Monitoring of Tin Residues in some Canned Food Collected from the Egyptian Local Markets during the Period of 1998 - 2000

Salwa M. Dogheim, A. M.El-Marsafy, Sohair A. Gad Alla, and Mona A. Khorshed
Ministry of Agriculture, Agricultural Research Centre, Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Dokki, Egypt.

ABSTRACT

Poor handling, transportation and bad storage practices might cause problems in canned food through denting or damage due to the can seams. A total of 196 of locally manufactured and imported samples of some types of canned food were collected from eight Egyptian local markets located in Cairo Governorate and all samples were examined for tin residues. Overall, 24% of the total samples were found to be free from tin residues, however 76% of the samples were found to contain detectable residues and 7.4 % out of total samples analyzed exceeded tin Maximum Limits (ML's) according to Egyptian Organization Standardization (EOS) ML's . It was found that the solid canned food samples showed higher contamination rates (85.1%) than liquid canned food samples (47.9%). Solid canned food exhibited a violation of 7.4%, while in liquid canned foods there was no violation above the established tin ML's. Dietary exposures to tin contaminant was mathematically estimated to see if there are any risks to health from the levels of this contaminant found in some canned food. Therefore, the mathematical calculated results showed that dietary exposures to tin are not a cause of the risk of any chronic health effects for the consumers.

KEY WORDS: Tin, canned food, monitoring, dietary intake

INTRODUCTION

Food canning is a long established and well-understood technique, which has served consumers well for nearly 200 years. This technique produces shelf stable products that can be stored at ambient temperatures. Tin occurs in the earth's crust with an average abundance of 2 mg/kg and is concentrated in areas of tin bearing minerals. Tin occurs in the earth's crust mainly as tinstone (SnO_2), which is the main source of tin production (Beliles, 1994). Combustion of fossil fuels releases tin into the air (Codex Alimentarius Commission 1998). Secondary tin sources are tin plate scrap, solders and other alloys. The present major source of tin in the diet is food contact materials; especially the release from tin cans to acidic foodstuffs (Codex Alimentarius Commission, 1995). Tin cans are actually steel cans with a thin coating layer of metallic tin (tinplate) (Beliles, 1994). There is often an internal resin-based coating layer on the tinplate. Tinplate is mainly used in cans, can ends, and closures mainly for glass bottles and jars. However, the use of tin in cans has been decreased in Europe and USA in the latest years. Tin is present in the diet only in small quantities of complex bound. Tin occurs in most foodstuffs at its levels which they generally less than 1mg in unprocessed foodstuffs (WHO ,1980). Higher concentrations are found in canned foodstuffs from dissolution of the tinplate to form inorganic tin compounds or complexes (Codex Alimentarius Commission ,1998). A maximum limit of 250 mg/kg for tin in solid foods in cans and a maximum level of 200 mg/kg for liquid foods in cans where suggested by the Codex Alimentarius Commission (1998).

Tin is on the Hazardous Substance List because it is regulated by Occupational Safety and Health Administration, (OSHA) and mentioned by American Conference of Governmental Industrial Hygienists (ACGIH) and National Institute for Occupational Safety and Health {NIOSH). Therefore, the aim of the present investigation is to estimate the actual dietary tin exposure throughout the consumption of some canned food sold in the Egyptian markets (either they are imported or locally manufactured). The monitoring program is designed as a rolling program.

MATERIALS AND METHOD

The followed method is applicable for the detection of tin in canned fruits and vegetables that migrated from the can, where the tin content is higher than the natural content (>20 mg/kg). After wet digestion of the sample with a mixture of sulfuric acid and nitric acid, the tin content is determined by using accredited colorimetric method (NMKL ,1985).

Sampling:

A total of 196 samples (148 of solid canned food plus 48 of liquid canned food) from locally manufactured and imported canned food products were collected from different Egyptian local markets located in Cairo Governorates during the period of 1998 - 2000. The number of samples analyzed from each commodity is presented in Table (2). Canned food sample of each type was homogenized with an electrical blender . The samples were stored in a refrigerator (+4°C) before homogenization or in a freezer (-18°C) after homogenization.

Reagents:

Sulfuric acid 96 % (Merck) , Nitric acid 68 % (Merck), Hydrochloric acid 37% (Merck) Hydrogen peroxide, 30% (Merck), ethanol 94 % (Lab scane), Qurecetin (Merck), Thiourea solution(Merck) and NaOH pellets (Riedel-de Haen) .Commercial tin stock standard solutions (1000 ug/ml) (Merck) was used as reference standards .

