THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

I. The Conditions of the Formation of Crystals in Canned Sea Foods

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Crystals of magnesium-ammonium-phosphate are sometimes found in various canned sea foods. Their presence has been reported in canned shrimp[1], in canned salmon[2)3)], and they have also been found in canned crab and canned cod[8] in the U.S.A. In Japan, they have been found also in canned seasoned bonito[4] and canned tuna[5]. As marine products, Guillerm[6] has found them in Nuoc-man of French India. Amano[7] has found the crystals in cooked juice of sardine, dried salted shark meat, fish-shoyu or in nutrient media of *Pseudomonas fluorescens* and *Clostridium fissum*.

The crystals have been identified by various investigators as hydrated magnesium-ammonium-phosphate or "struvite" with the chemical formula $MgNH_4PO_4 \cdot 6H_2O$[8)9)]. These crystals are hard and colorless, and though harmless, they are frequently mistaken by the consumer for minute broken glass. Their presence, therefore, has a definitely adverse effect upon the marketing of the canned products. The crystals in large size have been found recently in canned crab which was processed in a floating cannery. The crystals which were found in canned crab of land cannery were small, therefore no marketing claim occurred.

The authors have studied the mechanism of the formation of the "struvite" crystals and have reached some interesting conclusions. As Amano[7] stated a few years ago, the formation of the crystals is considered to be inevitable under the presence of magnesium, ammonium and phosphorus.

Experimental

The authors have observed the existence of the crystals which are visible and are tangible to finger and tongue, or are microscopic in size by the following treatment. Visible crystals on the surface of parchment paper in canned crab or on the surface of the meat of canned products, were picked up and put on a slide glass. The sizes and shapes of the crystals were observed microscopically. Invisible crystals were also raked up from the same surface with a platinum loop and put on a slide glass, and observed under the microscope. Visible crystals formed in the liquid portion of the cannd foods were gathered as follows: An aliquot of the liquid portion was centrifuged, 5 cc of water added to the precipitate and centrifuged again, and the treatment was repeated three times. The last precipitate was observed under the microscope (×600). The crystals in the last precipitate were ascertained to be not crystals of sodium chloride by

dissolving in 1% nitric acid solution and adding 1% silver nitrate solution. Invisible crystals in the juice of the canned foods were observed under the microscope.

Experimental Results

(1) *The size of the crystals which can be detected by the naked eye or by tangibility*

The following results were obtained. (1) The visible crystals (Planero crystals) having the smallest size are 60~100 μ, and microscopic crystals (Crycto crystals) are 17×5 μ in size. (2) The visible crystals in the juice of the canned crab are also 60~100 μ and the shape is needle like as shown in Fig. 1. (3) There are many microscopic small crystals in the juice of which the size is 15×5 μ in average. (4) The crystals in the upper transparent part of the juice are invisible, but there are many microscopic small crystals having irregular shape of 4.3×2.1 μ in size. The number of the crystals in the juice was 10^6~2×10^6 per cc according to Thoma's haemacytometer. (5) The size of crystals which are raked up from the surface of parchment paper and which are sensible to the end of the tongue or teeth is about 100 μ, and those which are tangible to the finger tip were above 150 μ. Those crystals can be seen by the naked eye with close observation.

Fig. 1. Visible crystals in the juice of the canned crab (550×)

(2) *Conditions of the formation of the crystals*

As above stated, there are always crystals having visible or microscopic size in the juice of canned crab. Here, the authors have detected the existence of those crystals in the juice of other canned marine products, e.g., canned boiled salmon, saury, mackerel, etc.

In canned mackerel, all of five cans examined included microscopic crystals. In canned salmon, four or five cans had microscopic crystals, but one can had no microscopic crystals. In canned saury (mackerel-pike), there were also no microscopic crystals. In nine of the cans there were visible crystals. All the cans which had no visible crystals were prepared by the training factory of our Faculty by employing city water throughout the course of the processing period.

(3) *The difference of conditions between the cans containing crystals and those containing no crystals*

Yamada et al[10] have recently said that there is no difference between the washing by fresh water or sea water, and between rapid cooling or slow cooling after the pro-

cessing of canned foods. As previously observed, the reason for the difference of the formation of the crystals in the canned food of same kind of fish are an enigma. However, the present authors have found a remarkable interesting difference of relative viscosity between the cans in which crystals had found and those in which no crystal had formed as shown in Table 1. As seen in Table 1, in the juice having larger value

Table 1. Relative viscosities of liquid portions in the cans containing crystals and those containing no crystals

Kinds of can	Factory	Relative viscosity	Crystal	
			Visible	Microscopic
Salmon	Floating cannery	2.1	none	less
	Land cannery	2.5	none	less
	Training factory	2.8	none	less
Saury	Training factory	2.8	none	much
Mackerel	Training factory	2.8	none	much
Crab	Floating cannery	1.4	Much of large crystals	much
	Land cannery	1.4	Much of small crystals	much
	Training factory	1.4	Much of very small crystals	much

of relative viscosity there is no visible crystal, or there are some microscopic crystals. But in the juice having smaller value of relative viscosity, for example, in canned crab, there are many visible or microscopic crystals. This fact may show, as Nagai[11] has said, that the visible or microscopic crystals are difficult to crystallize out in the colloid-like solution. In canned fish meat, the reason for the larger value of relative viscosity of the juice, is the gelatinization of the collagen of fish skin.

