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

X. General Consideration

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It has been known that glass-like crystals occur in canned sea foods. Those crystals are called struvite, of which chemical formula is $MgNH_4PO_4 \cdot 6H_2O$; they are dissolved in acid, and harmless for human beings.

The cause of the formation of the crystals in the canned foods has been studied by many investigators. However, the exact cause was not determined. In this series of papers, the authors have described their studies on the mechanism of the formation of the crystals in test tubes and the obtained experimental results have been demonstrated practically in the processing of canned sea foods.

From many experiments the following results were obtained: chemical components of magnesium and phosphate which are contained in the canned fish meat and ammonium which is generated from the muscle protein are combined in the heating process of the sterilization, the compound crystallizes out in larger size during the slow cooling processing after sterilization and the formed crystals furthermore grow to larger sizes during storage at comparatively high temperature.

The solubility and the shape of the crystals in the test tube are influenced by the temperature. The maximum solubility of the crystal is at about 50°~60°C. But above 50°C, the shape of the crystals is amorphous, while below 50°C, the crystal is needle-shaped having regular faces. In the present discussion the crystallizing temperature in canned foods is below 50°C.

The crystals which generate at 50°~30°C are particularly large and have beautiful regular faces. The authors have called the range of 50°~30°C **"Zone of the formation of large crystals"**. At the cooling of the canned foods after sterilization, when the temperature of the can passes rapidly through this zone, the crystals formed are small and numerous. If the formation of the crystals, even if they are invisible, is inevitable in the canned sea foods, the size of the crystals should be remained as small as possible. For that purpose, rapid cooling should be carried out strictly. However, even the invisible small crystals will grow to larger visible size during storage at as high temperature as 50°~30°C, so the storage temperature also should be lower.

The value of ion pH of canned food has an influence also upon the solubility of the crystal. In the acidic side below pH 4.0, the solubility becomes larger, therefore the crystals do not easily form in the acidic side. As far as the taste of the canned food permits, the addition of acids may be a method for preventing the formation of the crystals. But in many cases, the addition of acids makes the taste poor.

The ion concentration of the components, magnesium, ammonium and phosphate, will exert influence upon the formation of the crystals. Especially the amount of magnesium is important, because the amount of magnesium is sufficient if there is only one third of the amounts of the other components of the crystal. That is to say, when magnesium is contained above 0.0012%, the visible crystals may possibly form. In many canned sea foods the amount of the contained magnesium is above the amount required to form the crystals. Therefore the formation of the microcrystals is inevitable. The amounts of the components of the crystals in the pickle of the canned foods vary with the kind, the condition of the content and the freshness of the raw material. For example, when the raw material was unfresh, in spite of the increasing of the amount of ammonia, the number of crystals was small. This may be owing to the decrease of the amount of magnesium by the washing of the meat before packing, or by the decomposition of the meat.

It was described in paper I that in such canned foods, mackerel, saury, salmon etc. having high viscous juice, the size of the crystals formed was small. When the juice of the canned foods is high viscous, the crystallization is slow, but if the crystals once are formed, they have possibility to attain large size, and to become to have beautiful regular faces. Therefore, it is impossible to discuss the formation of the crystals in the various kinds of canned foods having various properties of contents only on the basis of the difference of the viscosity of the juice. The fact that there are only a few crystals in canned mackerel or saury is perhaps due to the low concentration of the components in the juice of the large quantity and to its being agitated by the rapid transfer of the heat in the juice during the cooling process. In those respects the condition of the formation of the crystals in canned mackerel or saury is different from that of canned crab.

Thus the various factors influencing the formation of the crystals are considered. Among those factors the most important one is considered to be the temperature and the concentration of the components of the crystals. As the formation of the crystals in the canned sea food is inevitable, the size of the crystals formed should be kept to invisible ones (microcrystals). The fact that the formation of the crystals in canned sea foods is not greatly influenced by the difference between the use of fresh water or sea water as factory water means perhaps that a very small quantity of magnesium is sufficient to form the crystals. Even if fresh water is used, the amount of magnesium in the raw fish material is already sufficient to enable formation of the crystals

However, recently Fujii and Yamada[1] have suggested that the formation of the crystals may be due mainly to the fresh raw material. They have estimated the amount of the crystals in canned foods by separating the crystals by means of the difference of the specific gravities of carbon tetrachloride and sodium iodide followed by determining the amount of magnesium in the separated crystals. By this method of estimation, they have studied the causes of the formation of the crystals. According to the obtained results, they have suggested (1) that the difference of the cooling velocities did not exert influence upon the formation of the crystals (size and shape), (2) that the using of sea water is not necessarily the cause of the formation of the crystals and (3) that the raw material itself contains the principal cause of the formation of the crystals. In their method for the estimation of the amount of the crystals, they have said that visible crystals (above 0.2～0.3 *cm* ～ 0.1 *cm*) can be separated by using carbon tetrachloride and that crystals of one-tenth the size of the visible crystal can be separated by using sodium iodide. However, in the present authors' experiments, not only visible size crystals, but also invisible size (microcrystals) (13×8 μ) pass into the layer of carbon tetrachloride. To summarize Fujii and Yamada's paper[1] practically reaches the conclusion that the quantity of magnesium of the visible crystals and some part of the microcrystals can be estimated. On trial, the difference of the formation of the crystals owing to the cooling velocities is shown in Table 1.

