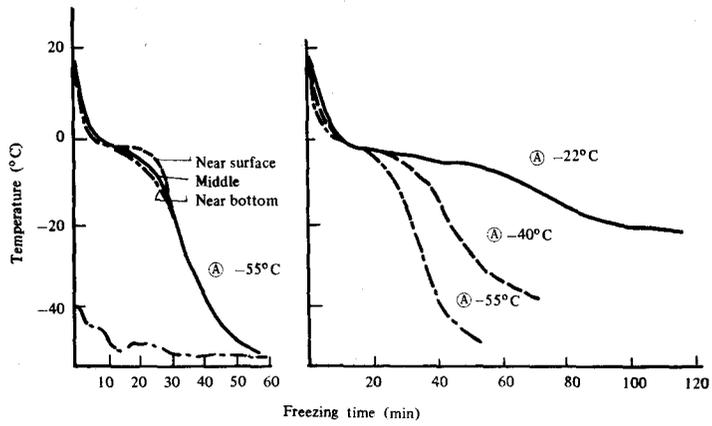
Fig. 8. Freezing curve of Whale meat
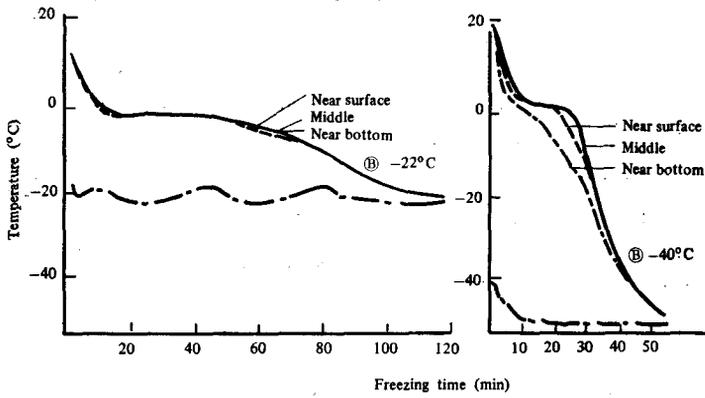
Fig. 9.　Freezing curve of Whale meat
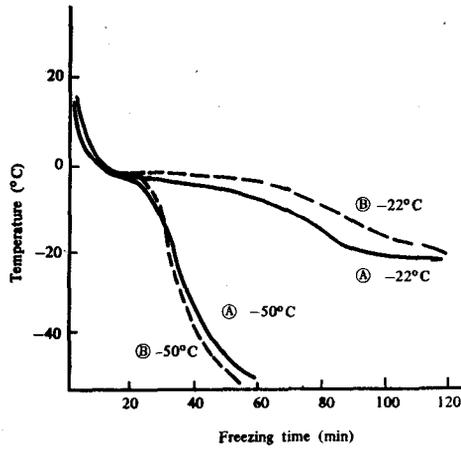
Fig. 10.　Freezing curve of Whale meat
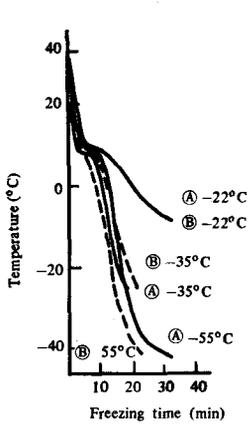
Fig. 11.　Freezing curve of Salmon meat
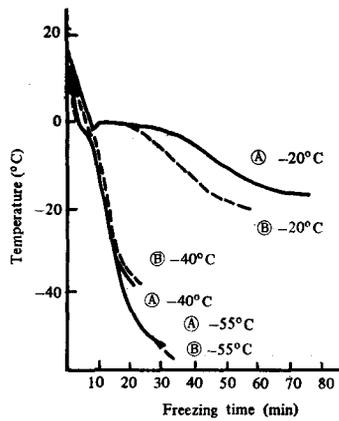
Fig. 12.　Freezing curve of Prawn

its wider surface area compared with its volume. The ratio[80] (surface-area)/ (volume) of a prawn becomes twice that of a plate type fish meat.

(b) Both fresh meat and boiled meat made as a plate type with more than 20 mm in thickness, are considered to be rapidly freezing even under –40°C. However, whale meat is considered to be slow freezing because of having less heat conductivity in comparison with other meats, a fact that is attributable to the scarcity of water content, and of being much fatty.

(c) The boiled meat reduced its water content and contracted itself, so the heat conductivity decreased. But, when the heat capacity has also decreased, the freezing-rate rises promptly.

The author got the following conclusions from the above deductions;

For this experiment, marine products with 10 mm in thickness froze by slow freezing not lower than –22°C, and by rapid freezing below –50°C.

(2) Evaporation freezing

An evaporation freezing process of marine products is carried out by loading them into a vacuum cabinet without heating. The latent heat removed from the marine products for evaporation progressively lowers the temperature of the materials and ice formation commences just when the vacuum degree reaches 4 mm Hg. This process seems to be useful to shorten the drying time because of the possibility to evaporate about 15~20% water contents in an initial drying stage. In certain circumstances, the case-hardening occures because vapour diffusion does not follow surface sublimation. Therefore, evaporation freezing is not always applied to every material.

As shown in the microphotographs of an evaporation-frozen tuna tissue, the contraction and crumbles are so noticiable that the application of this method to fish meats is considered to be useless.

In order to examine the temperature changes of a material when this method is applied, the author has made some tests on potatoes which seem to have almost constant water content at any points of it, and get evaporation freezing curves either when fresh or boiled. Table 7 and Fig. 13 show the freezing curves of a fresh potato when the initial temperature was kept at 16°C. Table 8 shows the freezing curves of both boiled and fresh potatoes with various kinds of shapes and sizes when the initial temperature is different. Fig. 14 shows four kinds of freezing curves when shapes and sizes are varied.

From the results described above, the author may explain that the optimum temperature near the middle of a fresh potato varied according to its size, the larger the size is, the lower the temperature becomes, but that the optimum one of a boiled potato at the same place, reached always a constant value –30°C no matter the size or the initial temperature.

Table 7. Evaporative freezing of Potato

Sample		cube	rectangle	cube	cube
Shape		cube	rectangle	cube	cube
Size	(mm)	$10 \times 10 \times 10$	$20 \times 20 \times 10$	$20 \times 20 \times 20$	$30 \times 30 \times 30$
Surface area	(cm²)	6	16	24	54
Volume	(cm³)	1	4	8	27
Initial water content	(%)	80	80	80	80
Initial temp.	(°C)	16	16	16	16
Ultimate temp. of sample	(°C)	−9	−12	−14	−20
Lowest vacuum	(mmHg)	0.06	0.06	0.06	0.06
Initial weight	(gr)	1.212	4.430	8.437	30.553
Weight after dehydration	(gr)	0.685	2.885	6.500	24.857
Dehydrated water	(gr)	0.527	1.575	1.937	5.696
Condenser temp.	(°C)		−55		
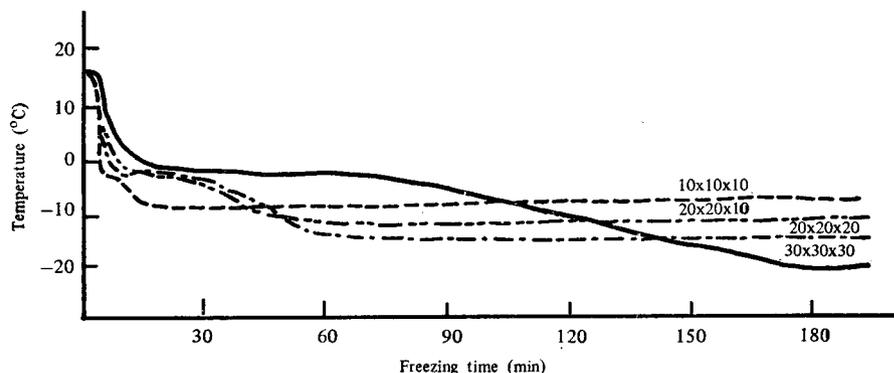
Fig. 13. Evaporative freezing curve of Potato

As already mentioned, evaporation freezing is the initial stage of a vacuum drying without heating, and an enthalpy corresponding to the initial temperature causes the evaporation of water component in a low pressure. A latent heat is consumed by evaporation, so a material temperature consequently falls. Freezing begins from a surface towards the inside at less than 4.5 mmHg in vacuum, and passes through the zone of maximum ice crystal formation. If an ice sublimation continues successively after most parts of water contents refrigerate, the material temperature falls more and more. Therefore, the optimum temperature is fixed according to the evaporating rate, subliming rate and heat capacity of a material. As for a fresh potato, the temperature drop is small because of an interference for vapour passage by a contraction and a case-hardening arising at the biginning of evaporation. On the contrary, a temperature drop of a boiled potato is great because of the development of many small crushes from the surface to the

Table 8.　Evaporative freezing condition of Potato

Sample	Potato							
Shape	Cube		Rectangle		Cube		Cube	
Size (mm)	10×10×10	10×10×10	20×20×10	20×20×10	20×20×20	20×20×20	30×30×30	30×30×30
State	fresh	boiled	fresh	boiled	fresh	boiled	fresh	boiled
Surface area (cm²)	6	6	16	16	24	24	54	54
Volume (cm³)	1	1	4	4	8	8	27	27
Initial water content (%)	84.9	77.4	84.9	77.9	84.9	77.4	80.4	79.8
Initial temp. (°C)	20	12	17	17	15	17	14	30
Ultimate temp. of sample (°C)	−6	−30	−13	−31	−16	−30	−22	−30
Initial weight(gr)	1.40	1.40	4.60	4.70	8.70	9.50	30.23	27.02
Weight after dehydration (gr)	1.20	1.15	3.85	3.85	7.30	7.90	26.45	21.73
Dehydrated water (gr)	0.20	0.25	0.75	0.85	1.40	1.60	3.78	5.29
Lowest vacuum (mmHg)					0.07			
Condenser temp. (°C)					−55			
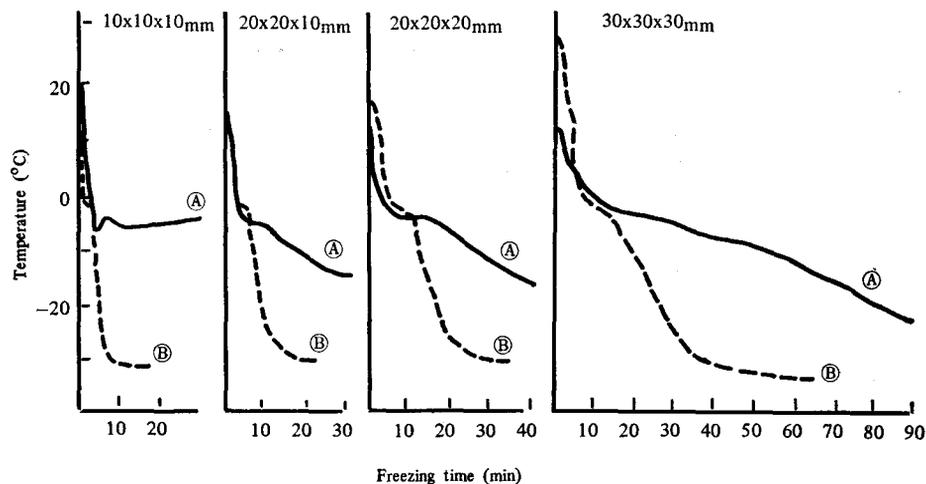
Fig. 14.　Evaporative freezing curve of Potato

inside of a material, which makes evaporation able to continue from the inside.

The reason of offering various kinds of temperature drops in accordance with sizes of a fresh material, — namely, the temperature of a small size potato is higher than that of a large one — is that, as shown in Fig. 13, a small potato has a small heat capacity, so its temperature drop is faster at the biginning of evaporations smaller and harder ice crystals are made in a material, sometimes, a surface contraction and case-hardening occur, consequently, a subliming evaporation is limited in small extent, finally, the temperature drop is small.

Here, the author has come to the conclusion that the evaporation freezing process is not suitable for all marine products because of the possibility of an extent of damages on a material tissue greater than the pre-freezing process, and besides, of the difficulty to get a desirable freezing temperature, which depends too much on the characteristics, shape and size of a material.

VI. Experiments on Freeze-Drying

As already mentioned in the introduction, the object of this study is to clarify the mechanism of freeze-drying, to investigate the possibility of applying this technique on marine products, to compare with the characteristics and similarities among freeze-dried marine foods. Then, the author has tried to practise freeze-drying on twelve kinds of marine products selected among the most popular marine foodstuffs in Japan. The author has obtained drying curves with whole samples, calculated and plotted the relations between the residual moisture content — drying time, drying-rate — residual moisture content, drying-rate — drying time, and then discusses on their freeze-drying characteristics and similarities. Furthermore, for the purpose of examining the tissue fiber changes, many microphotos of samples of fresh state, freeze-dried state, and reconstructed state were taken.

Here, as a determined shape, size, and uniform water content are necessary to examine the effects of freeze-drying on thick specimens, a potato was conveniently used for offering an adequate sample.

The materials used and the contents of this experiment are shown in the next Table.

Material	Contents of experiment
(1) Potato	What characteristic effects can result from a freeze-dried sample when its thickness changes ?
(2) Atka mackerel meat	What characteristic effects can result from a freeze-dried sample when the drying temp. changes ?
(3) Tuna meat	What characteristic effects can result from a

		freeze-dried sample when pre-freezing temp. changes ?
(4)	Halibut meat	Ditto
(5)	Squid meat	Comparison with a fresh meat and a boiled meat What characteristic effects can result from a freeze-dried sample when holes are made in it ?
(6)	Octopus	Comparison with a squid meat
(7)	Abalone	Effects following the making of holes.
(8)	Scallop adductor muscle	Effects following the repeated freeze-drying process
(9)	Short necked clam	Effects following the making of holes
(10)	Clam (Ezo-Bakagai)	Comparison with a fresh meat and a boiled meat
(11)	Prawn	Effects following pre-freezing temperature
(12)	Matured eggs of Sea urchin	Effects following the repeated freeze-drying process
(13)	Kelp (Makonbu)	Effects following pre-freezing temperature

VII.   Synthetic Interpretation of the Results

(1)   First of all, the author will discuss on the accuracy of this experiment and the results obtained.

(a)   In order to keep the surface temperature of the material at 40°C in most experiments, the Voltstat (variable transformer) which is connected to the ultra rays heating tubes is controlled by the confirming temperature of both the mercury thermometer and the theromocouple touching the material surface. But the author had some doubt whether those two thermometers were sure enough to indicate correctly the temperature of the surface heated by radiation in vacuum, because the thermometer indication in radiation and vacuum depends on its absorption ability for radiation, or on the adherent moisture on it which is apt to cause the thermometer temperature fall by its evaporation. Furthermore, when the radiant heat is not balanced with the subliming latent heat, the material température changes, and to let the Voltstat control follow with this temperature change is very difficult on account of its time lag.   So the author has tried to keep the radiant heat output constant during the drying process.   By this method the large temperature variation could be checked, but the small variation was probably presented by its kind or construction, even if the same shaped and sized sample was used.

(b)   Setting the limit of the radiant heat only within the material surface is difficult.   Some quantities of radiation inevitably occur from the side of a material or from the balance dish in contact with the bottom of a material, and

then cause some subliming evaporations from the side or bottom of the
material.

(c) The clam, prawn and sea urchin, having their own shapes, were dried just
as they were, so the drying processes differ from other type marine products,
then comparing their drying curves with those of the other fish meats was not
fair, because of the maximum projective area is used in the calculation as
effective subliming area.

(d) The technical accuracies of the differenciation on a diagram, in order to get
a drying curve for the measuring of weight decreases, came into question.