(4) *The relation between the crystal formation and amounts of magnesium, phosphorus and ammonium contents in canned crab meat and other canned marine fish*

Phosphorus exists in fresh lobster meat in the range from 0.13 to 0.16% in the form of inorganic phosphorus and 0.26 to 0.3% in the total phosphorus content, and 0.05~0.12% of the inorganic phosphorus in the pickle of canned lobster[12]. The present authors have analyzed the amount of phosphorus content of the pickle and that of the meat in canned crab, and have obtained as shown in Table 2.

Table 2. Magnesium and phosphor contents in canned crab meat

	Solid portion			Liquid portion		
	Soluble (%)	Insoluble (%)	Total (%)	Soluble (%)	Insoluble (%)	Total (%)
Mg	0.018	0.089	0.106	0.004	0.004	0.008
P	0.055	0.086	0.146	0.093	0.076	0.177

According to Hollett[12], the concentration of magnesium varied from 0.0227 to 0.0234% in the meat of fresh lobster muscle, and in the pickle of canned lobster was in the range of 0.010 to 0.028%. In other raw fish meat, 0.58% in shark meat[13], 0.55% in Anko fish (*Lophius litulon JORDAN*), 0.76% in mackerel[13], 0.62% in Nibe fish. The authors have analyzed the magnesium content in the meat and in the pickle of canned crab, and have obtained the results shown in Table 2. According to the authors' previous experiments[14], the concentration of volatile basic nitrogen which is mainly ammonia nitrogen is 8~12 *mg%* in fresh crab meat, 9~10 *mg%* in fresh mackerel meat, 4~14*mg%* in fresh Atka-mackerel meat. According to the data of Reed[15], in fresh lobster meat the amount of ammonia is approximately 0.005%. The concentration of the ammonium ions was 0.010~0.035% nitrogen in the pickle of canned crab (*Paralithodes camtschaticus*).

The amounts of magnesium, phosphorus and ammonia content necessary for the formation of crystals must be above a certain definite minimum quantity which will be described below, and the minimum quantities of those components exist in many marine fish meat. Especially when the sea-water is used in the procedure of canning fish meat, the amount of magnesium increases. According to Hollett[12], sea-water of 3.5% salinity contains 0.132% magnesium; furthermore the concentration of magnesium in the pickle and in fish meat in the can became often more than doubled by using sea-water in at least two steps of the canning procedure. In canned crab in which the amount of magnesium content exists above the minimum quantity needed to form the crystals, it often occurs that neither visible nor microscopic crystals have been found in the can. This fact may perhaps be due to the difference of relative viscosity of the juice of canned foods.

(5) *The microscopic crystals exist in canned marine products in the preparation of which sea-watar has been used*

As seen in Table 1, various canned products of salmon, mackerel, saury and crab which were prepared at the training factory of our Faculty were made by using city water. In those cans, visible crystals were not found. That is to say, the use of fresh water prevents the formation of the visible crystals, because the amount of magnesium needed to form the crystals in the raw fish meat exists below the minimum concentration.

(6) *The difference of the formation of crystals in canned products*

It has been said that the size of the crystals in canned crab which was prepared at land canneries is smaller than that prepared in floating canneries. This fact may also be noted in Table 1. The largest size of crystals in canned crab which was prepared in land canneries was 2×0.1 mm; on the other hand, the largest size of those from the floating cannery product was 5×2 mm. But the size of crystals from products of the

training factory of our Faculty is very small. However, microscopic crystals are found in the juice of canned crab of land caneries or from the training factory. Those facts are considered to be due to the difference of the velocities at which the cans were cooled after the processing. These facts were ascertained in the lately reported experiments which were carried out in vitro.

Summary

In a canned product containing magnesium, ammonium and phosphate ions, precipitation of $MgNH_4PO_4 \cdot 6H_2O$ will continue until equilibrium is reached between the precipitate and the concentration of the solution of the constituent ions. In vitro minimum concentration of magnesium of 0.018% combines with the minimum concentrations of magnesium of 0.013% of ammonia and 0.07% of phosphorus. This result agrees with the observation of Hollett[12] that the magnesium content of pickle is onethird or less that of ammonia or phosorus.

When the minimum concentration of constituent ions exists in canned products, especially in the pickle of small relative viscosity, e.g. in canned crab, the magnesium-ammonium-phosphate crystals visible or microscopic in size, are formed in the juice of the canned products. In this case, if the viscosity of the juice is large, e.g., that of canned salmon, saury, mackerel etc., the formation of the crystals is prevented or the size becomes microscopic. The viscosity of the juice of fish meat canned with the skin becomes viscid after the processing as a result of the gelatinization of the collagen of the skin. If the canned products are rapidly cooled, the size of the crystals is small, but the number is great; on the other hand, if the cans are slowly cooled, the size of the crystals is large, but the number is small. Those facts will be demonstrated in the later experiments.

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