Original Research

Determination of Tin in Canned Foods by Inductively Coupled Plasma-Mass Spectrometry

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Abstract

Most foods contain very low concentrations of tin, usually below 10 mg/kg, although canned foods may contain higher concentrations as a result of the slow dissolution of the tin coating used on the inside of some food cans to protect the steel body of the can from corrosion. An inductively coupled plasma-mass spectrometry (ICP-MS) method following microwave digestion was developed and evaluated to determine levels of dissolved tin in canned foods. Accuracy of the method was tested by analyzing analytical standards containing tin at 2 levels (0.5 and 5 ppm). Amounts of tin found for the 0.5 and 5 ppm standards were 0.505 and 5.12 ppm, while repeatability relative standard deviations (RSD) were 2.42 and 1.87%, respectively. Recoveries of tin from spiked products with two levels of tin ranged from 91.3 to 105.2%. The detection limit for tin standard solution was about 0.01 ppb. The developed method was used to determine levels of tin in several kinds of canned foods from the present market. Samples of canned pineapple, mandarins, fruit cocktail, carrots, mushrooms, peas, beans, corn, peeled tomatoes, and tuna were evaluated. The relationships between tin concentrations and time periods after opening were studied.

Keywords: ICP-MS, microwave digestion, dissolved tin, canned food

Introduction

Because metals have been extensively used in agricultural, industrial, and medical applications, environmental contamination is widespread, and exposure to metals and metal compounds continues to be a significant public health problem [1].

Trace elemental determination and in particular heavy metals in foods is a concern for the food safety community due to the potential toxicity of these metals.

Tin exists in oxidation state 0 as pure metal and in alloys, in oxidation states +II and +IV in inorganic tin compounds (stannic and stannous salts), and as organotin compounds of tetravalent tin (e.g. tributyltin). Each of these species has different properties that influence bioavailability and lead to a different fate [1].

Some studies suggest that tin is an essential trace element for humans. However, organotin compounds have been proven to be of toxicological relevance. Triorganotin compounds are particularly toxic, explaining their wide use as biocides (e.g., in antifouling paints or pesticides) [2]. Due to their toxic properties, a high propensity to accumulate in live organisms, and slow degradation in the environment, organotin compounds constitute a group of pollutants of organic origin that is dangerous for the marine environment [3].

Interest in tin has focused on its toxic potential in humans through the contact of foods with tin-coated cans

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and tinfoil. Large amounts of tin can accumulate in foods in contact with tin plate unless these are lacquered or coated with resin [4]. The acute toxicity of inorganic tin is manifested as gastric irritation, nausea, vomiting, and abdominal discomfort. Inorganic tin salts are poorly absorbed by the gastrointestinal tract and rapidly excreted. Nevertheless, there are several reports of gastric irritation and vomiting in humans consuming canned foods or beverages, particularly sour fruit products packaged in tinplate cans and containing high levels of tin [5]. High concentrations of tin bring serious interference to the metabolism of zinc [6].

From published data, there appears to be a small amount of evidence suggesting that consumption of food or beverages containing tin at concentrations at or below 200 ppm has caused adverse gastrointestinal effects in an unknown but possibly small proportion of those exposed [7]. On the other hand, when the contamination reaches this level the organoleptic properties of the food can be seriously affected [8].

The Joint Expert Committee on Food Additives of the Food and Agriculture Organization and the World Health Organization (JECFA) has 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) effects [9]. This PTWI is equivalent to 120 mg/day for a 60 kg person.

According to the Food and Agriculture Organization of the UN/World Health Organization (FAO/WHO) the maximum limit for tin in canned foods is 250 mg/kg [10]. The EU legislation (EC No. 1881/2006) [11] suggests a maximum limit of 200 mg/kg for inorganic tin in canned foods, of 100 mg/kg for canned beverages, and of 50 mg/kg for canned liquid foods for young children.

Most foods contain very low concentrations of tin, usually below 10 mg/kg, although canned foods may contain higher concentrations as a result of the slow dissolution of the tin coating used on the inside of some food cans to protect the steel body of the can from corrosion.

Many factors influence the amount of tin that is taken up by canned foods from the internal coating of the can. These include: the type and composition of the product itself (including the acidity, the presence of organic acids and pigments and certain ions such as nitrate); the type of can (including the quality and thickness of the tin coating, the amount of the tin coating that is exposed to the can contents, and the presence or absence of a layer of lacquer over the tin plate); the canning procedure (including the amount of air in the container at sealing and the internal vacuum and 'headspace' between the fill level of the product and the lid), and storage (time from canning and temperature during storage) [12].