As above mentioned, there were several inaccuracies about the obtained values,
but for the purpose of making these values intentional, it is necessary to proceed
with the experiment with the utmost care, especially in the next points;

Measurement as correct as possible

Precise graphical differenciation

Uniformity of freeze-drying condition

Correlation of characteristics rather than individual measuring values

Now, in order to make an analysis on freeze-drying characteristics of twelve
kinds of marine products, the author adopted the most representative "drying-rate
— residual moisture content curve".   As shown in Fig. 15, I, II, two type curves
of the first stage of a decreasing drying-rate are roughly devided, one is a straight
line type and the other is a curved line type.   But even in the case of the same
material, two types of curves become interchangeable when the freezing condition
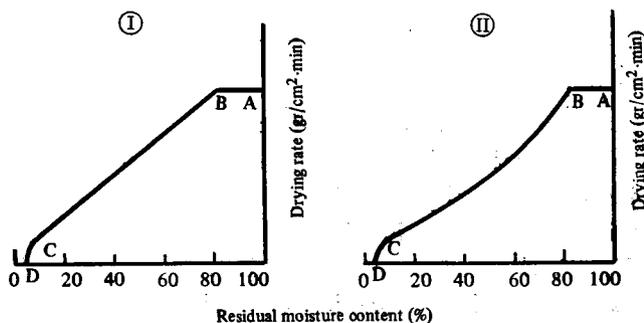
AB; Stage of the constant rate of drying
B; First critical residual moisture consent
BC; First stage of the decreasing rate of drying
C; Second critical residual moisture content
CD; Second stage of the decreasing rate of drying
D; Equilibrium moisture content

Fig. 15.   Two patterns of decreasing rate of drying I; Linear type II; Hyperbolic type

changes or the artificial working is done to the material construction.

Now, as the equation (2) shows, the drying-rate is considered to be antiproportional to the thickness (l) of the formed drying layer, and the residual moisture content is also proportional to the thickness, then, when the vapour transfer coefficient (φ) is regarded to be constant, the drying-rate — the residual moisture content curve is to become the hyperbolic type. When the case-hardening or surface contraction occurs, and therefore, the vapour transfer coefficient decreases, the drying-rate rapidly reduces, and the inclination of the curve becomes a steep slope.

On the contrary, when there are cracks or holes in a material, the surface sublimation can grow from inside it, and the stage of constant subliming-rate becomes longer.

As the resistance of the dried layer with cracks or holes for the vapour transfer is smaller than that of a precise layer, the drying-rate does not fall with the fromation of the dried layer, therefore, the drying-rate — residual moisture content curve become approximately linear.

Beside this, the following conditions have influences on the drying-rate;

(e)   Owing to the asymmetric surface evaporation, several small dried areas appear on the surface and the subliming effective area decreases.

(f)   On the way to the drying process, the material temperature rises up due to the excessive radiant heating.

(g)   The surface contraction or case hardening causes the decrease of (φ), the shrinkage of the tissue fiber causes the increase of (φ).

(h)   Evaporation from the side or bottom of the material

(2)   Secondarily, the author will discuss the relation between the material thickness and the drying time.

(a)   In the stage of the constant rate of drying:
This stage has no relation with the thickness of a material.
Let subliming water quantity be (F_1) in g,
      drying time   (t_1) in min.
      subliming effective surface area   (S) in cm^2,
      constant rate of drying   (q_A) in g/cm^2. min

then

$$t_1 = \frac{F_1}{q_A \cdot S} = \frac{(100 - f_B)(W_o - W_d)}{q_A \cdot S \cdot 100}$$

Where
    f_B=first boundary residual moisture content in %
    W_o-W_d=initial water content in %

(b)   In the first stage of the decreasing rate of drying:
    b–1),   Linear type characteristic curve:
        Let subliming water quantity be (F_2) in g
           drying time (t_2) in min.
           thickness of a dried layer (l) in cm
           second boundary residual moisture content (f_c) in %
           drying-rate at the points of (l) and (f) q, q_c in g/cm².min
           total thickness of material (L) in cm
           line inclination $(\varPhi)$
           weight of ice quantity per unit (ρ) in g/cm³
then

$$\frac{(q - q_c)}{(L - l)} = \varPhi$$

$$q = \rho \cdot d\,l/d\,t$$

    from above two equations

$$d\,l/d\,t = q_c + \varPhi \cdot (L - l)$$

Integrate this from 0 to L

$$t_2 = \frac{\rho}{\varPhi} \cdot ln\,\frac{q_A}{q_c} = \frac{\rho \cdot L}{q_A\,q_c} \cdot ln\,\frac{q_A}{q_c}$$

    Therefore the drying rate is proportional to the thickness.
Where

$$q_A/q_c = f_B\,/f_c$$

Then

$$t_2 = \frac{\rho}{\varPhi}\,ln\,\frac{f_B}{f_c}$$

and

$$\rho \cdot L \cdot S = F_2$$

    Where (q_c) is negligibly small compared with (q)
Then

$$t_2 \fallingdotseq \frac{F_2}{q_A \cdot S} \cdot ln\,\frac{f_B}{f_c}$$

    b–2),   Hyperbolic type characteristic curve:
From equation (2)

$$\rho \cdot \frac{d\,l}{d\,t} = \varphi \cdot \frac{(p_s - p_a)}{l}$$

Integrate this from 0 to L

$$t_2 = \frac{\rho \cdot L^2}{2\,\varphi \cdot (p_s - p_a)}$$

Namely, the drying time is in proportion to the (thickness)^2 and

$$F_2 = \rho \cdot L \cdot S$$

Then

$$t_2 = \frac{F_2 \cdot L}{2\,\varphi\,S\,(p_s - p_a)}$$

(c) The second stage of the decreasing rate of drying:

This stage is considered to be the term of less than several % residual moisture contents. The drying time during this stage is greatly affected by the end point determination which is so difficult to determine that the residual water content after drying has remained unsolved.

Now, comparing the drying-rate — residual moisture content curve with the drying time curve, the author could find that the drying time of the constant rate of drying is achieved within 30 minutes, but the evaporative water quantities could reach 20–40%. And what is more, this initial constant rate of drying has influences upon the initial decreasing rate of drying and drying time, too, and is affected by the drying temperature and the ice quantities on the material surface. In the case of fresh meat, the initial drying rate reaches 5 mg/cm^2.min, but boiled meat 3 mg/cm^2.min.

Two important factors having serious effects on the decreasing rate of drying are (K) and (φ). (K) is heat conductivity and (φ) is vapour transfer coefficient. Very few measurements on (K) have been done, one of them was done by Harper.[53] He has obtained the (K) value of dried meat as 0.03 Kcal/m.hr.°C (=0.005 cal/cm.. min°C).

The author could not get the true (K) value of samples by these experiments, because of the radiant heating. Then the (K) value, described in the next chapter should be considered as a certain value of a dried layer in proportion to the absorption ability of radiant heat. The dried layer having many cracks and holes is gererally expected to present small heat conductivity, but really shows a large value rather than a precise dried layer in radiant heat.

The (φ) value of a dried layer is not always constant during the drying process, because its construction and organization may be changing, then the (φ) value which is described in the next chapter is the one at the middle point of the residual moisture content (it corresponds to the middle point of material thickness).

VIII.   Individual Interpretations of the Results

(1)   Potato

As shown in the evaporation freezing curve, the subliming drying technique is more easily applied to the boiled potato than to the fresh one. Table 9 shows the freeze-drying conditions and the measuring values.

Table 9.   Freeze-drying condition of Potato

Object of test	effect of sample thickness	time	weight	weight	weight
Sample	Potato		A	B	C
Treatment	boiled in 90°C hot water	0	2.20	3.40	5.70
Shape	rectangle	30	1.70	3.05	4.95
Freezing temp.	−50°C	1.00	1.30	2.40	4.25
Condenser temp.	−55°C	1.30	0.85	2.05	3.75
Vacuum	0.06~0.07 mmHg	2.00	0.65	1.70	3.15
Drying temp.	40°C	2.30	0.60	1.40	2.80
Size	A; 20×20×5mm	3.00	0.55	1.15	2.50
	B; 20×20×10mm	3.30	0.53	1.00	2.20
	C; 20×20×15mm	4.00		0.90	2.00
		4.30		0.80	1.80
		5.00		0.75	1.65
		6.00			1.40
		7.00			1.25
		8.00			1.20

Fig. 16 shows the drying cruve, Fig. 17, the drying time — residual moisture content and Fig. 18, relation between the thickness of a material and the time needed to dry up to 10% residual moisture content.   The drying time is nearly proportional to the thickness and the thicker a material is, the faster the constant rate of drying becomes.   The reason is that the sublimation from the side of the material is added to the surface sublimation.   The temperature near the center of the material shows almost a constant value, and immediately after the drying interface passes through the center of the material, its temperature rapidly rises up, which indicates one side of an ideal drying process, but the dullness of weight decrease at that time shows, on the other hand, the end of drying is approaching and the center of the material is the last place for drying, which is due to the evaporation not only from the upper surface but also from the side or bottom. Really, the remaining ice layer is generally found out near the middle or under the center of a material, but never above the center.
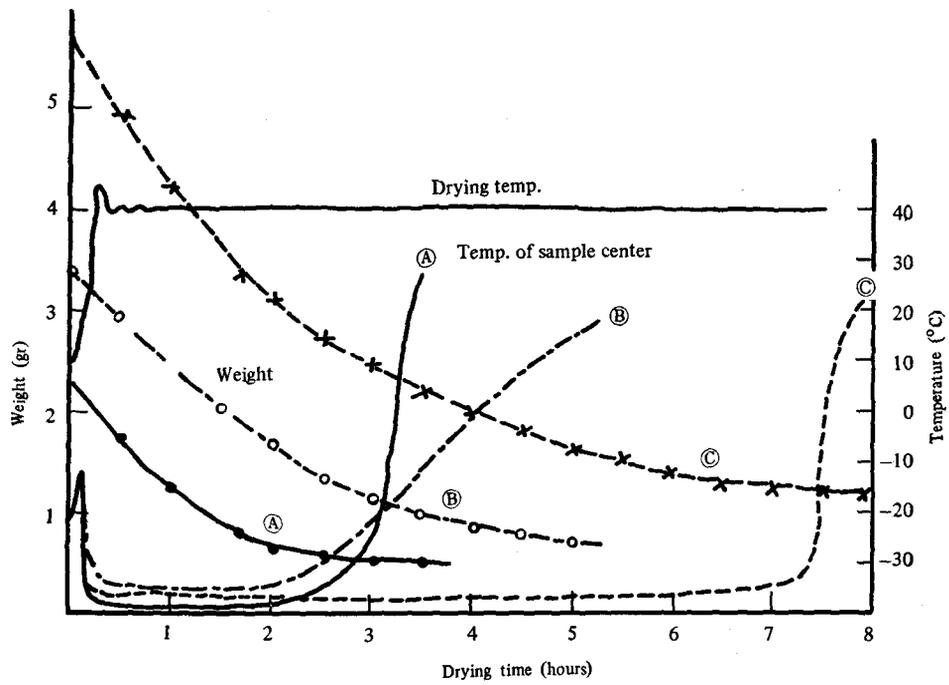
Fig. 16.　Drying curve of Potato
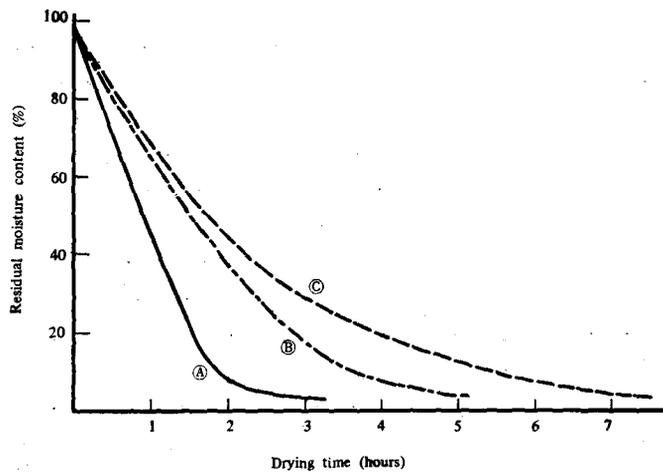
Fig. 17.　Residual moisture content-drying time curve
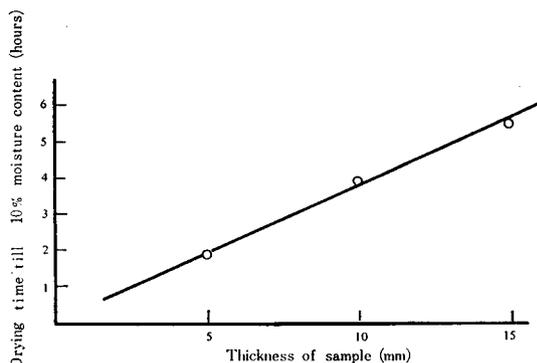
Fig. 18. Relation between drying time and thickness of sample

(2) Atka mackerel meat

Table 10 and Fig. 19 show the freeze-drying conditions and the measuring values, and Figs. 20~22 show the freeze-drying characteristics of the Atka mackerel meat.

Table 10. Freeze-drying condition of Atka mackerel

Object of test	effect of drying temp.	time	weight	weight	weight
Sample	Atka mackerel		A	B	C
Treatment	fresh	0	3.70	3.90	3.90
Shape	flatwise	30	3.25	3.15	2.85
Freezing temp.	−50°C	1.00	2.80	2.25	2.00
Condenser temp.	−55°C	1.30	2.40	2.15	1.45
Vacuum	0.06~0.07mmHg	2.00	2.04	1.70	1.15
Size	A; 18×15×12mm	2.30	1.79	1.45	0.94
	B; 18×17×11mm	3.00	1.60	1.20	0.80
	C; 18×19×13mm	3.30	1.40	0.90	0.80
Drying temp.	A; 25°C	4.00	1.20	0.90	
	B; 40°C	4.30	1.00		
	C; 60°C	5.00	0.80		
Initial water	75.5%	5.30	0.80		

Fig. 23 shows the relations of the drying time up to 10% residual moisture content, and the constant rate of drying against the drying temperature plotted on the semi-logarithmic paper.

As shown in the drying-rate — residual moisture content cruve, the stage of decreasing rate of drying begins in the hyperbolic type curve, and then changes into a linear type curve.   The constant rate of drying is very fast because the Atka mackerel meat is so weak that crashes and holes are apt to grow inside it.