Apparatus:

Spectrophotometer UV: double - beam Unicam SP 1800. (England) was used for measuring at 437 nm.

Digestion:

Two to five grams of homogenized sample were weighted into the digestion tube and 2 ml of conc. sulfuric acid and 10 ml conc. nitric acid were added. Then the mixture was heated by raising the temperature gradually and then to boil for 72 hours, depending on the sample material. The residue was transferred with 10% hydrochloric acid into 25-ml volumetric flask. The reagent blanks (2 replicates) are prepared as samples starting from the wet digestion step.

Determination:

Two millitres of the wet digestion solution had been taken into 50-ml volumetric flask. Also, eight ml of water, 5 drops of 10% sodium hydroxide, 10 ml 10% thiourea solution, and 5 ml quercetin solution were added. Then the solution was diluted to as known volume with ethanol 94%. The calibration solutions were prepared using 2 ml of different concentration of tin standards (10, 20,40, 100 and 150 µg/ml). The calibration blank is prepared using 2-ml acid mixture. Absorbance of the samples, reagent blank, calibration solution and calibration blank are measured at the wavelength 437 nm using 10 mm cuvette.

Quality assurance procedure

Tin method was fully validated as part of the laboratory quality assurance system and are audited and accredited by the Centre of Metrology and Accreditation, Finnish Accreditation Service (FINAS), Finland. This quality system is referred to EN 45001, ISO/IEC Guide 17025 (Anonymous, 1996). The criteria of quality assurance of the Codex Alimintarius Committee were followed to determine the performance of tin. The average recovery of tin from different commodities (Tomato, Guava, Orange and Mango) on 30-125 mg/kg level varied between (87-102 %) Table (1). The reproducibility expressed as relative standard deviation is < 10%. The limits of determination in canned samples were 25-30 mg/kg. The measurement uncertainty including random and systematic error (on 95% confidence level) for Tin is less than ± 22%. The Limit of detection for tin is 10 µg/ml. The details of such results represented in Table (1).

Table 1. The average recoveries, the standard deviation and coefficient of variance percentages of tin metal in different spiked commodities.

Commodity	Tin Conc. level (mg/kg)	No. of analyzed samples	Mean	Recovery %	RSD *	CV** %
Tomato	30	10	26	87	1.9	7.3
Mango		10	30.5	102	5.6	5.6
Orange		10	28.9	97	2.3	7.9
Guava		13	28.9	96	1.7	5.8
Mango	40	15	37.5	97	2.2	8.0
Orange		15	38.2	95	3.9	10.2
Guava		15	38.5	95	3.1	5.8
Tomato	50	7	47.3	95	4.6	9.6
Tomato	125	6	115.4	94	2.1	1.96
Guava		14	122.8	98	7.9	6.4
Mango		15	122.5	98	5.0	4.0
Orange		15	122.7	99	10.4	8.5

* RSD: relative standard deviation ** Coefficient of variance

RESULTS AND DISCUSSION

A total of 196 samples of different types of canned foods, collected from different Egyptian local markets, were examined for tin as a contaminant. The Egyptian Organization of Standards Limit (EOS) (150 mg/kg) was used for comparison. The detected tin levels, contamination range and the number of violative samples are given in Table (2). Overall, 76% of the total numbers of liquid and solid canned food samples analyzed were contaminated with tin residues, of which 7.4% exceeded Maximum Limits of tin. Data demonstrated in Table (2) showed that solid canned food recorded the highest contamination percentage (85.1%), while that percentage for the, liquid canned food was 47.9%. No exceeding of the levels of tin above limits in the liquid canned food was found, however, the violation percentage of solid canned samples reached 7.4%.

Solid canned foods:

Table (2) illustrated that fruit cocktail samples showed the highest contamination and violation rates, where the percentages were 100% and 15.4%, respectively. Pears and peach samples showed higher contamination percentages (i.e. 100% and 85%, respectively), nevertheless these levels were less than the EOS ML's. Also, data showed that the contamination rates of pineapple and tomato paste were 97% and 74%, respectively. However, the violation percentages were 9.4% and 9.1%, respectively.

Liquid canned foods:

The demonstrated data in Table (2) illustrated that apricot juice recorded the highest contamination percentage (78%), followed by orange juices (64%) and tomato juices (58%). However no violation was observed in apricot, orange, and tomato juices above EOS Limits. Apple, grape, and guava juice samples were free from tin contamination.