Under normal circumstances the shelf life of canned foods is set so that the tin content of the food remains well below the legal limit throughout the product's shelf life. However, under certain circumstances tin dissolution can accelerate, causing unacceptably high tin concentrations in the food within its shelf life [13].

Table 1. Operating conditions for ICP-MS.

ICP-MS, model Elann9000	
Rf power (W)	1000
ICP torch	fassele type
Torch injector	ceramic alumina
Nebulizer	tip cross flow
Nebulizer gas flow (l/min)	0.93
Sweeps/reading	20
Reading/replicate	2
Number of replicates	5

The tin content indicates the extent of corrosion of the container and the acceptability of the contents. Consequently, the determination of tin in various canned foods is important for assessing food quality [14].

Several international methods exist for the determination of tin. ISO proposes a spectrophotometric method [15] while the AOAC Int. describes an atomic absorption spectrophotometric (AAS) method [16]. A survey of the literature shows that several techniques are available to the analyst for tin analysis in foods, including spectrophotometry [17, 18], X-ray fluorescence spectrometry [4], atomic absorption spectrometry [5, 19-25], and electrochemical methods [26-28]. A few spectrofluorimetric methods [8, 29] and inductively coupled plasma-atomic emission spectrometry (ICP-AES and ICP-OES) [14, 30-33] have also been reported for determination of tin in food samples.

Spectroscopic methods such as mass spectrometry or atomic emission spectrometry with inductively coupled plasma (ICP-MS, ICP-AES) belong to the most universal, sensitive, and selective methods of detection utilized both in speciation analytics of organometallic compounds and in determinations of total contents of metals [34].

In this paper, we describe a relatively simple and reliable analytical method for determining levels of tin in canned foods by inductively coupled plasma-mass spectrometry (ICP-MS) combined with microwave digestion of the sample. This method was used to determine tin levels in several canned food samples from the present markets.

Materials and Methods

Instrumentation

A Perkin-Elmer ICP-MS (model ELAN 9000) was used for method development and applications. Parameter settings for ICP-MS operating are summarized in Table 1.

The nitric acid digestions were done in a Milestone Microwave Labstation, max. 1200 W, maximum pressure 100 Bar, maximum temperature 200ºC, with 75 ml TFM vessels and a 10-hole heating block.

Table 2. Conditions for microwave digestion.

Step	1	2	3	4	5	6
Temperature (ºC)	80	80	120	120	200	Cooling
Power (W)	200	200	400	400	600	0
Run time (min)	5	2	15	2	10	20

Samples

Canned food samples made from different kinds of fruit, vegetables, and fish were purchased at local markets and analyzed. Each sample was analyzed six times and the relative standard deviation in repeatability conditions was calculated. Tin concentrations in canned foods can vary considerably between individual cans in the same production batch. Therefore, tin concentrations were measured in three separate cans from the same batch for each product sampled, and the average tin concentration for the three cans was used to determine repeatability relative standard deviations (RSD).

Reagents and Chemicals

High-purity water was prepared using a Basic TWF system. Nitric acid (65%, Fluka 84380), hydrochloric acid (37%, Riedel-de-Haën 30721), and hydrogen peroxide (30%, Fluka 95302) were of analytical purity. Tin standards were prepared by dilution of a 1000 mg/l tin stock solution (Fluka 96524).

Sample Preparation

For microwave digestion, sample quantities of approximately 2.5 g were introduced into the TFM vessels, after which 5 ml 65% nitric acid and 2 ml 30% hydrogen peroxide were added. The heating program is given in Table 2. Reagent blanks were included in each series of digestions.

The vessel content was transferred to a 50 ml volumetric flask and make up to the mark with ultrapure water. The test solution was properly diluted with ultrapure water in order to attain the calibration range.

Linearity, limit of detection, accuracy, recovery of tin from spiked food products and repeatability were estimated.

Results and Discussion

Calibration and Linearity

A study was made on the linearity of tin calibration. Two calibration ranges were evaluated since tin may occur in most foods at low levels (several mg/kg), but may also

Table 3. Tin concentrations in different cans just after opening.