The muscle fiber in the dried layer becomes thin with the drying process, and then the resistance against vapour transfer through the drying layer may be decreasing.
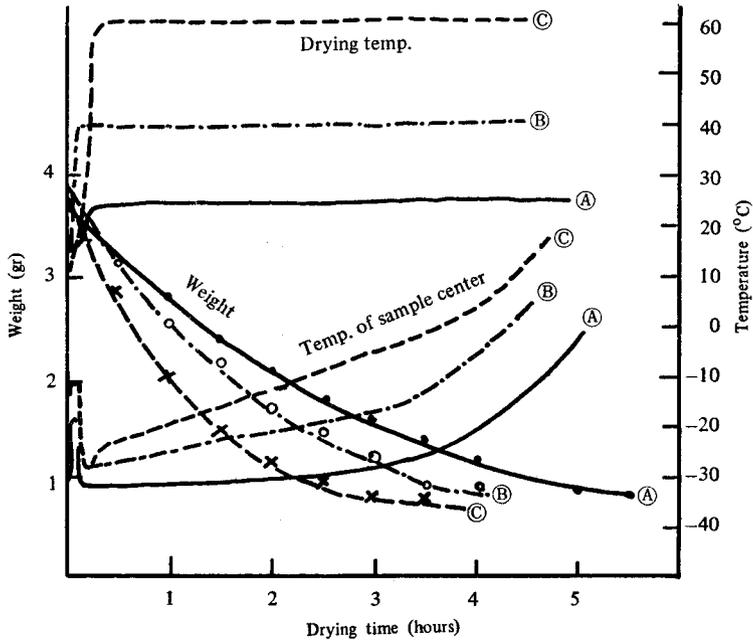
Fig. 19.　Drying cruve of Atka mackerel
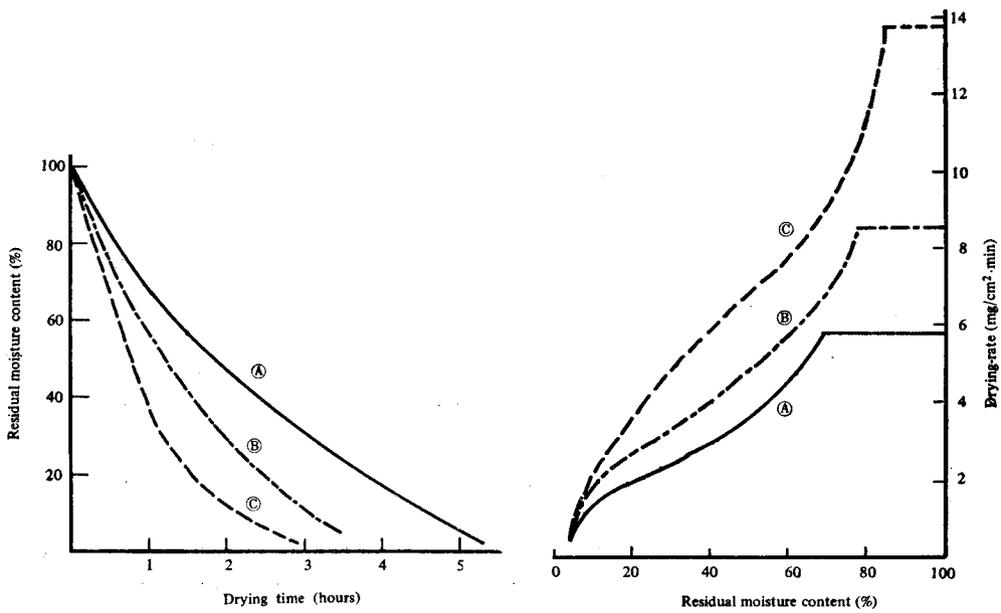
Fig. 20

Fig. 21

Fig. 20.　Residual moisture content-drying time curve of Atka mackeral meat
Fig. 21.　Drying rate-residual moisture content curve of Atka mackerel meat
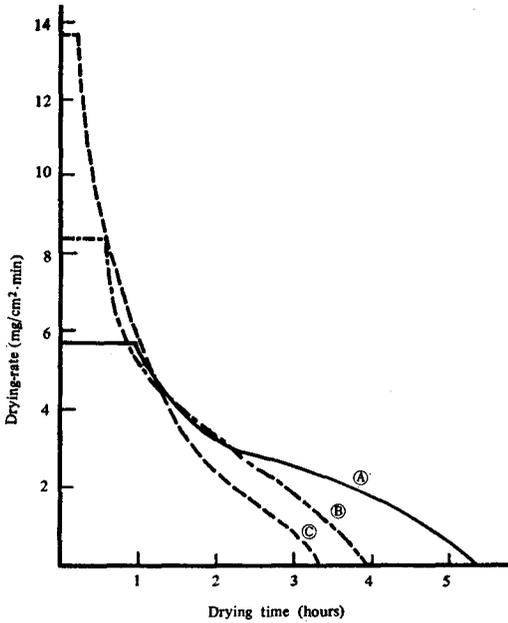
Fig. 22

Fig. 23

Fig. 22.　Drying rate-drying time curve of Atka mackerel meat
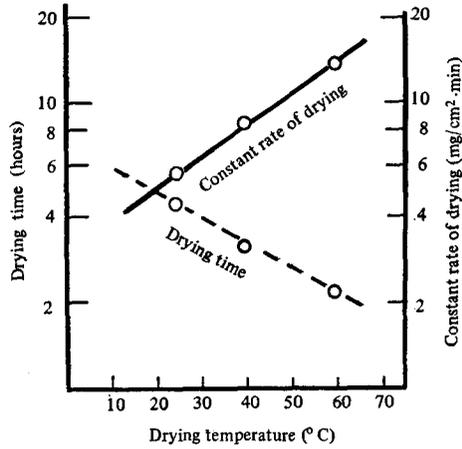
Fig. 23.　Drying time, constant rate of drying-drying temperature curve of Atka mackerel

The microphotos in Plate I show the muscle fiber construction changes after drying.　Fig. 23 explains the next empirical equation;

$$t = t_0 \cdot e^{-x\theta}$$

$$q_A = q_0 \cdot e^{\eta\theta}$$

where

t=drying time in hr

t_0=drying time during the drying temperature 0°C

θ=drying temperature in °C

q_A=constant rate of drying in g/cm^2.min

q_0=constant rate of drying during drying temperature 0°C in g/cm^2.min

x, η=constant values depending on material character

　The author has tried to get (K) and (φ) values of the dried meat.　Assuming the mid value of the residual moisture content as the mid point of its thickness, from the curve (A) in Fig. 22, the next value can be read thus;

　　L=1.2 cm,　θ=25°C,　q=2.9,　l=0.6 cm,　residual moisture content = 40%,

　　The necessary time to dry up to 40% moisture presence may be got from the curve in Fig. 20 as 2·1/3 hours, and the temperature at the center of the material at this time is read as –30°C from Fig. 19. The saturated vapour pressure corresponding

to this temperature is 0.28 mmHg, and the atmospheric pressure is 0.06 mmHg. Inserting these values into the equation (2)

$$2.9 = \varphi \cdot (0.28 - 0.06)/0.6$$

Then (φ) can be got

$$\varphi = 7.9$$

and from (3), (K) can be got

$$K = 0.023$$

In the cases of the curves (B) and (C) in Fig. 22, the subliming latent heat is not balanced with the conductive heat quantities, so the drying temperature of the material interface is gradually rising up, then (K) and (φ) values were not obtained.

(3) Tuna meat

In order to examine the effects of freezing temperature on the drying character-istics of a marine product, two pieces of tuna meat were tested, one was pre-frozen rapidly at –50°C, the other was slowly at –22°C. Under the same drying conditions, these meats dried up.   Table 11 shows the drying conditions and the measuring values, Fig. 24, the drying cruve, Figs. 25~27, the drying characteristics.

Table 11. Freeze-drying condition of Tuna meat

Object of test	effect of freezing temp.	time	weight	weight
Sample	Tuna meat		A	B
Shape	flatwize	0	3.55	3.42
Treatment	fresh	15	3.20	3.00
Condenser temp.	–55°C	30	2.95	2.65
Vacuum	0.07 mmHg	1.00	2.50	2.15
Size	30×20×5 mm	1.30	2.10	1.77
Drying temp	40°C	2.00	1.80	1.50
Freezing temp	A; –50°C	2.30	1.55	1.30
	B; –20°C (dilatory)	3.00	1.35	1.15
Initial water	A; 74.6%	3.30	1.20	1.02
content	B; 74.9%	4.00	1.10	0.97
		4.30	1.02	

The drying rate of the rapid frozen meat is less than that of the slow frozen one, then, during the drying time, it worked contrarily, for, the former makes small ice crystals but the latter large ones which makes sublimation easier.   The same result was obtained by Nei[81] who had made the test on rat blood and zeratin solution.

The microphotographs in Plate II show that the organization of the Tuna meat is finer than that of the Mackerel meat.

The absorbed water quantity is almost the same both on rapid and slow pre-frozen meats.   Assuming the subliming temperature at the surface to be –30°C, then (φ) and (K) values are got as follows;
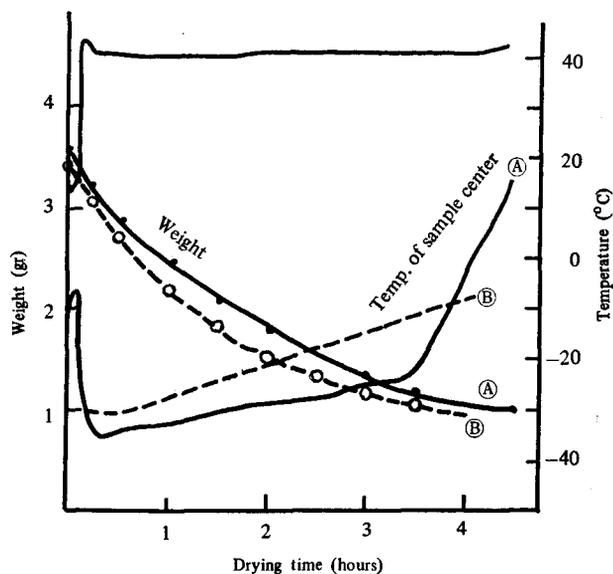
Fig. 24.　Drying curve of Tuna meat
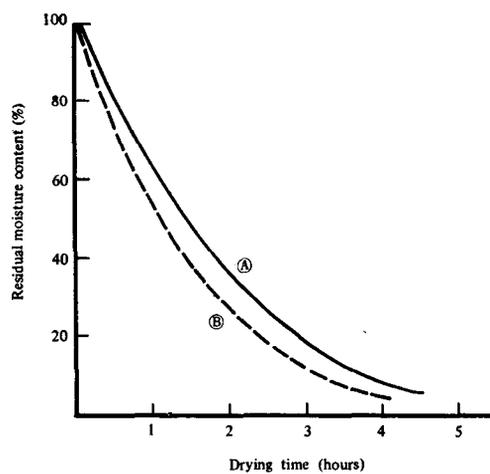
Fig. 25.　Residual moisture content-drying time curve of Tuna meat

A (pre-frozen –50°C) φ=1.65, K=0.0041
B (　　　　　–22°C) φ=1.93, K=0.0050

(4)　Halibut meat

In order to compare the Halibut meat with the Tuna meat, the author has tried to make the test by following the same condition.
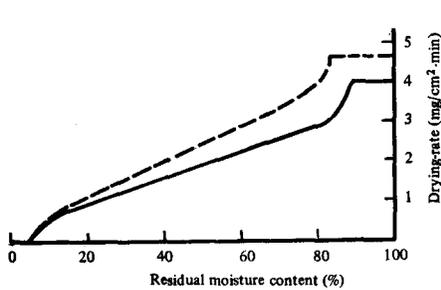
Fig. 26

Fig. 27

Fig. 26. Drying rate-residual moisture content curve of Tuna meat
Fig. 27. Drying rate-drying time curve of Tuna meat
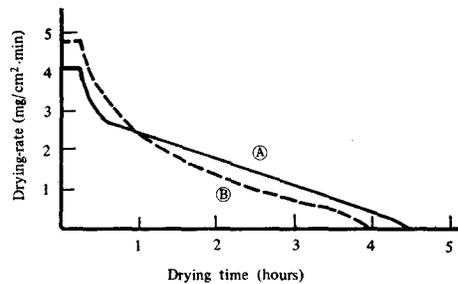
Table 12, Figs. 28–31 show the results of this test, the drying rate — residual moisture content curve of the Halibut meat nearly resembles that of the Tuna meat. Rehydration is easy and its water quantity reaches 75.5% for the rapid frozen meat, and 52.7% for the slow meat, but the water holding capacity is not always large, that is due to many spaces among its tissue fibers.

The microscopic photographs shown in Plate III were taken to compare the freeze-dried meat with the reconstructed meat of rapid frozen fresh Halibut. They explain that the muscle tissues after being reconstructed could not go back to the former state of fresh meat, but many spaces still remain among the tissue fibers.

Calculations as the same as those of the forsaid method wherefrom (φ) and (K) values were as follows:

$\varphi = 1.85 \sim 2.01$
$K = 0.0046 \sim 0.0052$

Table 12. Freeze-drying condition of Halibut

Object of test	effect of freezing temp.	time	weight	weight
Sample	Halibut (fresh)		A	B
Shape	flatwize	0	3.50	3.45
Size	30×20×5 mm	15	3.07	2.95
Freezing temp.	A; −55°C	30	2.72	2.57
	B; −22°C (dilatory)	1.00	2.15	2.07
Condenser temp.	−55°C	1.30	1.70	1.70
Vacuum	40°C	2.00	1.40	1.40
Initial water	0.07 mmHg	2.30	1.15	1.15
content	A; 80.6%	3.00	0.97	1.00
	B; 80.9%	3.30	0.87	0.87
		4.00	0.80	0.77
		4.30	0.77	0.75
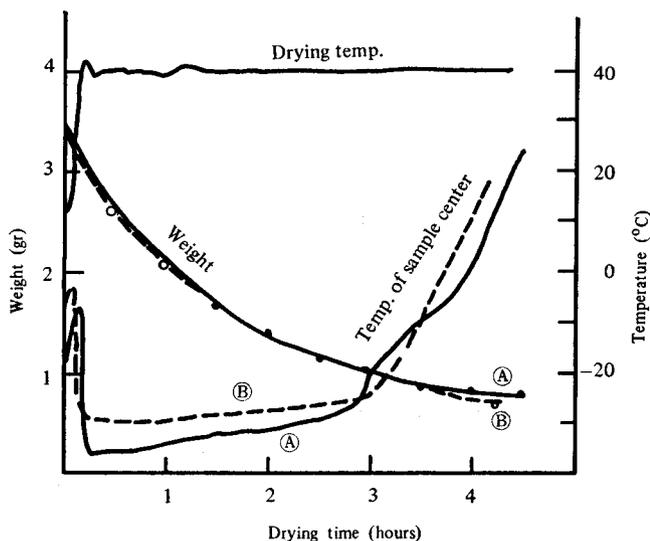
Fig. 28. Drying curve of Halibut
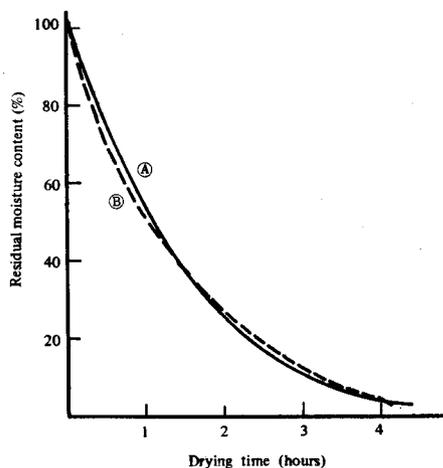
Fig. 29. Residual moisture content-drying time curve of Halibut

(5)   Squid meat

A squid meat has strong muscle tissue fibers which are finely crossed lengthwise
and breadthwise[82].   Damages are not so large as those of fish meat during pre-
freezing,   therefore,   the surface skin contraction and case-hardening are more
noticiable than those of fish meat which cause interruption for vapour transfer
passing through the dried layer.   In order to promote the passing of vapour, the
author has made many small holes through the surface skin to the bottom.   Three
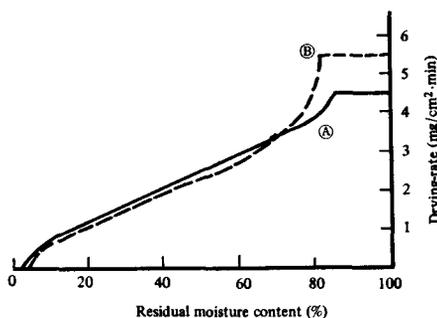
Fig. 30   Fig. 31

Fig. 30. Drying rate-residual moisture content curve of Halibut
Fig. 31. Drying rate-drying time curve of Halibut
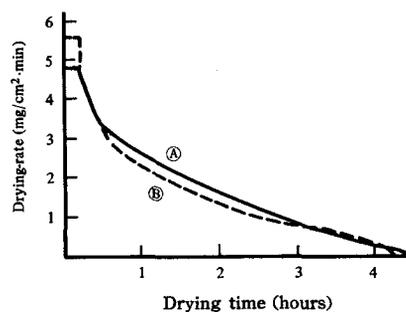
Table 13. Freeze-drying condition of Squid meat

Object of test	effect of pre-treatment	time	weight	weight	weight
Sample	Squid meat		A	B	C
Shape	flatwise	0	3.40	3.55	3.30
Freezing temp.	−50°C	15	3.12	3.32	3.05
Condenser temp.	−55°C	30	2.85	3.12	2.77
Vacuum	0.06−0.07 mmHg	1.00	2.40	2.70	2.25
Drying temp.	40°C	1.30	2.00	2.35	1.80
Initial water content	A; 79.7%	2.00	1.65	2.07	1.50
	B; 77.1%	2.30	1.40	1.87	1.25
	C; 76.1%	3.00	1.25	1.67	1.05
Size & treatment	A; 20×30×5mm fresh	4.00	1.05	1.35	0.90
	B; 20×30×6.5mm boil	5.00	0.92	1.10	
	C; 20×30×5mm boil, holes	6.00		0.97	

kinds of samples, fresh meat, boiled meat, and boiled meat with about thirty holes of 1.5 mm diameter were tested to compare with each other on their drying characteristics.

