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Determination of Tin in Canned Foods by X-Ray Fluorescence Spectrometry

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Wavelength-dispersive X-ray fluorescence spectrometry following a simple pretreatment was developed to determine levels of dissolved tin in canned foods. Sample syrup or a homogenate solution of fruit (meat) was freeze-dried and diluted with the same weight of cellulose powder. The mixed powder was then quickly formed into a pellet for X-ray measurements. This analytical method (detection limit, 5 ppm) was used to determine levels of tin in several kinds of canned foods from the present markets. The analytical results indicated that high concentrations (100–300 ppm) of tin were present in cans of many kinds of fruit, and a relationship was observed between the concentration and the length of time after manufacture. After a can was opened, the amount of dissolved tin rapidly increased. These results are consistent with those of Horio *et al*., which suggests that the issue of tin dissolving from cans has not been adequately addressed, despite their previous warning.

Key words —— tin, canned food, X-ray fluorescence spectrometry, dissolved tin

INTRODUCTION

Interest in tin has focused on its toxic potential in humans through the contact of foods with tin-coated cans and tinfoil. Large amounts of tin can accumulate in foods in contact with tin plate unless these are lacquered or coated with resin. In a comparison of the tin levels in various types of foodstuffs in either cans only partially, or not resin-coated (so-called plain can), cans entirely resin-coated, or non-tin packing, a complete resin-coating of tin-plated steel reduced the amount of tin in the foods by at least a factor of 50, as long as the coating remained intact.[1)] While ingested tin has low toxicity, due in part to its poor absorption and retention in tissues, abnormal dissolved-tin accidents have occurred, and many victim have suffered food poisoning with vomiting and diarrhea.[2–4)] Concerning the amount of tin dissolved from plain cans and the mechanism, comprehensive studies have already been reported by Horio *et al*.[5–9)] They alerted us to the problem of canned foods containing dissolved tin in 1965. Thus, it would be worthwhile to examine the tin concentrations in canned foods being sold today to verify that the problem of dissolved tin has been adequately addressed.

The techniques that are most commonly used for determining tin are colorimetry, polarography, and atomic absorption spectrometry.[10–15)] These methods require complex procedures, such as wet digestion. In contrast, X-ray fluorescence spectrometry (XRF) is a convenient analytical method and is suitable for many samples that contain tin at relatively high concentrations, such as syrup and fruit (meat) in plain cans. Nevertheless, little work has been done on XRF for determining tin in canned foods.

In this report, we describe a relatively simple and reliable analytical method for determining levels of tin in canned foods by XRF combined with a pretreatment procedure, *i.e*., a freeze-drying of sample solution and dilution with cellulose powder. This method was used to determine tin levels in several canned fruit samples from the present markets.

MATERIALS AND METHODS

Materials —— Canned food samples [13 different cans of fruit and one can of bamboo shoots can (plain cans), and a can of crab (resin-coated)] were purchased at a Japanese market. All reagents were of the highest quality available.

X-Ray Fluorescence Analysis —— Syrup samples (5 ml) were freeze-dried in a 100-ml flask and the same weight of cellulose powder as the freeze-dried powder was then added to the flask and mixed quickly. For fruit samples, 50 g (fresh weight) of sample was homogenized with water and one-tenth of it was treated as in the case of syrup. Each powdered sample (450 mg) was immediately pressed into a pellet of 2.0 cm in diameter at 10 t of pressure. If the powder was sticky, a thin (4.0 μm) prolene film (Chemplex Industries, Inc., Stuart, U.S.A.) between

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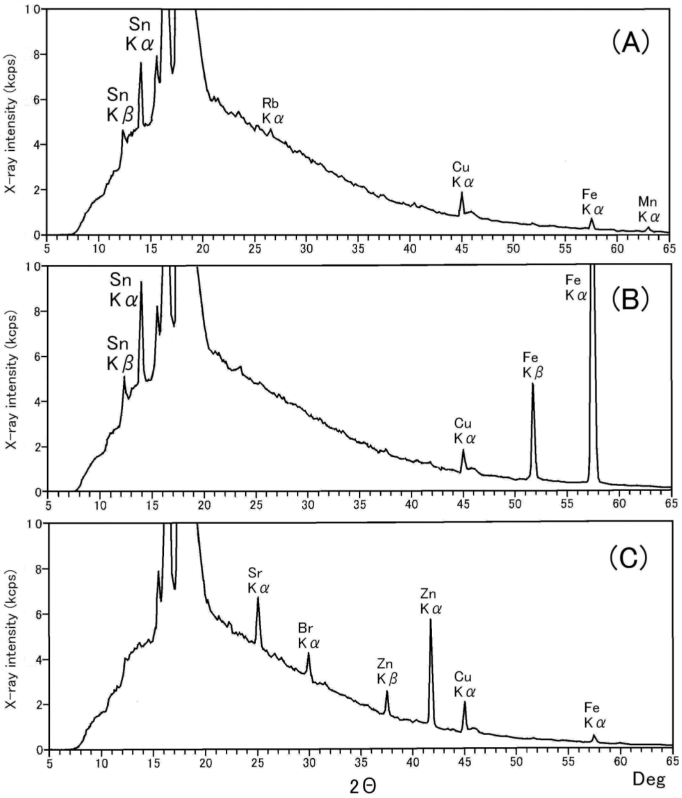