Although most foods contain very low concentrations of tin, usually below 10 mg/kg, canned foods can contain higher concentrations, which may increase with time as a result of the gradual dissolution into the food comes from the tin coating layer used on the inside of some food cans to protect the steel body of the can from corrosion (FAO, 1986). Also, tin concentrations in foodstuffs in the un lacquered cans may exceed 100 mg/kg, while foodstuffs stored in lacquered cans have tin levels generally below 25mg/kg (Corbin, 1970). Many factors can affect the amount of tin taken up by canned foods such as the type of food, the type of can, the canning procedure used and duration and conditions of storage. Foods packed in fully lacquered cans generally contain the lowest levels of tin (Bock, 1981).

The Dietary exposure of tin:

Dietary exposures to tin for the consumers of canned fruit and vegetables are well investigated within the safety guideline set by the Joint WHO/FAO Expert Committee on Food Additive. The Joint Expert Committee on Food Additives (JECFA)of the Food and Agriculture Organization and the World Health Organization recommended a Provisional Tolerable Weekly Intake (PTWI) for tin of 14 mg/kg body weight /week to protect against the risk of any chronic (long-term) health effects. This is equivalent to 120 mg/ day for a 60 kg person.

JECFA also stated that tin levels should be as low as practicable because of the possibility of gastric irritation (JECFA, 1989). The contribution of different canned foods to the total intake of tin based on GEMS/Food data of Middle East and estimated Provisional Tolerable Weekly Intakes (PTWI) are given in Table (3). Data showed that the total estimated intake of tin (0.154 mg/kg .bw /week) is lower than the established PTWI and contributing only 1.1 % of the established PTWI. Therefore, dietary exposures to tin are not a cause for concern. The major contributors to the total intake of tin are in descending order as follows : tomato paste (34.2%), apricot juice (16.64%), orange juice (13.43%), canned pear (11.8%), fruit cocktail (9.13%), peach (9%), pineapple (4.5%), and tomato juice (1.41%). In spite of the relatively high levels of tin found in pineapple, the contribution of fruit cocktail, and tomato juice, to the total intake of tin is minimal because of their low consumption.

These survey results do not raise any long term food safety concerns for consumers as chronic health effects and such effects are not expected even at the high tin concentrations found in the tested food products.

Table 2. Minimum, Maximum and Mean concentration of tin in mg/kg as well as frequencies, number, and percentages of contaminated samples, violated samples and the analyzed Tin residues in samples collected from Egypt during the period /of 1998 - 2000.

Commodity	Total No. of Samples	Contaminated samples of each commodity		Min. tin conc. mg/kg	Max. tin conc. mg/kg	Mean mg/kg	Violative samples	
		No.	%				No.	%
Solid canned food								
Pear(I)	11	11	100	18	100	47.3	-	-
Peach (I)	26	22	85	12	100	47.5	-	-
Fruits (I) cocktail	13	13	100	24	208	93.2	2*	15.4
Pineapple (I)	32	31	97	17	182	74.7	3	9.4
Tomato (D) paste	66	49	74	11	279	78.3	6	9.1
Total1	148	126	85.1				11	7.4
Liquid canned food								
Apricot (D) juice	9	7	78	23	80	49.1	-	-
Apple (D) juice	4	-	-	-	-	-	-	-
Grape juice (D)	4	-	-	-	-	-	-	-
Guava juice (D)	5	-	-	-	-	-	-	-
Orange juice (D)	14	9	64	3	39	24.44	-	-
Tomato juice (D)	12	7	58	8	122	62.3	-	-
Total 2	48	23	47.9				-	-
Total 1 + 2	196	149	76				11	7.4

Ml's: Maximum level
EOS: Egyptian Organization of Standardization 1995
(I) Imported
(D) Domestic = locally manufactured
*** Number of samples that exceeded the ML's according to EOS (150 mg/kg)**

Table 3. Estimated Provisional Weekly Intakes (PTWI's) of tin residues in some canned foods according to gained results .