Table 13 shows the freeze-drying conditions and measuring values, and Figs. 32–35 show the drying characteristics.

The results explain that the Squid meat with many holes has nearly a straight line of the decreasing rate of drying.

The constant rate of drying of fresh meat is larger than that of dried meat, and this fact is due to the poor water content at the surface of the boiled meat.

The boiled meat with many holes lost its water contents above 40% during the stage of constant rate of drying. The ratio of the rehydrated water content to the initial water content reaches 84.4% in fresh maet, 89.1% in boiled meat and 93.6% in boiled meat with holes.
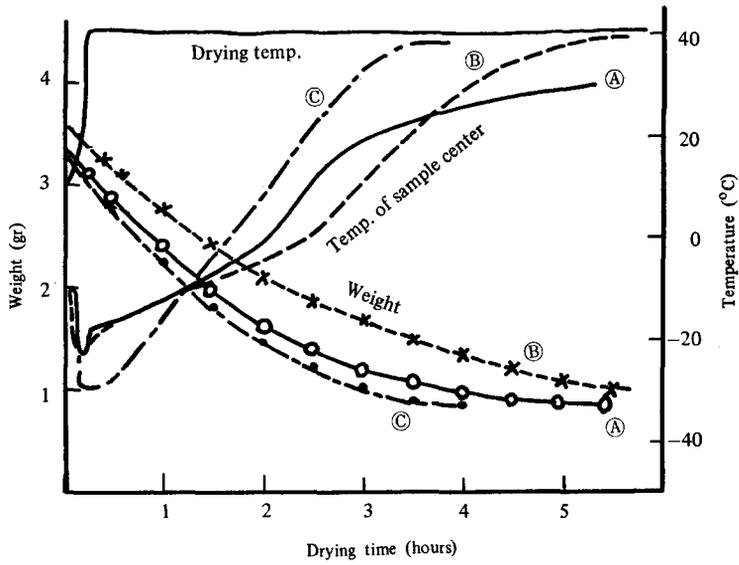
Fig. 32.   Drying curve of Squid meat
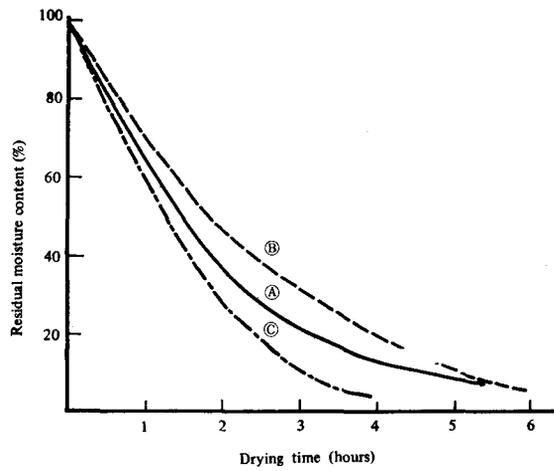
Fig. 33.   Residual moisture content-drying time curve of Squid meat
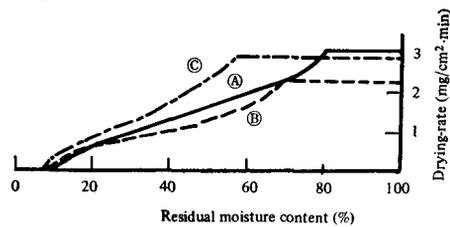
Fig. 34.   Drying rate-residual moisture content curve of Squid meat
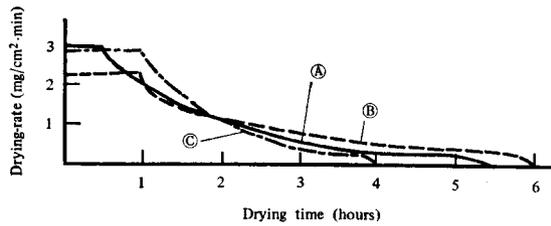
Fig. 35. Drying rate-drying time curve of Squid meat

The microphotographs in Plate IV show the very fine organization suffering little damage by freeze-drying and therefore has good reconstruction.

$\varphi=1.5$

$K=0.003$ both fresh meat and boiled meat

(6) Octopus meat

A boiled Octopus leg meat, sliced into thin discs, are pre-frozen at −50°C and then dried in the vacuum cabinet. Table 14 shows the freezing conditions and the measuring values. Figs. 36–39 show the drying characteristics.

As shown in Plate V, Octopus tissue fibers are arranged in good order lengthwise and breadthwise, and are very applicable for freeze-drying.

A reconstruced Ocpopus meat resembles fresh meat in taste and crisp, because its tissue fibers are strong and suffer little damage during freeze-drying. The absorbing water rate is 56.1% after 30 min of soaking in water.

$\varphi=2.7$

$K=0.008$

Table 14. Freeze-drying condition of Octopus

Object of test	comparison with Squid	time	weight
Sample	Octopus		
Shape	slice	0	3.95
Treatment	boiled	15	3.45
Condenser temp.	−55°C	30	3.10
Vacuum	0.07 mmHg	1.00	2.50
Size	30×30×5 mm	1.30	2.00
Drying temp.	40°C	2.00	1.62
Freezing temp.	−55°C	2.30	1.32
Initial water content	83(%)	3.00	1.10
		3.30	0.95
		4.00	0.85
		4.30	0.81
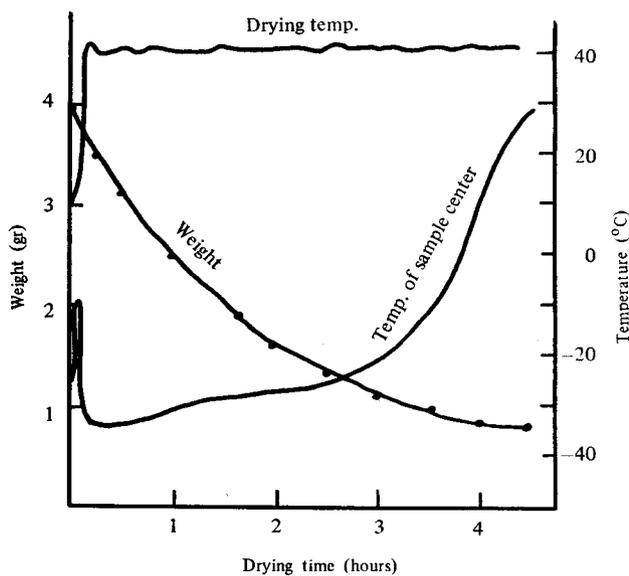
Fig. 36.   Drying curve of Octopus
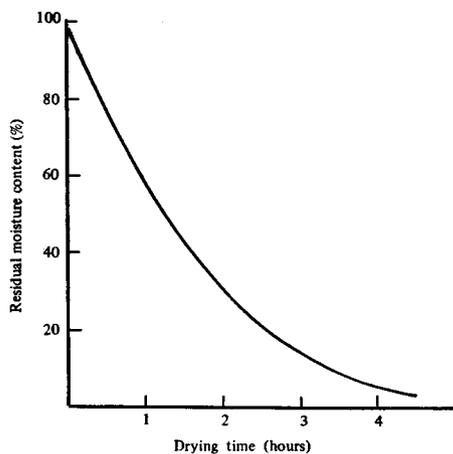
Fig. 37.   Residual moisture content-drying time curve of Octopus

(7)   Abalone

Two samples were prepared, one was a boiled Abalone meat which was soaked in 90°C hot water during 2–3 minutes and sliced into 5 mm thickness, and the other was a boiled meat with 30 holes pierced into it.

When the pre-freezing was over, they were dried in the same conditions. Fig. 43 shows the freezing curve.   Table 15, freeze-drying conditions, Figs. 40–44, the freeze-drying characteristics.
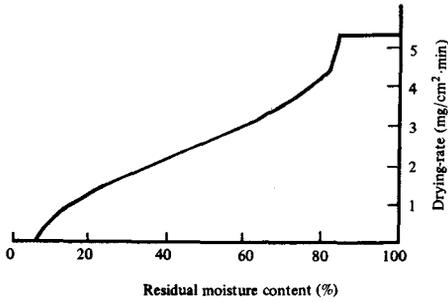
Fig. 38

Fig. 39

Fig. 38. Drying rate-residual moisture content curve of Octopus
Fig. 39. Drying rate-drying time curve of Octopus
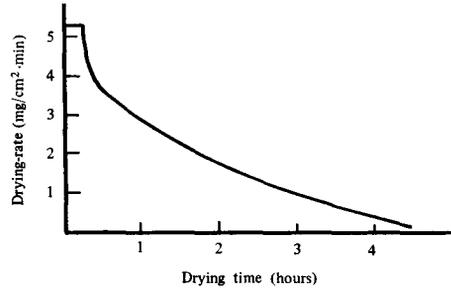
Table 15. Freeze-drying condition of Abalone

Object of test	effect of pre-treatment	time	weight	weight
Sample	Abalone		A	B
Shape	slice	0	2.90	3.00
Freezing temp.	−50°C	15	2.75	2.77
Condenser temp.	−55°C	30	2.60	2.57
Vacuum	0.06~0.07 mmHg	1.00	2.40	2.15
Drying temp.	40°C	1.30	2.25	1.70
Size	5.6 cm² × 0.5 cm	2.00	2.12	1.35
Treatment	A; boil	2.30	2.00	1.12
	B; boil & make fine holes	3.00	1.19	1.02
		3.30	1.80	0.98
		4.00	1.70	0.96
		4.30	1.60	
		5.00	1.52	
		6.00	1.45	
		6.30	1.42	

Abalone is one of several marine products to which this technique is very difficult to apply. Both fresh mat and boiled meat have little subliming vapour quantity, even if the drying temperatue is kept at more than 40°C.

Therefore, the material temperature rises up as shown in the drying curve and causes ice to melt. For instance, even if six hours of drying are given, more than 35% of the residual moisture contents still remain.

The Abalone muscle tissue is the strongest and finest of the three meats (Squid, Octopus, Abalone), and causes severer surface contraction, case-hardening and vapour transfer distrubance than the other two. But, the characteristics of Abalone meat with holes resemble those of Squid meat, and indicates 60% of subliming quantity at the first stage of constant rate.
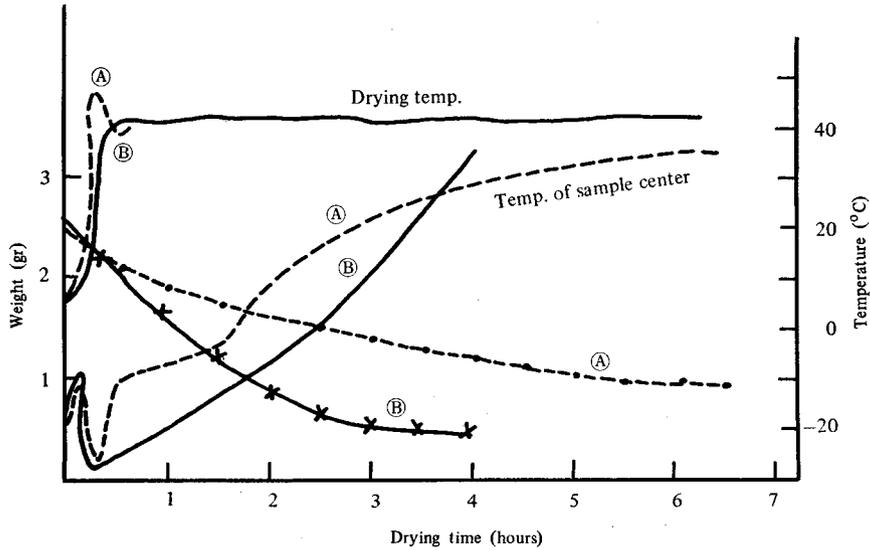
Fig. 40.   Drying curve of Abalone
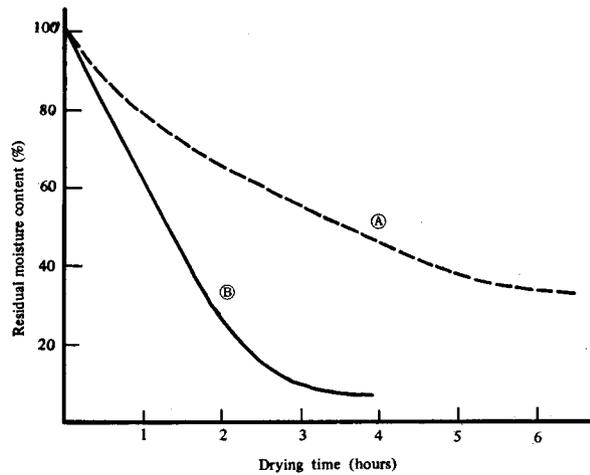
Fig. 41.   Residual moisture content-drying time curve of Abalone

The time necessary to reconstruction is very long, for instance, only 56.8% of suction of water can be given by 17 hours of soaking in water.

The microscopic photographs in Plate VI show that the tissue fibers of Abalone are very fine and complicatedly crossed.
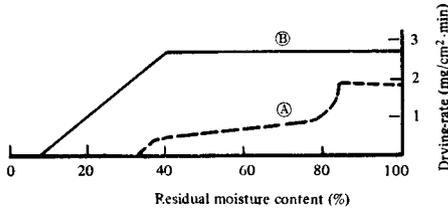
Fig. 42

Fig. 43

Fig. 42. Drying rate-residual moisture content curve of Abalone
Fig. 43. Freezing curve of Abalone
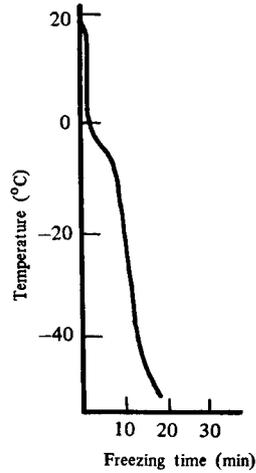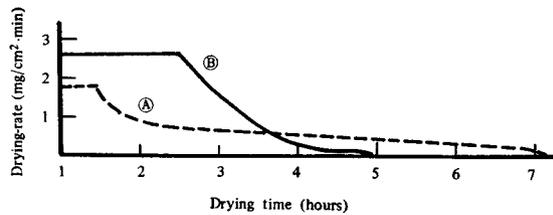
Fig. 44. Drying rate-drying time curve of Abalone

(8) Scallop adductor muscle

A Scallop adductor muscle was boiled in 90°C hot water for 2–3 minutes and was sliced into 5 mm thickness, its initial water content is 77.4% and specific gravity is 1.3. After pre-frozen at –55°C, it was dried under the condition shown in Table 16. This dried sample was soaked in water for reconstruction, after that, pre-freezing was repeated at –22°C, and then dried twice under the same condition. The purpose of this test is to ascertain the following two phenomena.

One is that if there were a remarkable change of the organizations after boiling and after reconstruction, some change would appear in the drying characteristics.