Fig. 1. X-Ray Fluorescence Spectra of Three Samples of Canned Foods

(A), pineapple (plain can, 10.5 years after manufacture) containing a high level of tin. (B), peach (plain can, 9.2 years after manufacture) containing a high level of tin. (C), crab meat (resin-coated can, 9.0 years after manufacture) containing an undetectable level of tin.

the sample powder and the surface of the stainless steel of the pressing device was used to help form the pellet. X-ray measurements were performed on pellet samples with a wavelength-dispersive X-ray fluorescence spectrometer (Rigaku ZSX100s) equipped with a rhodium anode X-ray tube. Concentrations of tin and other elements were analyzed using the fundamental parameter (FP) method with several standard samples.[16)]

RESULTS AND DISCUSSION

Figure 1 shows the X-ray fluorescence spectra for typical pineapple (A) and peach (B) samples containing high tin levels in plain cans and a normal crab meat sample (C) containing a very low tin level in a resin-coated can.

Qualitative analysis was easily performed based on the peak position (diffraction angle, 2θ) of the characteristic X-rays generated from the sample materials. The characteristic X-rays (Kα and Kβ) of tin appeared at specific positions (2θ: 14.0° for Sn-Kα, 12.5° for Sn-Kβ) in the upper and middle spectra (A, pineapple; B, peach, both in plain cans) with strong intensity, compared with that of the sample (C, crab meat) in the coated can (Fig. 1). In spectrum B, strong peaks of Fe-Kα and -Kβ were also seen, suggesting that iron dissolved from the can together with tin. All of the fruit can samples tested contained considerable amounts of tin. On the other hand, tin was not detected in the cans of fish and shellfish (data not shown), the inside of which were coated with resin.

Quantitative analysis requires correction for preliminary and secondary effects of the sample matrix. These effects can be represented by very complex equations. Most of the syrup and fruit contained light elements such as H, C, O, and N. The principal constituent in the fruit and syrup samples is a carbohydrate such as cellulose $(C_6H_{10}O_5)n$. The X-ray fluorescence technique should be applicable to nearly all elements heavier than sodium. Since the matrix effects could be calculated by assuming that the residual composition is cellulose, a quantitative analysis using the FP method is possible.[7,8)]

Table 1 shows the recovery rates of total tin added to the syrup from a certain can of oranges.

Recovery rates for 50, 100, 500, and 1000 ppm were between 95.2 and 102.5%. Thus, the recovery, reproducibility, and coefficient of variation were satisfactory.

Table 2 shows the analytical results for syrup and fruit (meat) from various cans by this XRF method, together with the results for a can of bamboo shoots (plain can) and a can of crab (coated can). Tin was detected in all of the plain can samples examined. Sixty–one hundred ppm of tin were observed for syrup samples ($n = 6$) and 79–160 ppm were observed for canned fruit meats ($n = 6$) in cans within 3 years after manufacture ("Best Before" date: 3 years after manufacture). These values were comparable to the maximum value (150 ppm) allowed for beverages in the Food Sanitation Law. On the other hand, cans that were more than 3 years old contained high levels of tin (more than 300 ppm). Quantitative analysis showed tin levels of 757 and 512 ppm in certain fruit (meat) samples of canned peach and pineapple, and 517 and 329 ppm for syrup in certain samples of canned pineapple and orange. In all of these samples, long times had passed since the can was produced (757 ppm for 9.2 years; 512 ppm for 11.4 years; 517 ppm for 11.4 years; and 329 ppm for 7.9 years). In addition, 290 ppm of tin was detected in the sample of bamboo shoots, suggesting that tin had dissolved from the can of bamboo shoots (plain). Tin was not detected in crab meat from the resin-coated can despite the long period of time after manufacture.

Table 1. Recovery Rates of Tin from Canned Food (Orange Syrup)

Added[a)]	Recovery (%)[b)]	C.V. (%)
1000	102.5	4.2
500	98.4	3.1
100	96.4	2.9
50	95.2	4.5

C.V., coefficient of variation. *a*) Amounts are expressed as ppm (μg/ml) of the syrup. *b*) Values are means (n = 5).