Sample (manufacturer)	Manufacture date	Years after manufacture	pH	Tin concentration* (ppm)	
				syrup	fruit (fish)
Pineapple (A)	2008.12.17	1.1	3.11	0.19±0.010	6.75±0.035
Pineapple (B)	2008.05.05	1.6	4.22	1.28±0.013	3.34±0.022
Pineapple (C)	2008.03.28	1.8	4.22	0.16±0.005	30.93±0.088
Pineapple (D)	2008.07.10	1.5	3.86	3.19±0.026	17.91±0.022
Mandarin oranges	2008.11.12	1.2	3.44	23.45±0.042	48.00±0.066
Fruit cocktail	2009.09.04	0.4	3.57	2.70±0.014	8.47±0.089
Small whole carrots	2009.07.31	0.5	4.93	0.14±0.006	0.38±0.014
Mushrooms	2009.03.19	0.8	4.96	0.70±0.009	0.91±0.026
Peeled tomato pieces in tomato juice (A)	2009.12.03	0.2	4.29	68.18±0.062	70.55±0.182
Peeled tomato pieces in tomato juice (B)	2007.12.31	2.1	4.28	69.59±0.054	73.68±0.156
Peas	2009.05.13	0.7	6.38	0.09±0.005	0.09±0.003
Cut green beans	2008.08.12	1.4	5.45	0.11±0.010	0.48±0.012
Whole kernel corn	2008.07.29	1.5	6.29	0.12±0.018	0.18±0.006
Tuna flakes in water	2008.12.31	1.1	6.24	0.56±0.015	0.70±0.014

*average tin concentration of six determinations±standard deviation occur at higher concentrations (several hundred mg/kg) in acidic products, e.g. fruit juices. The first range was between 0 and 1000 ppb and gave an R^2>0.9992, while the higher range was between 0 and 15 ppm with R^2>0.9995.

Limit of Detection

The limit of detection was calculated as 3× the standard deviation of the blank divided by the slope of the calibration curve for tin. The detection limit for tin standard solution was about 0.01 ppb.

Accuracy

The accuracy of the method was tested by analyzing analytical standards containing tin at 2 levels (0.5 and 5 ppm). Amounts of tin found for the 0.5 and 5 ppm standards were 0.505 and 5.12 ppm, while repeatability relative stan-