The other is that, the sample being pre-frozen two times before and after at different temperatures, the difference of non-frozen water quantity between before and after may appear by this test. But actually, no difference was recognized between before and after on its characteristic curve, and the difference of non-

Table 16. Freeze-drying condition of Scallop adductor muscle

Object of test	efIect of rehydration	time	weight	weight
Sample	Scallop adductor) muscle		A	B
Shape	disc	0	3.40	2.95
Freezing temp.	−55°C	15	3.12	2.69
Condenser temp.	−55°C	30	2.85	2.40
Vacuum	0.06∼0.07 mmHg	1.00	2.30	1.95
Drying temp.	40°C	1.30	1.85	1.52
Size	30×20×5 mm	2.00	1.47	1.25
Treatment	A; freeze-drying after	2.30	1.20	1.05
	boil	3.00	1.00	1.00
	B; freeze-drying A after	3.30	0.90	
	rehydration	4.00	0.80	
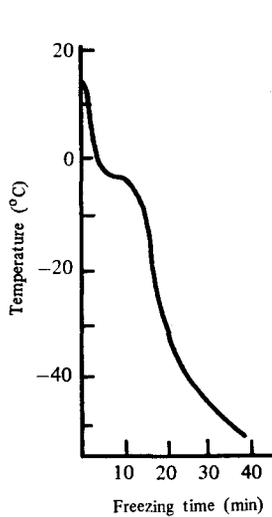
Fig. 45
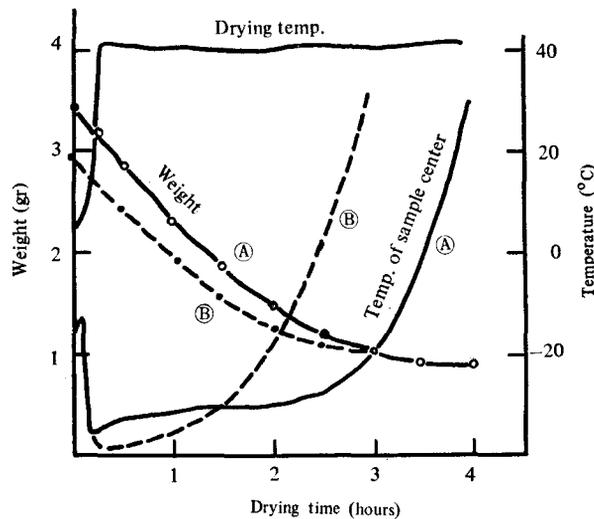
Fig. 46

Fig. 45. Ereezing curve of Scallop adductor muscle
Fig. 46. Drying curve of Scallop adductor muscle

frozen water quantity was so small that it is unreliable. The results of the first drying are shown in Figs. 45∼49, and the comparison of absorbed water quantities is in Fig. 50.

$\varphi=2.04$

$K=0.0043$

(9) Short necked clam

Two samples were prepared, one was boiled in 90°C hot water for 2 minutes, its initial water content was 75.1% and specific gravity, 1.04, the other was the same boiled meat with about 30 holes of 1.5 mm diameter each pierced into it.
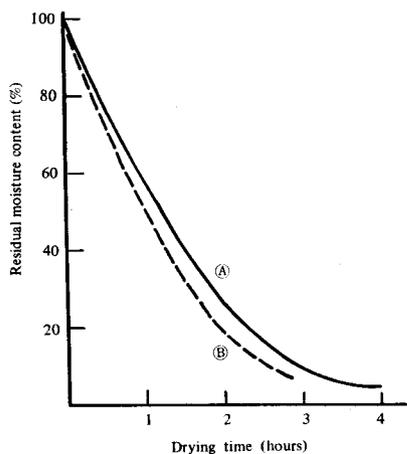
Fig. 47
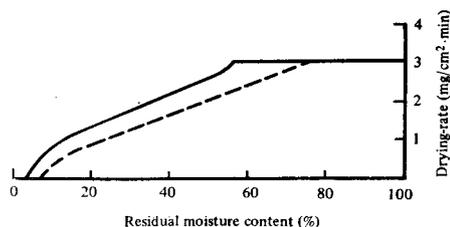
Fig. 48

Fig. 47. Residual moisture content-drying time curve of Scallop adductor muscle
Fig. 48. Drying rate-residual moisture content curve of Scallop adductor muscle
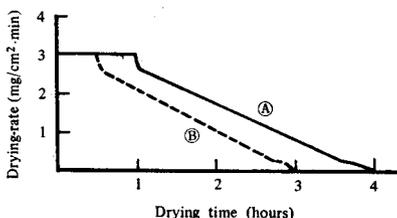
Fig. 49. Drying rate-drying time curve of Scallop adductor muscle

Table 17 shows the freezing conditions and the measuring values, Fig. 53, freezing curve of boiled mat and Figs. 51~55, characteristic curves of freeze-drying.

The two samples presented a similar drying rate curve, but the dying rate of the latter was faster than that of the former.

These samples were tested as they were (without cutting or slicing), so, it is mathematically unreasonable to compare the results with those of the other marine products, because, when the author made the calculations of the measuring values, he adopted the maximum projective area as the effective area.

$\varphi=1.0$ no hole
$K=0.008$ no hole
$\varphi=1.5$ with holes
$K=0.012$ with holes

Total Weight (gr)
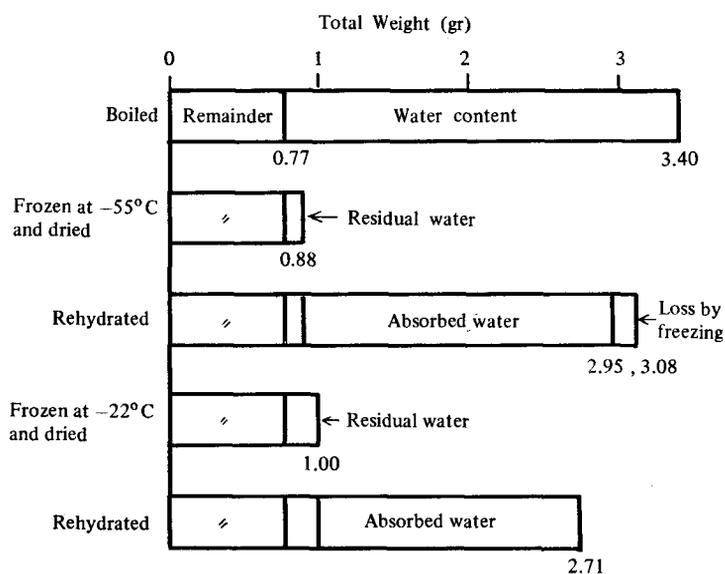
Fig. 50. Comparison of absrobed water content between Scallop adductor muscle dried
after freezing at –55°C, and that dried after rehdyration and freezing at –22°C

Table 17. Freeze-drying condition of Short necked clam

Object of test	effect of pre-treatment	time	weight	weight
Sample	Short-necked clam		A	B
Shape	stripped	0	4.10	4.25
Freezing temp.	–50°C	15	3.80	3.90
Condenser temp.	–55°C	30	3.50	3.60
Vacuum	0.06~0.07 mmHg	1.00	3.07	3.05
Drying temp.	40°C	1.30	2.70	2.65
Size	A; area 5.9cm	2.00	2.40	2.32
	max. thickness 1.1 cm	2.30	2.15	2.05
	B; area 5.8 cm	3.00	1.95	1.85
	max. thickness 1.2 cm	3.30	1.80	1.70
Treatment	A; boil & make fine holes	4.00	1.67	1.55
	B; boil	5.00	1.45	1.35
		5.30	1.35	1.29
		6.00	1.27	
		6.30	1.15	

(10) Clam (Ezo-Bakagai)

Two samples were tested, one was fresh meat and the other was boiled meat,
which was soaked in 90°C hot water for 1~2 minutes.

The freezing curve is shown in Fig. 58, and the result obtained is that the fresh
meat rich in water content needs a longer drying time than that of boiled meat.
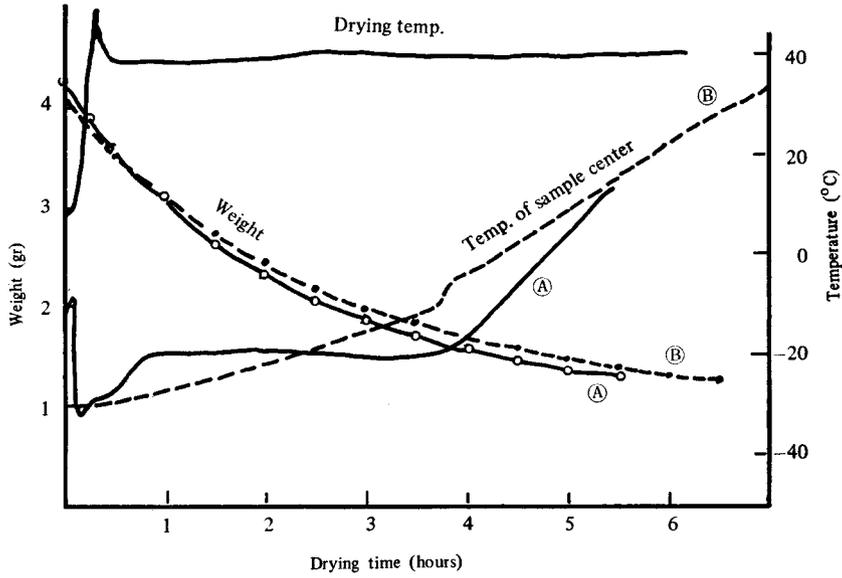
Fig. 51. Drying curve of Short necked clam
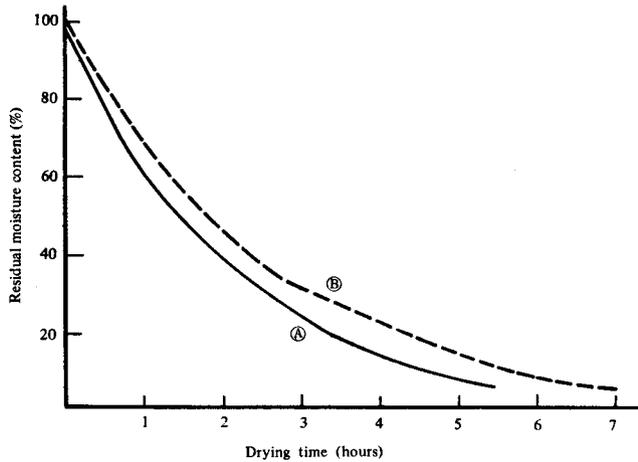
Fig. 52. Residual moisture content-drying time curve of Short necked clam

In the second place, the boiled meat was rapidly pre-frozen at –55°C, and dried under the condition of Table 18, then reconstructed by soaking in water. Besides, this sample was pre-frozen again at –22°C, and dried under the same condition as above. The object of this test is the same as in the case of Scallop.

Table 18 shows the freeze-drying conditions and measurig values, Figs. 56~60,
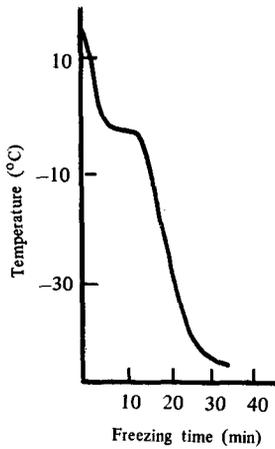
Fig. 53   Fig. 54

Fig. 53. Freezing curve of Short necked clam
Fig. 54. Drying rate-residual moisture content curve of Short necked clam
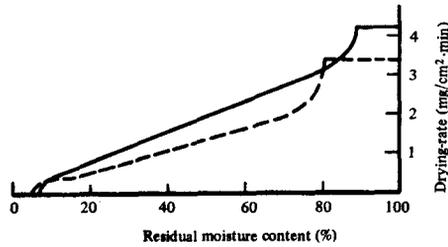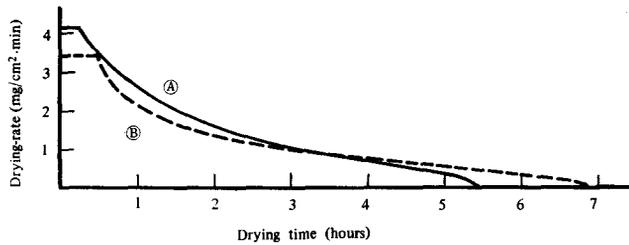
Fig. 55. Drying rate-drying time curve of Short necked clam

Table 18. Freeze-drying condition of Clam (Ezo-Bakagai)

Object of test	effect of rehydration	time	weight	weight
Sample	Clam (Ezo-bakagai)		A	B
Shape	stripped	0	2.90	2.40
Condenser temp.	−55°C	15	2.65	2.17
Vacuum	0.07 mmHg	30	2.45	1.95
Drying temp.	40°C	1.00	2.05	1.60
Size	4.8 cm²	1.30	1.75	1.35
	max. thickness 1.0 cm	2.00	1.45	1.17
Treatment	A; freeze-drying after	2.30	1.25	1.05
	biol	3.00	1.15	0.95
	freezing temp. −50°C	3.30	1.00	0.87
	B; freeze-drying A	4.00	0.95	0.80
	after rehydration	4.30	0.90	0.78
	freezing temp. −22°C	5.00	0.85	0.76
		5.30	0.80	
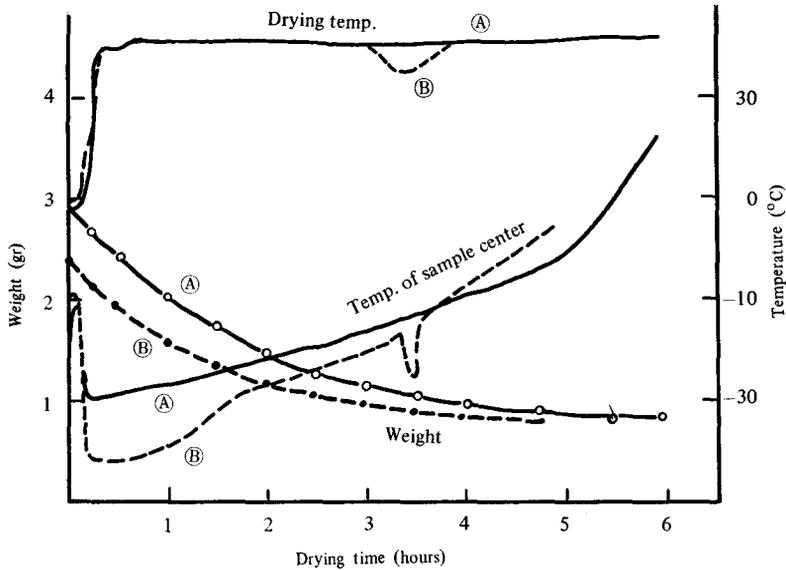
Fig. 56. Drying curve of Clam
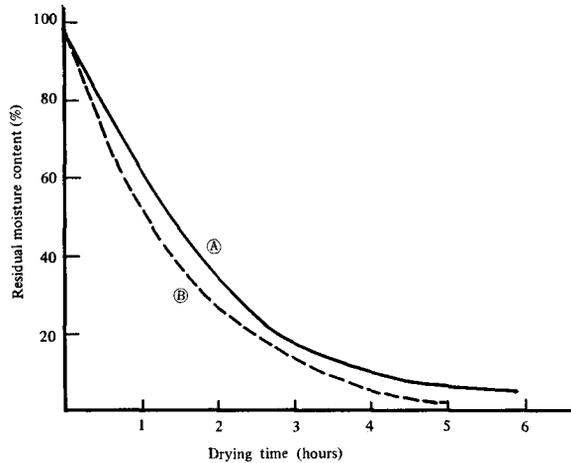
Fig. 57. Residual moisture content-drying time curve of Clam

the characteristic curves of freeze-drying, Fig. 61, the weight changes after dyring and after reconstruction. Fig. 60 explains that the residual moisture content after secondary processing is smaller than that after the first processing. This result is considered to be contrary with the one obtained in the case of Scallop, and it is due to the elongation of the end point of drying after reconstruction.