Figure 2 shows the relationship between the tin concentration and the number of years that had passed since manufacture. Within three years, the tin concentrations in both fruit and syrup were less than 200 ppm. However, at more than six years, the concentrations ranged from 200 to 800 ppm. An apparent positive correlation was observed between the tin concentration and the number of years after manufacture. Also, while peach accumulated tin at a higher level in fruit meat than in syrup, the tin concentration in pineapple meat was comparable to that in its syrup. A similar tendency was observed in the can of bamboo shoots (Fig. 3). These results might be accounted for by the adsorption capacity of tin on the surface of fruit meat.

Figure 3 shows the effects of standing in a plain can on the tin concentrations in syrup and fruit. After a can is opened, corrosion of the inner tin-plated surface is known to be greatly accelerated under air.[7)] In fact, after standing for only three hours at *ca*. 4°C,

Table 2. Tin Concentration (ppm) in Fruits Cans Just after Opening

Sample (manufacturer)	Manufacture date	Years after manufacture	Tin concentration (ppm) syrup	Tin concentration (ppm) fruit
Orange (L)	2003.02.01	0.8	60	97
Orange (H)	2002.12.31	1.3	63	140
Orange (M)	1996.01.26	7.9	329	392
Peach (L)	2003.06.26	0.3	69	136
Peach (H)	1994.09.07	9.2	282	757
Pineapple (M)	2002.12.24	0.9	71	79
Pineapple (S)	2002.10.01	1.5	99	119
Pineapple (D)	2000.12.16	2.9	81	83
Pineapple (L)	1999.05.25	4.5	166	149
Pineapple (S)	1998.02.04	5.8	304	217
Pineapple (K)	1993.05.02	10.5	222	227
Pineapple (L)	1992.06.04	11.4	517	512
Pineapple & Orange (H)	2003.03.20	0.7	82	115 (Pineapple), 159 (Orange)
Bamboo shoot (F)	1996.04.07	5	33	290
Crab (H)	1992.09.16	9	< 5	< 5

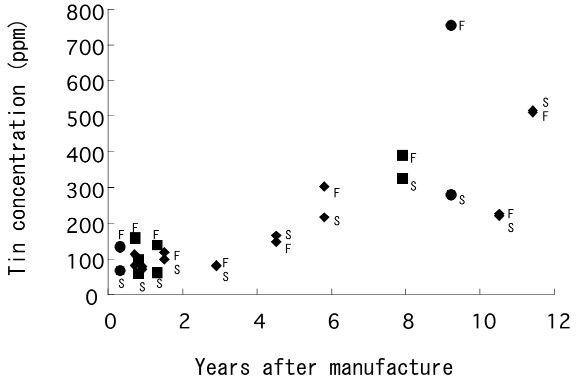

Fig. 2. Relationship between Tin Concentrations of Canned Foods and Years after Manufacture

◆: pineapple, ●: peach, ■: orange. F: fruit meat, S: syrup.

in almost all of the syrup samples in cans within three years after manufacture, the amount of dissolved tin more than doubled (from 60–70 ppm to near 150 ppm). Two days later, the concentrations reached 200–600 ppm. In cans over three years old, the tin concentrations in syrup (200 to 500 ppm when the cans were first opened) reached 300–600 ppm, after standing for two days at *ca*. 4°C. Consequently, the can contents should be transferred to glass vessels as soon as possible after the cans are opened.

In the Food Sanitation Law, the tin concentration in canned beverages should not be more than 150 μg/ml (ppm). (In the Codex Alimentarius Committee on Food Additives, the concentration should