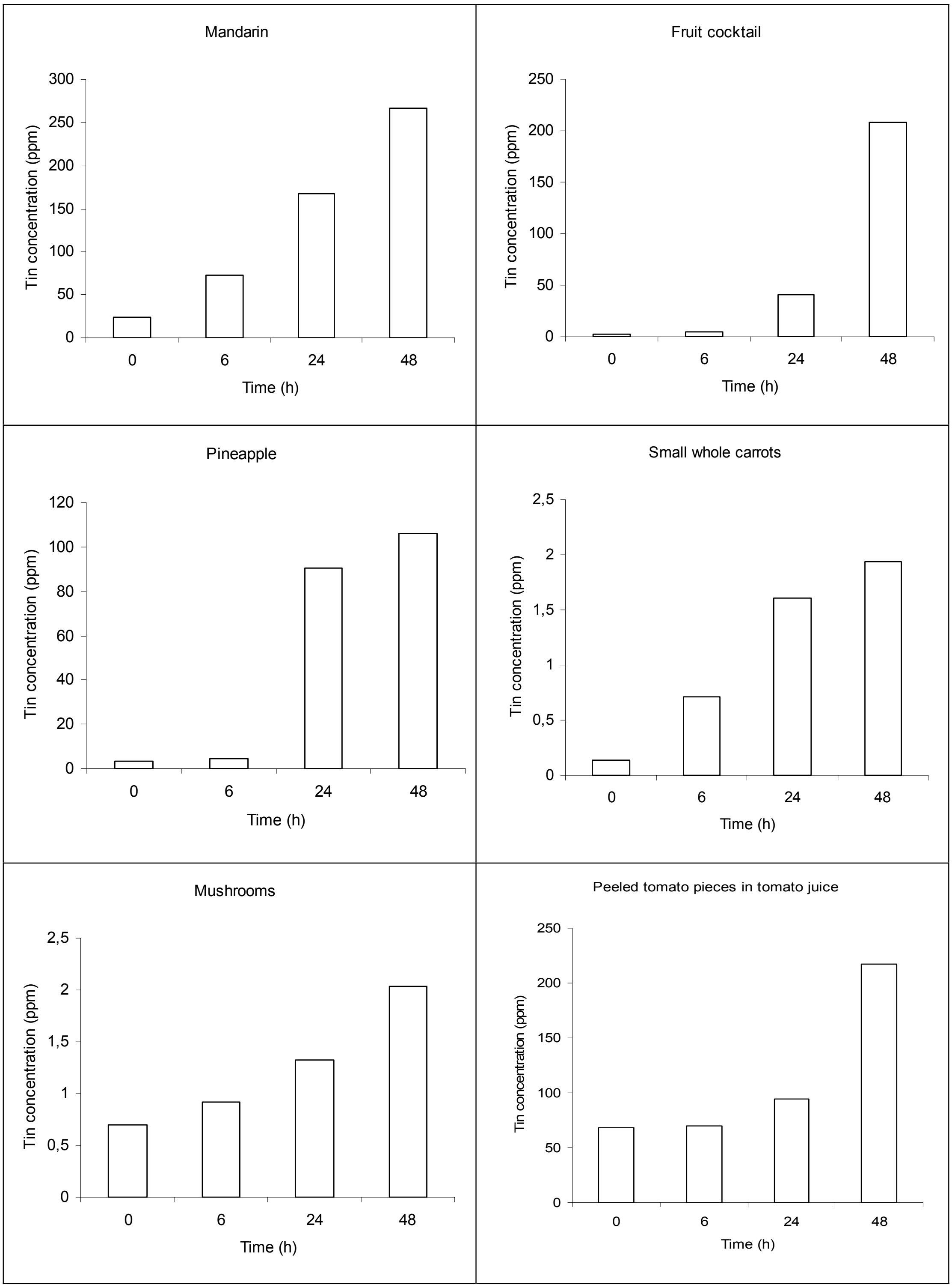

Fig. 1. Effects of standing in an opened can (at 20ºC) on tin content in syrup.

dard deviations (RSD) were 2.42 and 1.87%, respectively. RSD for unspiked samples varied from 2.2 (fruit cocktail) to 5.8% (peeled tomato).

Recovery

Recovery of tin from 6 canned foods spiked at 2 levels (25 and 100 ppm) ranged from 91.3 to 105.2%.

Survey of Tin Concentrations in Canned Foods

Table 3 shows the results for syrup and fruit (fish) from various cans by ICP-MS. The analytical results indicated total tin concentrations from 0.09 ppm to 73.68 ppm in different cans just after opening.

The maximum permissible level for tin of 200 ppm was not exceeded. The very low amounts (less than 4 ppm) of tin were observed for carrots, mushrooms, peas, green beans, corn, and tuna. The higher contents of tin were observed in cans with tomato, mandarin, and pineapple.

Different concentrations of tin between syrup and fruit (fish) were observed. The concentration of tin was higher in solid parts than in syrup. These results might be accounted for by the absorption capacity of tin on the surface.

Corrosion seems to be affected less by the number of years that had passed since manufacture (within two years) but more by the chemical composition of a specific food. As indicated by previous studies [35], the highest tin levels occurred in aggressive foods like fruits and tomato products in unlacquered tin cans. Components that may affect it are most probably the organic acids due to their H^+ concentrations, or by their ability to bind free stannous ions, resulting from interaction between the tin plate container and food, in stable chelates, particularly at the low pH values commonly encountered in fruits and tomatoes.

The relationship between the concentration and time period after opening was studied. For this experiment we used samples of canned mandarins, fruit cocktail, pineapple, carrots, mushrooms, and peeled tomatoes. Cans were stored at 20ºC and the concentrations of tin in syrup after 6, 24, and 48 h were determined. Fig. 1 shows the effects of standing in an opened can on the tin concentrations in syrup.

After a can is opened, corrosion of the inner tin-plated surface is known to be greatly accelerated under air [4]. In fact, after standing for only six hours at 20ºC, in all of the syrup samples the amount of dissolved tin increased, while two days later, the concentrations exceed 200 ppm in mandarin, fruit cocktail and tomatoes samples. Consequently, the can content should be transferred to glass vessels as soon as possible after the cans are opened.

Conclusions

A rapid and accurate method has been developed for determination of tin in canned food by ICP-MS. The results of this work showed that all the investigated canned food samples contained less than 200 ppm. The highest concentrations of tin were found in canned sour fruits and tomatoes, while the lowest concentrations were found in canned vegetables (peas, corn, beans) and fish, the inside of which were coated with resin.

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 200 ppm were observed. These results suggest that consumers should 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 improving the treatment of the can surface to supress the dissolving of tin.

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