Plate IX shows the microphotos of the sample.
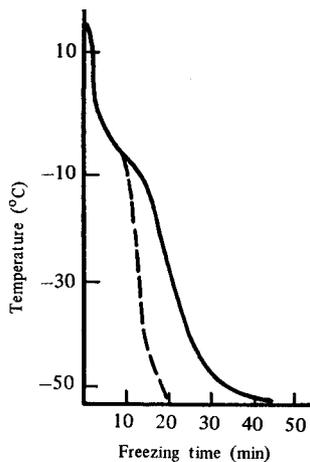
Fig. 58   Fig. 59

Fig. 58. Freezing curve of Clam
Fig. 59. Drying rate-residual moisture content curve of Clam
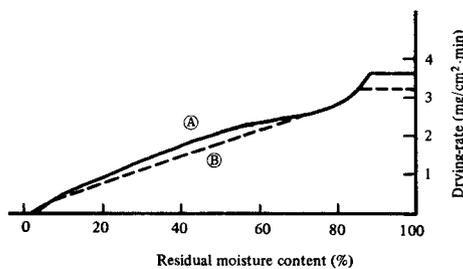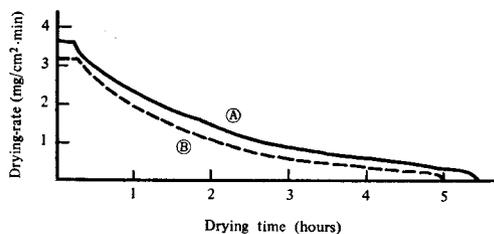
Fig. 60. Drying rate-drying time curve of Clam

Comparing with the Short necked clam which has a form similar to this sample, the author found that the drying-rate of this clam was faster than that of the Short necked clam, and that it seemed to be based on the lack of freshness of this sample, which was bought at the market in the state of a strip.

$\varphi = 2.3$

$K = 0.0095$

(11) Prawn

The influence of pre-freezing temperature on a prawn was examined.

Table 19 shows the freeze-drying conditions and the measuring values, Figs. 62~65, the freeze-drying characteristics.

The muscle fibers of a prawn are regularly arranged parallel to the body length. When a prawn is boiled, its muscle fibers become thin and are contracted both lengthwise and breadthwise, so the spaces are grown among the fibers, which makes rather easy the evaporation from inside a material.

Total Weight (gr)
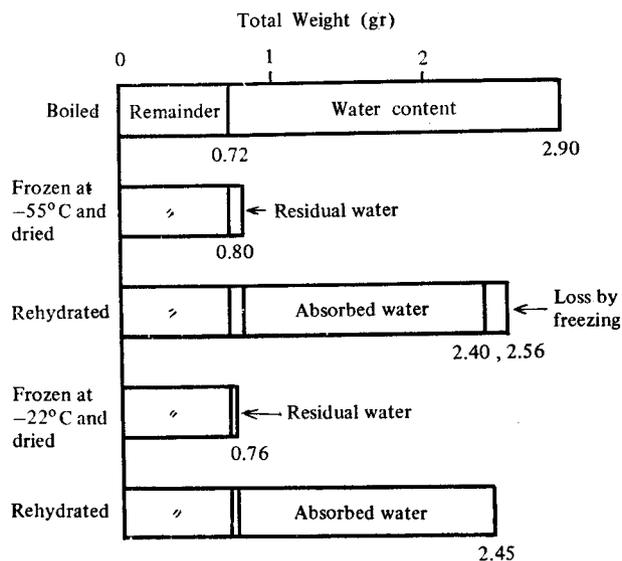
Fig. 61. Comparison of absrobed water content between Clam dried after freezing at –55°C
and that dried after rehydration and freezing at –22°C

Table 19. Freeze-drying condition of Prawn

Object of test	effect of freezing temp.	time	weight	weight
Sample	Prawn		A	B
Treatment	boil after stripped	0	4.05	4.80
Condenser temp.	–55°C	15	3.50	4.55
Vacuum	0.07 mmHg	30	3.15	4.20
Drying temp.	40°C	1.00	2.50	3.65
Size	A; dia.10 mm	1.30	2.10	3.30
	length 28 mm	2.00	1.80	2.70
	B; dia. 15 mm	2.30	1.55	2.45
	length 30 mm	3.30	1.05	1.95
Freezing temp.	A; –22°C	4.00	1.00	1.75
	B; –55°C	4.30	0.96	1.65
Initial water	A; 77.4%	5.00	0.95	1.50
content	B; 75.4%	6.00		1.35

Generally, a prawn has good teste after reconstruction, but its freshness has
a considerable effect on the drying-rate, which has not yet been tested by the author.

Owing to the cylindrical form of a prawn, the freeze-drying process differs from
other flat type samples. Calculating the subliming rate per unit area, the author
used the maximum projective area, but actually, subliming evaporation being
plactised from the whole surface area, so the drying-rate is faster than that of a
flat type sample.
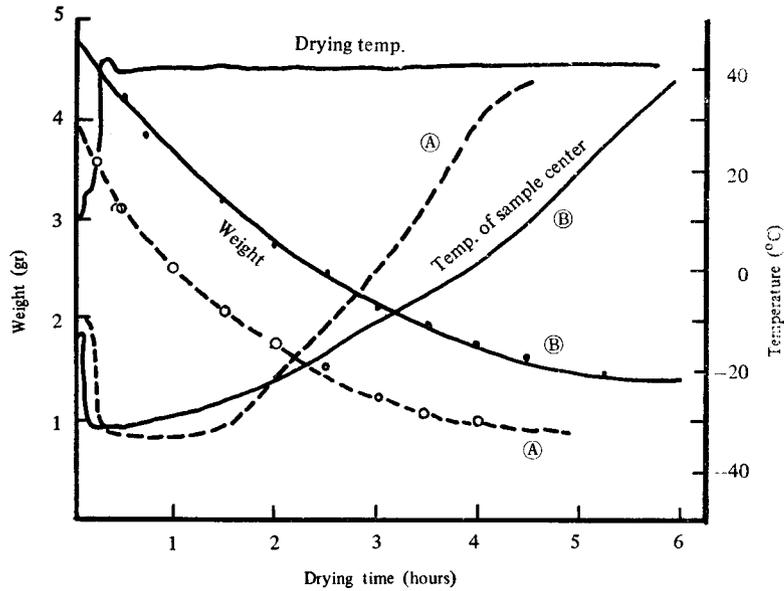
Fig. 62.   Drying curve of Prawn
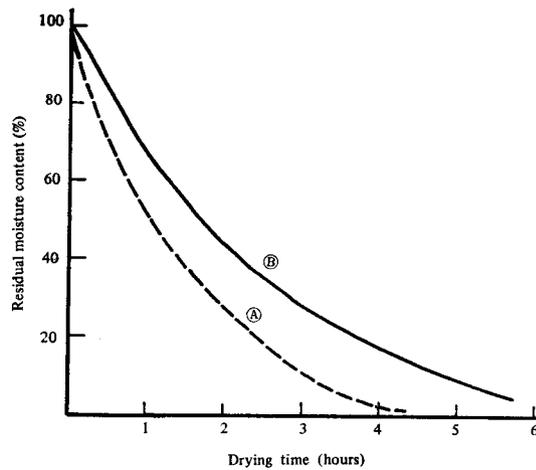
Fig. 63.   Residual moisture content-drying time curve of Prawn

Plate X shows the microphotos of a prawn.

$\varphi=7.5$ rapidly frozen at $-55°C$

$K=0.054$ ″

$\varphi=9.8$ slowly frozen at $-22°C$

$K=0.048$ ″
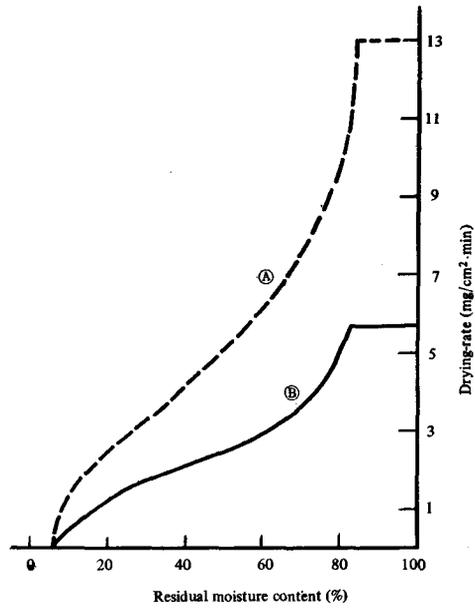
Fig. 64. Drying rate-residual moisture content curve of Prawn
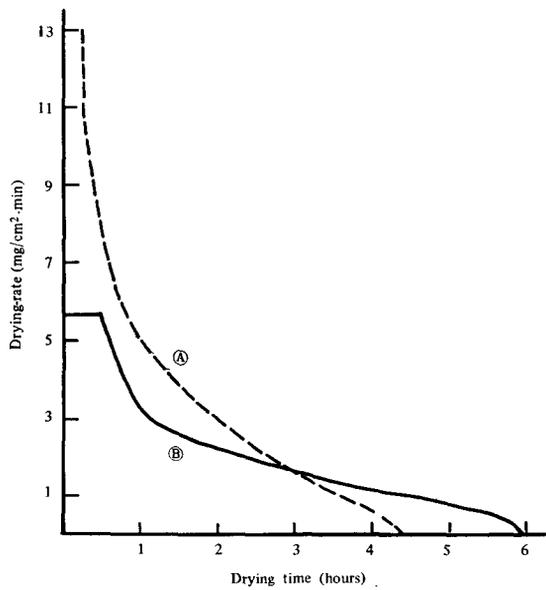
Fig. 65. Drying rate-drying time curve of Prawn

(12)   Matured eggs of sea urchin

The freeze-drying technique is very easily applied to the Sea urchin. The dried one can be quickly reconstructed, but has very brittle organization and is apt to go into pieces.

After rapidly pre-frozen at −55°C, the sample which has been bought at the market was dried int the vacuum cabinet. Table 20 shows the freeze-drying conditions and the measuring values, Figs. 66~69, drying characteristics, Fig. 70, freezing curves. The abosrbed water quantities reached 60.7%.

Table 20.   Freeze-drying condition of Sea urchin

Object of test	effect of rehydration	time	weight	weight	weight
Sample	Sea urchin		A	B	C
Condenser temp.	−55°C	0	3.25	2.20	1.80
Vacuum	0.07mmHg	15	2.98	1.95	1.55
Size	base area of ellipsoid	30	2.70	1.65	1.30
	5.2 cm²	1.00	2.25	1.30	0.97
	max. thickness 6mm	1.30	1.85	1.05	0.80
Drying temp.	40°C	2.00	1.55	0.90	0.70
Treatment	A; fresh	2.30	1.30	0.85	0.67
	B; after rehydration A	3.00	1.10		
	refreeze at −55°C	3.30	1.00		
	C; after rehydration	4.00	0.95		
	the same kind of A				
	refreeze at −22°C				
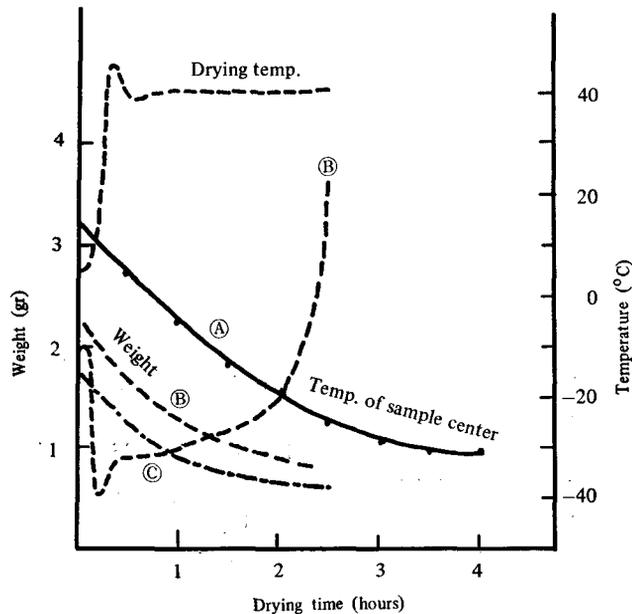
Fig. 66.   Drying curve of Matured eggs of sea urchin

Fig. 67
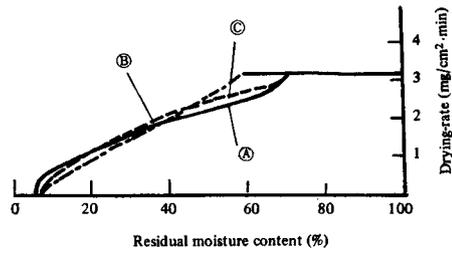
Fig. 68
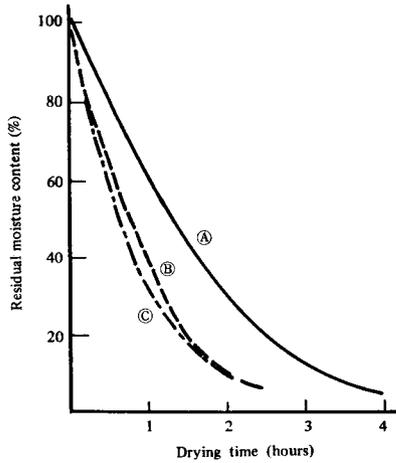
Fig. 67. Residual moisture content-drying time curve of Matured eggs of sea urchin
Fig. 68. Drying rate-residual moisture content curve of Matured eggs of sea urchin

Fig. 69
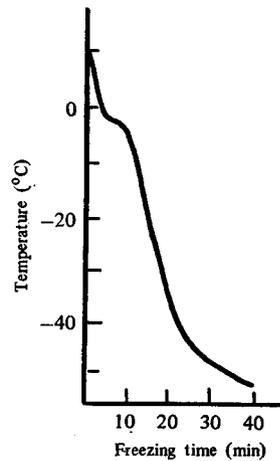
Fig. 70
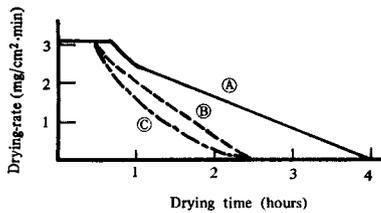
Fig. 69. Drying rate-drying time cruve of Matured eggs of sea urchin
Fig. 70. Freezing curve of Matured eggs of sea urchin

The short stage of constant rate of drying, in spite of its drying easily, is due to the small quantity of the initial water contents (74.3%) and the phlegmatic temperament covering the surface of a sea urchin.

Plate XI shows the microphotos of a sea urchin.

$\varphi=2.57$

$K=0.052$

(13) Kelp

The sample were collected near Hakodate Bay in June, and cut off some sheets of 40×35×2.25 mm size.   Its initial water content was 78.8%.

First, two samples were pre-frozen at –55°C and –22°C respectively, then dried under the conditions shown in Table 21.   Figs. 71~74 show the freeze-drying characteristics of the samples.   Temperature   readings seem to be uncertain because the Kelp is too thin to keep the thermometers at the center of its thickness.

