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Inductively Coupled Plasma Atomic Emission Spectrometric Determination of Tin in Canned Food

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Various canned foods were digested sequentially with HNO_3 and HCl, diluted to 100mL, and filtered, and then tin was determined by inductively coupled plasma atomic emission spectrometry (ICP/AES). Samples of canned Satsuma mandarin, peach, apricot, pineapple, apple juice, mushroom, asparagus, evaporated milk, short-necked clam, spinach, whole tomato, meat, and salmon were evaluated. Sample preparations did not require time-consuming dilutions, because ICP/AES has wide dynamic range. The standard addition method was used to determine tin concentration. Accuracy of the method was tested by analyzing analytical standards containing tin at 2 levels (50 and 250 μg/g). The amounts of tin found for the 50 and 250 μg/g levels were 50.5 and 256 μg/g, respectively, and the repeatability coefficients of variation were 4.0 and 3.8%, respectively. Recovery of tin from 13 canned foods spiked at 2 levels (50 and 250 μg/g) ranged from 93.9 to 109.4%, with a mean of 99.2%. The quantitation limit for tin standard solution was about 0.5 μg/g.

Key words: inductively coupled plasma atomic emission spectrometry, tin, canned food, wet digestion method, standard addition method.

Both tin plate and lacquered cans are used for food storage. Tin plate cans are used when the can-food interactions are not significant or when the quality of the food is better in tin plate can. In canned foods packed in tin plate can, tin dissolves into the food because of the interaction between container and contents. The tin content indicates the extent of corrosion of the container and the acceptability of the contents. Estimation of tin in various canned foods is important in assessing food quality. The Japanese regulatory limit for tin in canned beverages is 150 μg/g. The Canadian regulatory limit for canned food is 250 μg/g. An excellent review of commonly used methods of determination of tin in foods has been presented by Horwitz (1). The photometric determination of tin using salitylidenamino-2-thiophenol as a reagent (2), not cited in the review, has been authorized by the pharmaceutical society of Japan (3). Determinations of tin in canned foods by atomic absorption spectrometry (AAS) have been investigated very actively (4, 5). Inductively coupled plasma atomic emission spectrometry (ICP/AES), however, offers wide dynamic range and relative freedom from interferences compared with AAS.

The objective of the present study was to establish a method for the rapid determination of tin in canned foods by ICP/

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AES. Wet digestion with a combination of concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) was used for sample preparation.

Experimental

Reagents

(a) *Concentrated HCl (35% v/v), concentrated HNO_3 (61% v/v), and acetone.*—Analytical grade (Wako Pure Chemical Industries Ltd., Osaka, Japan).

(b) *Tin stock solution.*—Dissolve 1.000g tin (>99.999% pure, Wako Pure Chemical Industries Ltd.) in 50mL concentrated HCl. Dilute to 1L with 3N HCl

(c) *Tin metal plate.*—A thickness of 0.2 mm, purity of 99.99% (Rare Metallic Co. Ltd., Tokyo, Japan). All canned foods were purchased from local markets.

Apparatus

(a) *Inductively coupled plasma atomic emission spectrometer.* — Model ICPS-1000 III (Shimadzu, Kyoto, Japan) interfaced under standard operating system.

(b) *Water purification system.*—Elgastat UHQ (Elga Ltd., Lane End, United Kingdom).

Preparation of Analytical Standards

To check the accuracy of the method, analytical standards were prepared as follows. An accurately weighed tin metal plate (50 × 260 × 0.2mm) was dipped in 300g fresh Satsuma mandarin juice in a bottle. The bottle was tightly capped with a screw cap and placed in a constant-temperature oven at 90℃ for 41.5h. The tin plate was then removed from the juice, washed with acetone and then water, dried at 60℃, and cooled to room temperature in a desiccator. The weight of the tin plate was taken. The amount of dissolved tin (98.8mg) was estimated from the difference in the weight of tin before and after it was placed in mandarin juice. Two levels of analytical standard (50 and 250μg/g) were prepared from the remaining mandarin juice by quantitative dilution with fresh mandarin juice.

Preparation of Samples

Homogenize canned food with a Waring blender. Accurately weigh 40g of homogenate or analytical standards into 300mL Erlenmeyer flask. Dry homogenate in oven at 110℃. In a hood, add 30mL HNO_3 to flask and heat mixture gently to initiate digestion; avoid excessive frothing. When frothing has subsided, gently boil mixture at moderate temperature for 2h or until sample begins to dry at the bottom of the flask. Do not let sample char. Add 20mL HCl to flask and heat mixture gently ca 15min. Increase heat and boil 1.5h. Remove flask from heat. Transfer digest to 100mL flask and then thoroughly rinse Erlenmeyer flask twice with water. Let the solution cool to room temperature and dilute to volume with water. Fat floating on top shoud not be considered part of volume. Mix well and filter under reduced pressure through dry Whatman No.1 paper into a clean, dry bottle.