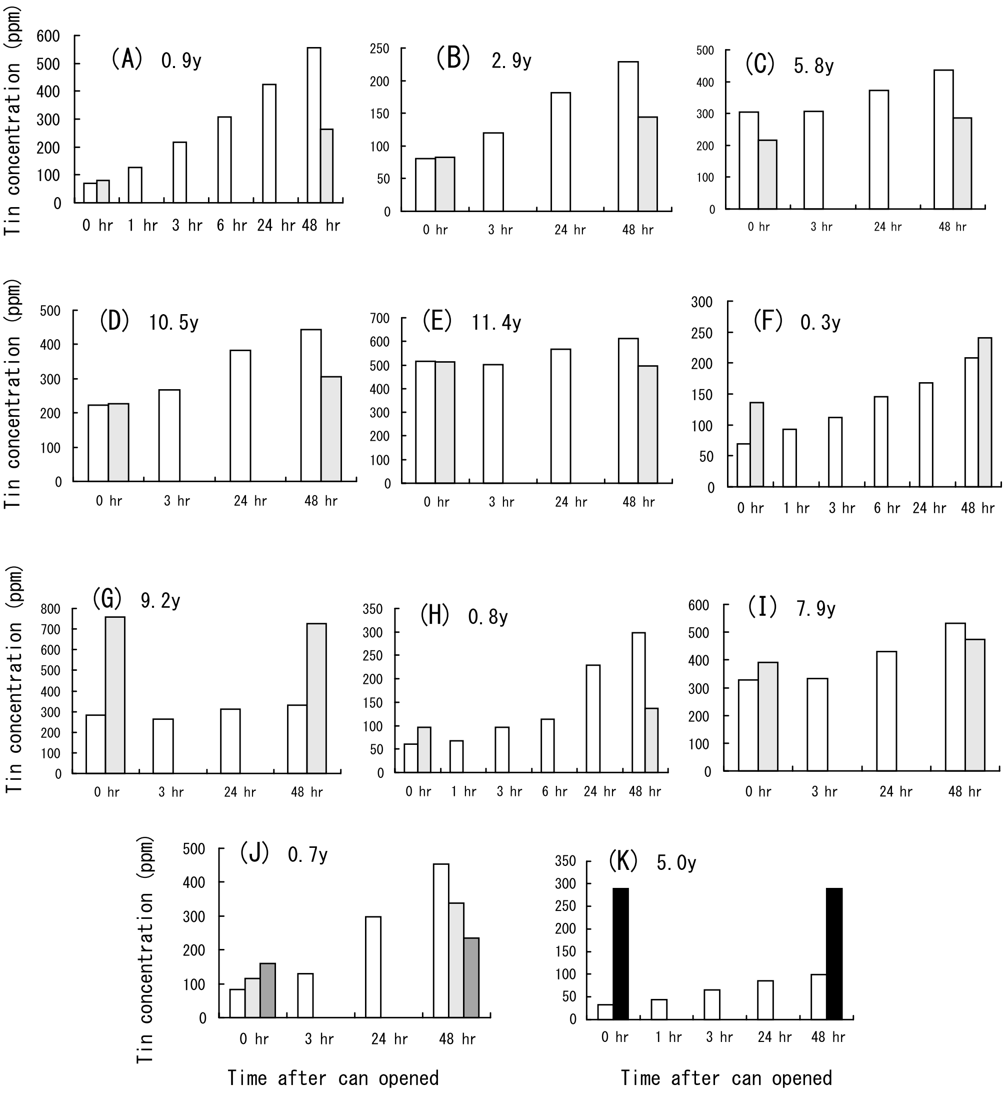

Fig. 3. Effects of Standing in an Opened Can (at *ca*. 4°C) on Tin Concentrations in Syrup and Fruit

(A)–(E): pineapple, (F) and (G): peach, (H) and (I): orange, (J): pineapple and orange, (K): bamboo shoots. □: syrup, □: fruit meat, ▨: orange meat, ■: bamboo shoots meat. The number of years after manufacture was indicated just after an alphabetic code.

not be more than 150 or 250 ppm for liquid food or solid food, respectively.) However, there are no regulations regarding the tin concentrations in other canned foods in Japan. Although tin shows low toxicity, it is known to cause abnormal metabolism of calcium.[17–19] In addition, high tin levels in juice have led to several incidences of food poisoning. This suggests that the tin concentration of canned foods should be regulated. The levels of tin in canned juice that caused poisoning were 200–600 ppm, which are comparable to the concentrations observed in canned fruit more than 6 years after manufacture or which had been allowed to stand open for over 1 day in a refrigerator. These results suggest that there is a high likelihood of unhealthy tin intake under these conditions. Since the tin in canned foods is known to have dissolved from the tin-plated surface of the inside of the can, a resin coating on the surface should help to inhibit the dissolving of tin. The tin concentrations in canned foods from Japanese markets should be carefully examined to obtain accurate information. The present XRF method could be suitable for determining tin levels in large numbers of samples of canned foods.

In summary, to determine tin levels in canned foods, we developed a relatively simple and reliable XRF (using the FP method) in which the sample is only homogenized, freeze-dried, diluted with cellulose powder, and formed into a pellet for X-ray measurements. The analytical results for several canned foods indicated that both syrup and fruit (meat) in plain cans contained tin at higher concentrations (60–757 ppm) than those (less than 5 ppm) in cans that were entirely coated with resin. Within the “Best Before” period, the tin concentrations were comparable to the upper limit allowed by Japanese law for beverages (150 ppm), and levels of 300–750 ppm were observed in older samples. When cans were opened and allowed to stand, the dissolving of tin from the can surface into syrup was enhanced, and tin concentrations of more than 150 ppm were observed. These results suggest that consumers should avoid eating canned foods after the “Best Before” date and immediately pour the contents out of a can into a glass vessel after a can is opened. For can manufacturers, there is still room for improvement in treatment of the can surface to suppress the dissolving of tin. In addition, a criterion for tin concentrations in all canned foods should be established.

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