Table 21.   Freeze-drying condition of Kelp

Object of test	effect of freezing temperature	time	weight	weight
Sample	Kelp (Makonbu)		A	B
Shape	flatwzie	0	3.55	3.80
Size	40×35×2.25 mm	15	3.15	3.32
Condenser temp.	–55°C	30	2.75	2.85
Vacuum	0.07 mmHg	1.00	2.05	2.15
Drying temp.	40°C	1.30	1.15	1.57
Treatment	fresh	2.00	1.25	1.27
Freezing temp.	A; –55°C	2.30	1.10	1.20
	B; –22°C (dilatory)	3.00	1.08	1.18
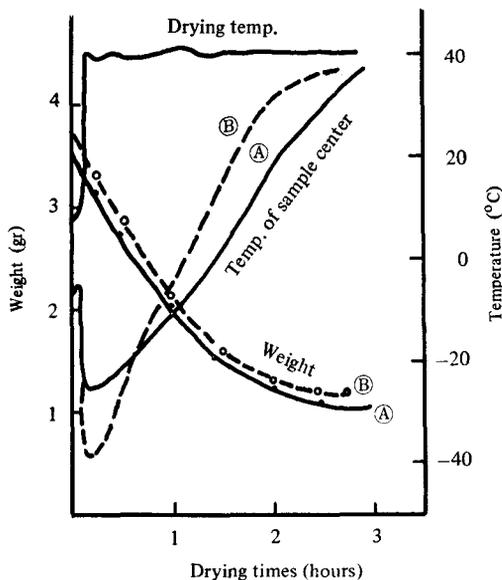
Fig. 71

Fig. 72

Fig. 71.   Drying curve of Kelp
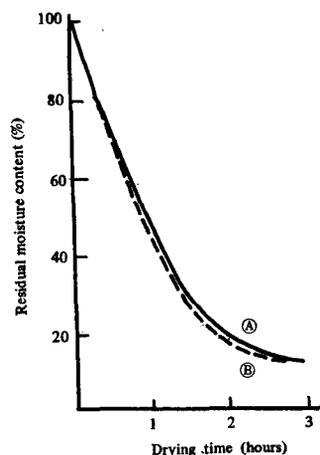
Fig. 72.   Residual moisture content-drying time curve of Kelp
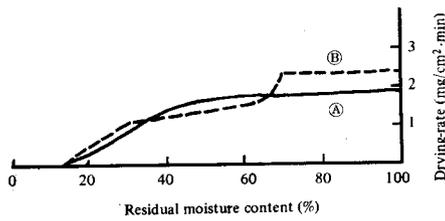
Fig. 73

Fig. 74

Fig. 73. Drying rate-residual moisture content curve of Kelp
Fig. 74. Drying rate-drying time curve of Kelp
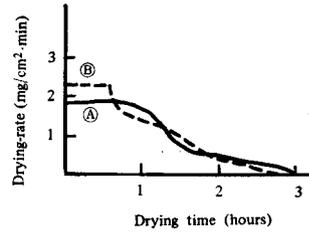
It is rare that the drying-rate curve shows the convex type in the case of rapid freezing, and also shows the convex type at the decreasing rate of drying in the case of slow freezing.

The constant rate of drying of the Kelp is small compared with the other marine products, because of the phlegmatic temperament covering its surface and some ice quantities.

The special convex type of the drying-rate of the Kelp is due to the size of the ice crystal, the place of ice growth, the size of the crack at its surface, etc., but those effects remaining uncertain, it is necessary to continue this test.

Plate XII shows the microphotos of the Kelp.

$\varphi = 4 \sim 6$

$K = 0.0087 \sim 0.013$

IX. Summary

Considering the mechanism of freeze-drying of marine products on the bases of experimental results above obtained, the author has come to the following conclusions:

(1). The most important process of freeze-drying seems to be mass transfer in a vacuum cabinet which is followed by heat transfer and phase change. Mass transfer is mainly determined by vapour transfer coefficient which is affected by the construction of the porous dried layer. The value of (φ) is in direct proportion to (d^4), where (d) is dia of hole, and in inverse proportion to (l), where (l) is hole length. Calculated (φ) value from experimental results presents the mean value of vapour transfer coefficient of many ununiform holes.

(2). Putting the drying-rate — residual moisture content curve as a representative of drying characteristics of marine products, three stages are shown in this curve, they are the constant rate, the first stage decreasing rate and the second stage of decreasing rate of drying. The stage of constant rate of drying is due to

the surface sublimation in vacuum, and the larger the surface area is, the higher
the drying temperature is, the lower the vacuum is, the richer the ice crystals
are, and the faster the drying rate becomes.   The first stage of the decreasing
rate of drying is due to the decrease of heat conductivity with the formation of
a porous dried layer and increase of resistance for vapour passage through the
dried layer.   Two types of drying-rate curves appear owing to the difference of
the decreasing rate of the drying process, one is the straight line type and the
other is the curved line type.

The second stage of the decreasing rate of drying is due to the necessary term
to remove a part of the bound water which was unfrozen during the pre-
freezing, and remove some melted water by temperature rising.

In order to remove these water contents, a lot of heat quantities and time
period are necessary.

(3).   The first stage of the decreasing rate of drying is considered as a main
process of freeze-drying.   Let's imagine the ideal process of the first stage
of the decreasing rate, thereupon, the equation (1), (2), (3) hold good, and a
subliming interface temperature (θ_s) is kept constant without any connection
with the thickness, whereas an ice layer is being formed, if drying temperature
and atmospheric vacuum degree are settled.

Moreover, the value of (θ_s) is determined by heat conductivity (K) and vapour
transfer coefficient (φ), and has a distinct feature to approach the constant
value owing to the maintaining of the dynamic equilibrium at the beginning
time of drying.

(4).   On the other factors offering some effects upon drying characteristics:

(a)   Drying temperature

When the drying temperature rises up, the subliming interface temperature
also generally rises up, and prompts the drying-rate of evaporation by the
increasing of conductive heat quantities and the driving power.

But optimum drying temperature should be determined with material,
because of the quality denaturation caused by too high temperature.   Even if
the drying temperature rises up, too small a vapour transfer coefficient causes
the material temperature to rise which is apt to melt the ice crystals.

(b)   Effective surface area

Subliming vapour quantities are in proportion to the effective surface area.
Whereupon, an effective surface area means the whole faces in contact with
the atmosphere from which heat and mass transfer can be done effectively
throughout the material.   Then, the cracks or artificially made holes are
included in the effective surface area.

(c)   Thickness of material

The drying time is prolonged with material thickness, and the aspect of

elongation is affected by the drying characteristics of the material.

(d) Initial water content

The author[83] has tried to test on the effect of initial water content upon the freeze-drying characteristics with Messers. Noda and Yoshida, and obtained the following consideration.

The constant rate of drying increases in compliance to the initial water content, for a large water quantity naturally makes a large ice quantity on the surface of a material. But the subliming interface evaporation is not so much affected that little change is perceived in the decreasing rate of drying.

In a word, the initial water content does not offer any effects on the decreasing rate of drying, but some drying time elongation does on the constant rate of drying.

(e) Pre-freezing temperature

From the view point of dried food quality, rapid pre-freezing is said to be more preferable for the freeze-drying than slow pre-freezing, because the former offers little demage on the cell organization, but as to the drying time or the effectiveness of the drying process, the latter is preferable to make large ice crystals and facilitate the passage of the subliming vapour throughout the dried layer. But the latter has bad effects on taste of dried food.

(f) Vacuum

The vacuum degree is controlled by the trap temperature, and the lowest limit is within the saturated vapour pressure corresponding to the trap temperature. As shown in equation (6), the subliming interface temperature (θ_s) is so affected by the vacuum degree that a necessary vacuum to get adequate temperature (θ_s) should be secured by cooling the trap. But the drying rate increase produced by lowering the vacuum degree is not so large as the one by rising up the drying temperature.

(5). Microscopic photographs

They explain that fish meat revealed a lot of large spaces among the tissue fibers after freeze-drying, because its tissue fibers are remarkably reduced breadthwise and lengthwise and become very thin during freeze-drying, and its spaces can not recover as far as the orginal state by suction of water, but remain as they are.

Abalone, Octopus and Squid meat having strong tissue fibers suffer little damage during freeze-drying, and expand to fill up the spaces after reconstruction.

References

1) Bird, K.M. (1963).　A directory of freeze-drying, food processors, equipment firms and others.　*Freeze-drying report* 4, 10p.　Washington; U.S. Department of Agriculture.

2) Hara, T. Kubota, E. & Furuya, K. (1966).　Studies on the freeze-drying of tea extract. *Journal of Food Science and Technology* 13 (5), 178–180.

3) Flosdorf, E.W. (1949).　*Freeze-drying.* 280p. New York; Reinhold.

4) Hanson, S.E. (Ed. 1961).　*The accelerated freeze-drying method of food preservation.* 169p. London; Gt. Brit. Ministry of Agriculture, Fisheries and Food.

5) Fisher, F.R. (Ed. 1962).　*Freeze-dehydration of foods.* 237p. Chicago; The Quartermaster Food and Container Institute.

6) Mohrhardt, F.E. (1963).　*Freeze-drying of foods, a list of selected references.* 69p. Washington: National Agricultural Library U.S. Department of Agriculture.

7) Nei, T. (1954).　Bibliography on freeze-drying.　*Low Temperature Science, Series B, Biological Science* No. 12, 87–113.

8) Kimura S. (1962).　Problems of dehydrated food by freeze-drying.　*Food Industry* 5(3), 13–20.

9) ———— (1963).　*Dehydrated food.* 272p. Tokyo; Korin Shoin.

10) Kallistratos, G. & R. von Sengbush (1964).　Probleme um die gefriertrocknung von lebensmitteln.　*Zeitschrift fur lebensmittel untersuchung und forschung* 125(5), 344–356.

11) Yamada, K. (1963).　Development of freeze-dried food.　*Food Industry* 6(22), 153–155.

12) Bird, K.M. (1962).　Freeze-drying, progress and problems.　*Selected writing on freeze-drying of foods* No. 1, 1–5.

13) Stein, M. (1966).　Freeze-drying.　*Food Manufacture* 41(2), 51–54.

14) Shimakawa, J. & Mukaiyama, Y. (1962).　Problems on freeze-drying.　*Journal of Food Science and Technology* 9(2), 33–41.

15) Decareau, R.V. & Burke, R.F. (1964).　*Advance in food research* No. 13, 88p. New York; Academic Press.

16) Nei, T. (1961).　Electron microscopic study of microorganisms subjected to freezing and drying. I, *Low Temperature Science, Series B, Biological Science* No. 19, 79–93.

17) ———— (1962).　Ditto. II, *Ibid.* No. 20, 95–101.

18) ———— (1964).　Formation of cracks in specimens by freezing and drying. *Ibid.* No. 22, 133–138.

19) Jones, N.R. (1959).　Browning reactions and loss of free amino acid and sugar from lyoohilizid muscle extractive of fresh and chill stored colding.　*Food Research* 24 (6), 704–710.

20) Connel, J.J. (1957).　Some aspects of the texture of dehydrated fish. *J. Sci. Food and Agr.* 8(9), 526–537.

21) Kimura S. & Kaniuma, K. (1960).　Studies on the storage of dehydrated food by freeze-drying. Part I, *Journal for the Utilization of Agricultural Products* 7(3), 124–127.

22) Kuroki M. & Kimura S. (1961).　Ditto. Part II. *Ibid.* 8(6), 302–306.

23) Kimura S. & Shioda, K. (1963).　Ditto. Part III. *Ibid.* 10(5), 169–174.

24) ———— & ———— (1963).　Studies on the dehydration of food by freeze-drying. *Journal of Food Science and Technology* 10(7), 276–283.

25) ———— & ———— (1964).　Studies on freeze-dried food. *Ibid.* 11(3), 8–25.

26) ———— & ———— (1966).　Studies on dried food by freeze-drying, Part 7. *Ibid.* 13(3), 95–100.

27) ———— & Miyazaki, K. (1966).　Ditto. Part 8, *Ibid.* 13(3), 100–103.

28) ———— & Taki, M. (1966).　Effect on microwave dielectric heating on freeze-drying. *Ibid.* 13(4), 141–142.

29) Ueoka, Y. Oka, H. & Suemitsu, H. (1964).　Studies on the freeze-dried fish. Part I. *Ibid.* 11(1), 12–20.

30) ————, ———— & ———— (1964). Ditto. Part II. *Ibid.* **11**(11), 484–490.

31) ————, ———— & ———— (1965). Ditto. Part III. *Bulletin of the Ehime Prefectural Institute of Chemical Technology* No. 2, 32–35.

32) ————, ———— & ———— (1966). Ditto, Part IV. *Journal of Food Science and Technology*, **13**(1), 18–24.

33) ———— Ueda, M. Oka, H. & Suemitsu, H. (1965). Histological study on the dried fish. *Bulletin of the Ehime Prefectural Institute of Chemical Technology* No. 2, 36–45.

34) Shibazaki, K. Otani, S. Hirai, T. & Suzuki, M. (1964). Studies on freezing and freeze-drying of foods. Part I. *Journal of Food Science and Technology* **11**(2), 521–530.

35) ———— & Asano, M. (1965). Ditto. Part II. *Ibid.* **12**(4), 137–143.

36) ————, ———— & Ito, K. (1966). Ditto. Part III. *Ibid.* **13**(1), 7–13.

37) ———— Otani, S. Nakazawa, K. & Ito, Y. (1966). Ditto, Part V. *Ibid.* **13**(7), 274–280.

38) Tamoto, K. (1964). Study on freeze-drying of marine mammal. *Scientific Reports of Hokkaido Fisheries Experimental Station* No. 2, 60–70.

39) Takahashi, T. Kamina, K. Takei, M. & Tanaka, T. (1964). Protein denaturation of fish meat during freeze-drying and storing the dried meat. *Bulletin of Tokai Regional Fisheries Research Laboratory* No. 38, 149–155.

40) Toyomizu, M. Matsumura, Y. & Tomiyasu, Y. (1963). Lipid oxidation and protein denaturation in freeze-dehydrated fish. *Bulletin of the Japanese Scientific Fisheries* **29**(9), 854–859.

41) ———— Orita, F. & Tomiyasu, Y. (1963). Discololation of lyophilized fish. *Ibid.* **29** (11), 1037–1043.

42) ———— & Tomiyasu, Y. (1963). Discoloration of fish muscle by freeze-drying in storage. *New Food Industry* **5**(6), 2–6.

43) Yamazaki, H. Sunagawa, M. Iiyama, M. & Imai, H. (1966). Studies on the storage of dehydrated food by freeze-drying Part I. *Journal of Food Science and Technology* **13**(2), 64–70.

44) ———— & Imai, H. (1966). Ditto. Part II, *Ibid.* **13**(7), 281–285.

45) ———— Sunagawa, M. & Imai, H. (1966). Ditto. Part III. *Ibid.* **13**(7), 286–288.

46) Kobayashi, K. & Igarashi, S. (1963). Freeze vacuum drying of marine products I. *Bulletin of the Faculty of Fisheries Hokkaido University* **14**(2), 73–83.

47) ———— & ———— (1964). Ditto. II. *Ibid.* **14**(3), 163–169.

48) ———— & ———— (1964). Ditto. III. *Ibidl* **14**(4), 209–214.

49) ———— & ———— (1964). Ditto. IV. *Ibid.* **15**(1), 58–62.

50) ———— & ———— (1965). Ditto, V. *Ibid.* **16**(3), 164–170.

51) Kamei, S. (1966). *Theory and calculation of chemical equipment.* 564p. Tokyo; Sangyo Tosho KK.

52) Nei, T. (1961). Mechanism of drying during freeze-drying VIII. *Low Temperature Science Series B, Biological Sciences* No. 19, 59–72.

53) Harper, J.C. & Tappel, A.L. (1957). *Advance in Food Research.* No. 8, 172–234.

54) Takano, T. & Tadano, T. (1962). *Drying in Food Industry.* 293p. Tokyo; Korin Shoten.

55) Ueda, R. (1961). *Vacuum technique.* 211p. Tokyo; Iwanami-Shoten.

56) Ota, I. (1964). *Vacuum drying.* 270p. Tokyo; Nikkan Kogyo Shinbunsha.

57) ———— (1959). Theory and application of freeze-drying in food industry. *New Food Industry* No. 13, 59–64.

58) ———— (1959). Ditto. (continue). *Ibid.* **1**(8), 61–65.

59) Octjen, G.W. et al. (1962). *Temperature measurement and control of freeze-drying of foods.* 178p. Washington; National Research Counc.

60) Harper, J.C. (1962). Transport properties of gasses in porous media at reduced pressure with reference to freeze-drying. *J. Am. Inst. Chem. Eng.* **3**, 298–302.