Canned commodities	Food consumption (g/day)	Tin mean (mg/kg)	Estimated intake (µg/day)	% of total
Canned pear	3.3	47.3	156.1	11.8
Peach	2.5	47.5	118.8	9
Fruit cocktail	1.3	93.2	121.2	9.13
Pineapple	0.8	74.7	59.8	4.5
Tomato paste	5.8	78.3	454.1	34.2
Apricot juice	4.5	49.1	221	16.64
Apple	4.5	-	-	-
Grape	4.5	-	-	-
Guava	4.5	-	-	-
Orange juice	7.3	24.44	178.4	13.43
Tomato juice	0.3	62.3	18.7	1.41
Total		1328 µg/day or 1328 x 7 = 9296 9296 / 60 / 1000 = 0.1549 = 0.155 mg/kg.bw/week		100

Set (PTWI) = 14 mg/kg.bw/week

Total estimated intakes as a % of set PTWI = $\frac{0.155 \times 100}{14}$ = 1.1%

REFERENCES

Anonymous. (1996). General requirement for competence of calibration and testing laboratories. EN 45001, ISO/IEC Guide 17025.

Beliles, R.P. (1994). The metals. In: Patty's Industrial Hygiene and Toxicology, Fourth edition, Volume 2, Part C. Edited by Clayton, G.D., and Clayton, F.E. John Wiley & Sons, Inc.

Bock, R. (1981). Triphenyl tin compounds and their degradation products. Residue Rev., 79:1-270.

Codex Alimentarius Commission. (1998). Position paper on tin. Doc. No. CX/FAC 98/24. Joint FAO/WHO food standards program.

Codex Alimentarius Commission. (1995). Codex general standard for contaminants and toxins in foods. Doc. No. CX/FAC 96/17. Joint FAO/WHO food standards programme.

Corbin, H.B. (1970). Separation and determination of trace amounts of tin present as organotin residues on fruits. J. Assoc. Official Anal. Chemists, 53:140-146.

FAO. (1986) . Guidelines for can manufacturers and food canners. Prevention of metal contamination of canned foods. *FAO Food and Nutrition Paper No.* 36. Food and Agriculture Organization of the United Nations, Rome.

JECFA. (1989). Evaluation of certain food additives and contaminants. A report of the Joint FAO/WHO Expert Committee on Food Additives. World Health Organization, Technical Report Series 776.

NMKL. (1985). Tin - quantitative determination of the total content in food No.115.

WHO (1980). Tin and organotin compounds: a preliminary review. World Health Organization , Geneva, Swaziland.

الملخص العربي

تقصى متبقيات القصدير في بعض المعلبات الغذائية التي تم جمعها من الأسواق المصرية خلال الفترة من ١٩٩٨ إلى ٢٠٠٠

سلوى دغيم، أشرف المرصفي، سهير أحمد جاد الله ، منى خورشيد

وزارة الزراعة – مركز البحوث الزراعية – المعمل المركزي لتحليل متبقيات المبيدات والعناصر الثقيلة فى الأغذية – الدقى – جمهورية مصر العربية

تم تجميع عدد ١٩٦ عينة من المعلبات الصلبة والسائلة المستوردة و المصنعة محلياً من ٨ أسواق محلية فى محافظة القاهرة، ولقد أوضحت هذه الدراسة أن معظم العينات التى تم تحليلها تحتوى على عنصر القصدير. ولقد وجد أن ٢٤% من العدد الكلى من هذه العينات كانت خالية من متبقيات القصدير، بينما وجد أن ٧٦% من العينات كانت ملوثة منها ٧,٤% زاد فيها تركيز القصدير و تعدى الحدود القصوى التى أقرتها مصر (الحدود القصوى المصرية) . ولقد أوضحت هذه الدراسة أن نسبة تلوث المعلبات الصلبة بالقصدير كانت ٨٥,١% و هى أعلى من نسبة تلوث عينات المعلبات السائلة (٤٧,٩%) وكانت نسبة التعدى للحدود القصوى المصرية فى العينات الصلبة هى ٧,٤% ولكن فى عينات المعلبات السائلة لم تتعدى نسبة التلوث فيها عن الحدود القصوى . كما تم حساب المتناول اليومى والاسبوعى للفرد من عنصر القصدير نتيجة لتناوله الأغذية المعلبة وذلك لتحديد مدى خطورة ذلك على الإنسان نتيجة ما قد يتواجد من عنصر القصدير فى بعض المعلبات الغذائية. وقد أوضحت النتائج أن مقدار ما يتناوله الفرد من قصدير لا يسبب أى ضرر وأقل من النسبة المسموح بها عالمياً و يمثل فقط ١,١% من هذه النسبة العالمية .