Table 1. The state of the crystals formed in the course of cooling canned crab by various method (reprinted from Fujii and Yamada's report)

Sample No.	Cooling method	Amount of formed crystals (amount of Mg *mg*)				
		Perchment paper	Meat and juice		Total (*mg*)	Size of crystal on perchment paper
			CCl_4-layer	NaI-layer		
A	Cooled by fan (40 min.)	29.3	48.4	0.1	77.8	large
	Cooled in sea water (6°C, 10 min.)	62.6	47.4	2.0	112.0	middle
B	Cooled by fan (40 min.)	72.6	54.5	31.3	158.4	middle
	Cooled in sea water (6°C, 10 min.)	77.7	49.4	43.4	170.5	middle
C	Cooled by fan (50 min.)	30.3	85.8	24.2	140.3	small
	Cooled in sea water (3°C, 10 min.)	34.3	78.7	19.2	132.2	small
D	Cooled by fan (50 min.)	15.1	123.1	29.3	167.5	small
	Cooled in sea water (3°C, 10 min.)	31.3	119.1	10.0	160.4	middle

In presenting Table 1, Fujii and Yamada have said that there seems to be no difference in the amount and size of the crystals according to cooling velocities. But the present authors would like to comment the results in Table 1 with regard to the cooling velocity, Fujii and Yamada have not estimated the temperature in the can by a thermo-couple. The cooling by electric fan for 40 minutes in Table 1 makes the temperature at the center of the can 50°～45°C, for 50 minutes, 45°～40°C according to the present authors' experiences. When the cans are cooled by being submerged in sea water of 6°

or 3°C for 10 minutes, the temperature will be 35°~40°C. After having been submerged, when the cans are left in the air, the temperature falls very slowly. Their temperature passes very slowly through **"Zone of the formation of large crystals"**. In Fujii and Yamada's experiments, they have not discriminated the cooling velocies at all. So there was perhaps no difference in the formation of the crystals (size and number) in relation to the cooling velocities. However, if the cooling by an electric fan is defined to be **"slow cooling"** and the cooling by submergence in sea water is defined to be **"rapid cooling"**, the results except D-sample showed somewhat smaller sized crystals, or the same on the parchment paper of the canned crab cooled rapidly than that cooled slowly. As the total amount of magnesium in Fujii and Yamada's results may contain the visible and invisible microcrystals as stated above, the only amount of magnesium in the separated crystals which passed into the carbon tetrachloride layer should be compared. If the amounts of the magnesium are compared by cooling velocities, the amount in the cans cooled rapidly in sea water is less than that in those slowly cooled by an electric fan as seen in Table 1. In Fujii and Yamada's results, if the argument is as above, the comparison of the formation of the crystals from the cooling velocities is considered to be possible. According to Fujii and Yamada's results, difference in the formation of the crystals dependent upon freshness of the material was seen. The size of the crystals on the parchment paper and in the juice of the cans made from fresh raw materal, is larger than that from unfresh material. Those results agreed with the present author's results. However, the influence of the cooling velocity upon the formation of the crystals is clearly greater than that of freshness of raw material, according to the present authors' results.

It is advisable to use a complex-making agent in order to prevent the formation of the crystals in the canned foods. The present authors have used various kinds of complex-making agents, and found that the amount of sodium hexametaphosphate should be above 0.11~0.22 % of the content of the canned food, E. D. T. A. of 0.34~0.67 % and Mascolin "M" and "T" ($M_n+2P_nO_{3n+1}$) of 0.1~0.28 % in order to prevent the formation of the crystals. But the addition of any large amount of those complex-making agents exerts a bad influence upon the taste of the food and health of human beings. So the addition of complex-making agent should be less than 0.11~0.22 % of sodium hexametaphosphate and Mascolin "M"., "T".

As noted above, the formation of the crystals, $MgNH_4PO_4 \cdot 6H_2O$, is inevitable in canned marine foods. Therefore the size of the crystals formed should be controlled below visibility by rapid cooling after the sterilization in the retort or by the addition of a complex-making agent in quantity below the point where it would injure the taste or quality of the canned foods. However, it is difficult rapidly to cool the processed cans by a large amount of fresh water on the floating canneries, so the cooling method or the addition of adequate complex-making agent must be further considered in future.

Literature Cited

1) Fujii, H. & Yamada, A. *et al.* (1956). *The Research of Nippon Suisan Co., Ltd.* **7**, 31~38.