61) Sakai, T. (1939). *Physics IV, B. Thermodynamics.* 98p. Tokyo; Iwanami-Shoten.
62) Nei, T. et al. (1955). Mechanism of drying during freeze-drying I. *Low Temperature Science Series B, Biological Science* No. 13, 59–64.
63) Samukawa, T. (1948). *Theory and practice of automatic control I,* 210p. Tokyo; Japan Society of Mechanical Engineering.
64) Yoshida, J. & Nakayama, H. (1949).   Evaporating rate of water in vacuum. *Low Temperature Science* No. 2, 159–167.
65) Mizushima, M. & Akabori, S. (1956).   *Protein chemistry.* 265p. Tokyo; Kyoritsu Shuppan.
66) Azuma, K. (1947).   Problems of bound water. *Science* 17(5), 126–130.
67) Akiba, M. (1961).   Studied on bound water in fresh muscle. *Memoirs of the Faculty of Fisheries Hokkaido University* 9(2), 86–179.
68) Chiba, S. (1967). Mechanism of drying during freeze-drying II, *Low Temperature Science, Series B, Biological Science* No. 15, 75–94.
69) Kawakami, T. (1942). *Physical studies on fish dehydration.* 192p. Kyoto; The Faculty of agriculture, Kyoto University.
70) Nakamura, K. (1957). *Vacuum technique and freeze-drying.* 227p. Tokyo; Naya-Shoten.
71) Green, V.H. Fennema, O. & Powrie, W.D. (1965). A comparison of methods for microscopic examination of frozen tissue. *J. of Food Science* 30(4), 601–603.
72) Nagaoka, J. & Tanaka, K. (1959). *Science of cooler storage and refrigeration.* 398p. Tokyo; Koseisha-Koseikaku.
73) Nakagawa, M. (1962). *Refrigeration in food industry.* 230p. Tokyo; Korin-Shoin.
74) Tanikawa, E. & Akiba, M. (1942). *Science of cold storage II.* 263p. Tokyo; Kobundo.
75) Kato, M. (1966). *Theory and applciation of food refrigeration.* 1000p. Tokyo; Korin-Shoin.
76) Suzuki, T. Kamina, K. & Tanaka, T. (1964).   Studies on protein denaturation of frozen fish. *Bulletin of the Japanese Society of Scientific Fisheris* 30(12), 1022–1037.
77) Kuprianoff, J. (1962).   Some factors influencing the reversibility of freeze-drying of foodstuffs. *In Freeze-Drying of Food* (Edi. Fisher, F.R.)
78) Neumann, K.G. (1959). 5th Nati. Symp. *Vacuum Technology Trans.* 258p.
79) Hiroshi Fujioka (1963). *Theory and practice of Freon refrigerating machine.* 287p. Tokyo; Kaibundo.
80) Katayama, K. Saito, A. et al. (1966). *Exercises on heat transfer.* 217p. Tokyo; Jitsuyo Tosho K.K.
81) Nei, T. Sato, H. & Hanabusa, N. (1963).   Mechanism of drying during freeze-drying X, *Low Temperature Science Series B, Biological Sciences* No. 21, 71–79.
82) Migita, M. Tanikawa, E. (1958). *Chemistry and processing of cattle fish.* 242p. Hakodate; Hokkai-Suisan Shinbun K.K.
83) Noda, Y. Yoshida, N. & Kobayashi, K. (1963).   Foundamental research on freeze-drying. unissued.

Explanation of Plates

PLATE I (a)

Microscopic photographs of Atka mackerel
A.   Cross section of fresh meat   × 200
B.   Longitudinal section of fresh meat   × 200
C.   Cross section of freeze-dried meat (drying temp. 25°C)   × 200
D.   Long. section of freeze-dried meat (drying temp. 25°C)   × 200
E.   Cross section of rehydrated meat (drying temp. 25°C)   × 200
F.   Long. section of rehydrated meat (drying temp. 25°C)   × 200
G.   Cross section of freeze-dried meat (drying temp. 40°C)   × 200
H.   Long. section of freeze-dried meat (drying temp. 40°C)   × 200
I.   Cross section of rehydrated meat (drying temp. 40°C)   × 200
J.   Long. section of rehydrated meat (drying temp. 40°C)   × 200
K.   Cross section of freeze-dried meat (drying temp. 60°C)   × 200
L.   Long. section of freeze-dried meat (drying temp. 60°C)   × 200
M.   Cross section of rehydrated meat (drying temp. 60°C)   × 200
N.   Long. section of rehydrated meat (drying temp. 60°C)   × 200

PLATE I (b)

Comparative photographs of Atka mackerel during processing
A.   Fresh state
B.   Freeze-dried state
C.   Rehydrated state

PLATE II (a)

Microscopic photographs of Tuna meat
A.   Cross section of fresh meat   × 200
B.   Longitudinal section of fresh meat   × 200
C.   Cross section of freeze-dried meat (evaporative frozen)   × 200
D.   Long. section of freeze-dried meat (evaporative frozen)   × 200
E.   Cross section of rehydrated meat (evaporative frozen)   × 200
F.   Long section of rehydrated meat (evaporative frozen)   × 200
G.   Cross section of freeze-dried meat (pre-frozen at –22°C)   × 200
H.   Long. section of freeze-dried meat (pre-frozen at –22°C)   × 200
I.   Cross section of rehydrated meat (pre-frozen at –22°C)   × 200
J.   Long. section of rehydrated meat (pre-frozen at –22°C)   × 200
K.   Cross section of freeze-dried meat (pre-frozen at –50°C)   × 200
L.   Long. section of freeze-dried meat (pre-frozen at –50°C)   × 200
M.   Cross section of rehydrated meat (pre-frozen at –50°C)   × 200
N.   Long. section of rehydrated meat (pre-frozen at –50°C)   × 200

PLATE II (b)

Comparative photographs of Tuna meat during processing
A.   Fresh state
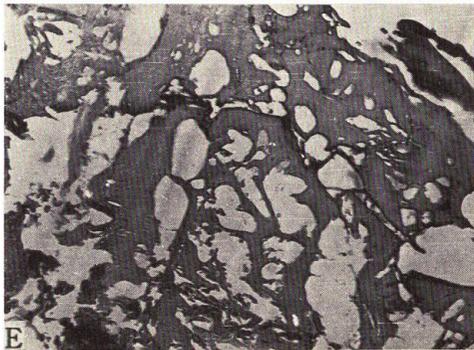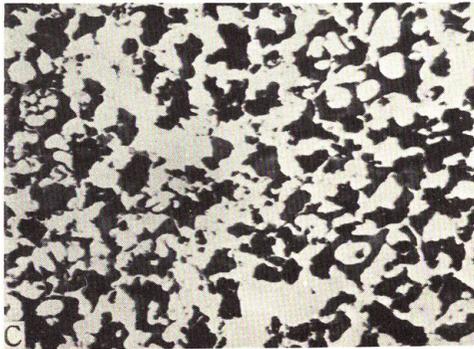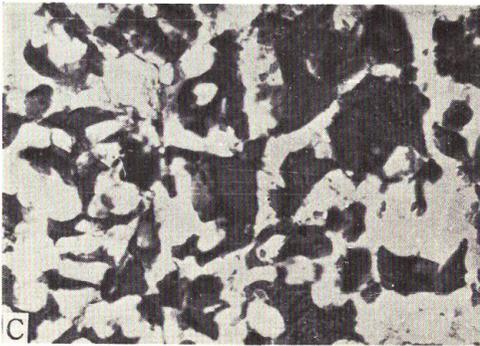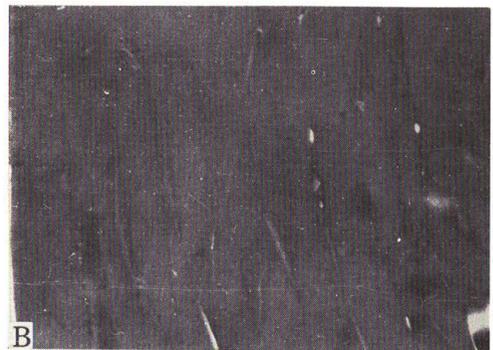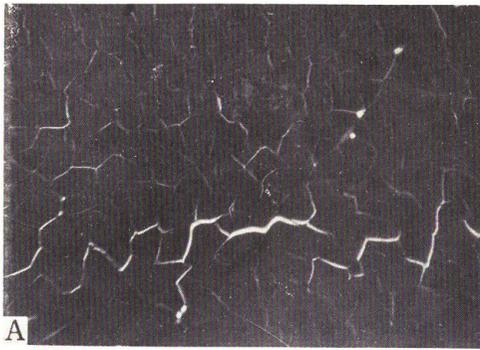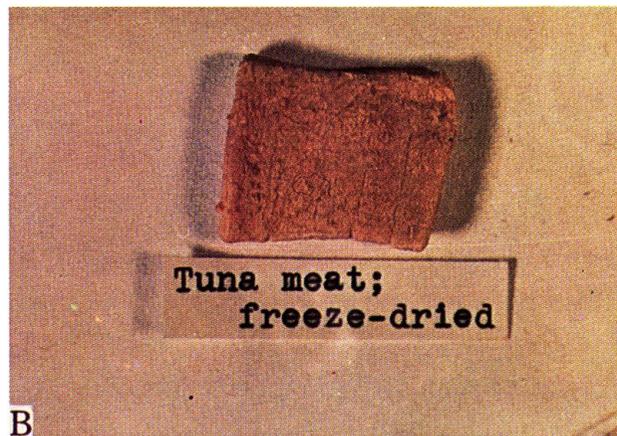B.   Freeze-dried state
C.   Rehydrated state

PLATE III (a)

Microscopic photographs of Halibut meat
A. Cross section of fresh meat   × 200
B. Longitudinal section of fresh meat   × 200
C. Cross section of freeze-dried meat (pre-forzen at –55°C)   × 200
D. Long. section of freeze-dried meat (pre-frozen at –55°C)   × 200
E. Cross section of rehydrated meat (pre-frozen at –55°C)   × 200
F. Long. section of rehydrated meat (pre-frozen at –55°C)   × 200

PLATE III (b)

Comparative photographs of Halibut meat during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE IV (a)

Microscopic photographs of Squid meat
A. Cross section of fresh meat   × 200
B. Long. section of fresh meat   × 200
C. Cross section of freeze-dried meat   × 200
D. Long. section of freeze-dried meat   × 200
E. Cross section of rehydrated meat   × 200
F. Long. section of rehydrated meat   × 200

PLATE IV (b)

Comparative photographs of Squid meat during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE V (a)

Microscopic photographs of Octopus meat
A. Cross section of boiled meat   × 200
B. Long. section of boiled meat   × 200
C. Cross section of freeze-dried meat   × 200
D. Long. section of freeze-dried meat   × 200
E. Corss section of freeze-dried meat   × 200
F. Long. section of rehydrated meat   × 200

PLATE V (b)

Comparative photographs of Octopus meat during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE VI (a)

Microscopic photographs of Abalone meat
A. Cross section of fresh meat   × 200
B. Long. section of fresh meat   × 200
C. Cross section of freeze-dried meat   × 200
D. Long. section of freeze-dried meat   × 200
E. Cross section of rehydrated meat   × 200
F. Long. section of rehydrated meat   × 200

PLATE VI (b)

Comparative photographs of Abalone meat during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE VII (a)

Microscopic photographs of Scallop adductor muscle
A. Cross section of fresh meat   × 200
B. Long. section of fresh meat   × 200
C. Cross section of freeze-dried meat   × 200
D. Long. section of freeze-dried meat   × 200
E. Cross section of rehydrated meat   × 200
F. Long. section of rehydrated meat   × 200

PLATE VII (b)

Comparative photographs of Scallop adductor muscle during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE VIII (a)

Microscopic photographs of Short-necked clam
A. Cross section of fresh meat   × 200
B. Long. section of fresh meat   × 200
C. Cross section of freeze-dried meat   × 200
D. Long. section of freeze-dried meat   × 200
E. Cross section of rehydrated meat   × 200
F. Long. section of rehydrated meat   × 200

PLATE VIII (b)

Comparative photographs of Short-necked clam during processing
A. Fresh state
B. Freeze-dried state
C. Rehydrated state

PLATE IX (a)

Microscopic photographs of Clam (Ezo-Bakagai)
A.   Cross section of fresh meat   × 200
B.   Long. section of fresh meat   × 200
C.   Cross section of freeze-dried meat   × 200
D.   Long. section of freeze-dried meat   × 200
E.   Cross section of rehydrated meat   × 200
F.   Long. section of rehydrated meat   × 200

PLATE IX (b)

Comparative photographs of Clam (Ezo-Bakagai) during processing
A.   Fresh state
B.   Freeze-dried state
C.   Rehydrated state

PLATE X (a)

Microscopic photographs of Prawn meat
A.   Cross section of fresh meat   × 200
B.   Long. section of fresh meat   × 200
C.   Corss section of freeze-dried meat   × 200
D.   Long. section of freeze-dried meat   × 200
E.   Cross section of rehydrated meat   × 200
F.   Long. section of rehydrated meat   × 200

PLATE X (b)

Comparative photographs of Prawn meat during processing
A.   Fresh state
B.   Freeze-dried meat
C.   Rehydrated meat

PLATE XI (a)

Microscopic photographs of matured eggs of Sea urchin
A.   Cross section of fresh egg   × 200
B.   Long. section of fresh egg   × 200
C.   Cross section of freeze-dried egg   × 200
D.   Long. section of freeze-dried egg   × 200
E.   Cross section of rehydrated egg   × 200
F.   Long. section of rehydrated egg   × 200

PLATE XI (b)

Comparative photographs of matured eggs of Sea urchin during processing
A.   Fresh state
B.   Freeze-dried state
C.   Rehydrated state

PLATE XII (a)

Microscopic photographs of Kelp (Makonbu)
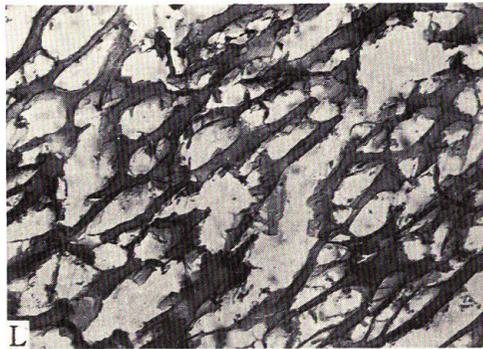
A.	Cross section of fresh Kelp	× 200
B.	Long. section of fresh Kelp	× 200
C.	Cross section of freeze-dried Kelp	× 200
D.	Long. section of freeze-dried Kelp	× 200
E.	Cross section of rehydrated Kelp	× 200
F.	Long. section of rehydrated Kelp	× 200

PLATE XII (b)

Comparative photographs of Kelp during processing
A.   Fresh state
B.   Freeze-dried state
C.   Rehydrated state

A — Atka mackerel; fresh

B — Atka mackerel; freeze-dried

C — Atka mackerel; rehydrated

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. Kobayashi: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI:　Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

A

Squid meat; fresh

B

Squid meat; freeze-dried

C

Squid meat; rehydrated

K. Kobayashi: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. Kobayashi: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

Scallop adductor muscle ; fresh

A

Scallop adductor muscle ; freeze-dried

B

Scallop adductor muscle ; rehydrated

C

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

A

Short-necked clam; fresh

B

Short-necked clam; freeze-dried

C

Short-necked clam; rehydrated

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

A. Clam (Ezo bakagai); fresh

B. Clam (Ezo bakagai); freeze-dried

C. Soft clam (Ezo bakagai); rehydrated

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

Prawn; fresh

A

Prawn; freeze-drying

B

Prawn; rehydrated

C

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

Mature eggs of sea urchin; fresh

A

Mature eggs of sea urchin; freeze-dried

B

Mature eggs of sea urchin; rehydrated

C

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products

K. KOBAYASHI: Studies on freeze-drying mechanism of marine products