Determination

The instrumental conditions are summarized in Table 1.

(a) *Preparation of standard addition sample.*—Pipet 25mL digested sample solution into three 50mL volumetric flasks, and then add 0, 1.0, and 2.0mL tin stock solution (1000μg/mL) into each flask and dilute to volume with water.

(b) *Standard addition method.* — Three standard addition samples were measured by

Table 1. Instrumental conditions for tin determination by ICP/AES

Parameter	Setting
Rf (radio frequency) generator frequency	27.120MHz
Vacuum spectrometer	
Grating	
Radius of curvature	1 m
Number of grooves	3600/mm
Wavelength range	160-458nm
Reciprocal linear dispersion	0.22nm/mm
Entrance slit width	20 μm
Exit slit width	30 μm
Plasma output power	1.2kW
Argon flow rate	
Coolant	14L/min
Plasma	1.2L/min
Carrier	1.0L/min
Purge	3.5L/min
Observation height in plasma	15mm
Integration time	5 s
Tin analytical line	189.989nm

ICP/AES after background correction. Background subtraction was done in the wavelength scan profile on a display by marking 2 suitable positions on the baseline of both sides of the peak. The results were plotted against the added concentrations. The plot was extrapolated to intercept the negative concentration axis. The concentration of tin in sample was calculated by using the extrapolated value, and allowing for sample weight dilution.

(c) *Calculations.*

$$\text{Tin, } \mu\text{g/g sample} = \mu\text{g tin/mL} \times (50/25) \times (100/m)$$

where 25, 50, and 100 are dilution factors and m is the sample weight in grams.

Results and Discussion

Immediately after a can is opened, the contents should be transferred to a glass vessel, because tin plated on the internal surface of the can rapidly dissolves into the contents in the presence of oxygen.

Most methods now rely on wet digestion to destroy organic matter, because dry ashing leaves the tin as insoluble oxides. The wet digestion used in this study was a modification of the AOAC official method for tin determination by AAS(6). It was difficult to digest fat and oil in fatty samples such as meat, salmon, and evaporated milk. In this method, the limit of fat and oil in sample is about 10-20%. We did not examine how to digest fat and oil.

Table 2. Results of accuracy test obtained by analyzing analytical standards[a] containing tin at 2 levels (50 and 250 μg/g)

Level of tin in standard, μg/g	Amount of tin found, μg/g	Average, μg/g	RCV, %[b]
50	52.2	50.5	4.00
	52.2		
	48.1		
	51.6		
	48.6		
250	264.6	256.0	3.73
	258.9		
	243.1		
	249.2		
	264.4		

[a] Prepared as described in text.
[b] RCV, repeatability coefficient of variation.

The analytical line of sulfur (190.027 nm) is adjacent to that of tin (189.989 nm) (7). If the sample contains large amounts of sulfur compared with tin, the method is inaccurate because the instrument catches the sulfur line instead of the tin line. In this case, a fixed-wavelength method should be used.

In the initial stage of this investigation, we attempted to determine tin by the internal standard method using yttrium as internal standard. However, we could not obtain correct results, because we could not match the matrix of sample solution with that of tin standard solution. The pronounced matrix effect may have been due to spectral or physical interference from organic materials and acids remaining in sample solution after digestion. Results of the standard addition method indicated that the most favorable method of determining tin in canned food is ICP/AES.

The accuracy of the method was tested by analyzing analytical standards containing tin at 2 levels (50 and 250 μg/g). Results are shown in Table 2. Amounts of tin found and repeatability coefficients of variation (RCV) for the 50 and 250 μg/g standards were 50.5 and 256.0 μg/g and 4.0 and 3.8%, respectively. Results for 13 canned foods are shown in Table 3. RCVs for unspiked samples varied from 0.91 (apple juice) to 10.3% (mushroom). Recovery of tin from 13 canned foods spiked at 2 levels (50 and 250 μg/g) ranged from 93.9 to 109.4%, with a mean of 99.2%. Recovery at the lower spiking level (50 μg/g) was slightly erratic compared with the higher spiking level (250 μg/g).

The quantitation limit was defined as the concentration at which RCV was less than 10% ($n=5$). By measuring 5 replicates of tin standard solutions ranging from 0.1 to 3 μg/g, we found that 0.5 μg/g tin was the minimum concentration at which RCV did not exceed 10%. The quantitation limit of the method was estimated to be about 0.5 μg/g.

Tin was not detected in foods packed in

Table 3. Recovery of tin from canned foods by standard addition method[a]

Sample	Found		Spike level, μg/g	Recovery	
	μg/g	RCV, %		%	RCV, %
Satsuma mandarin[b]	57.7	3.07			
			50	102.4	5.53
			250	94.1	2.44
Peach[b]	50.0	4.78			
			50	100.8	3.95
			250	96.4	3.16
Apricot[b]	87.7	3.27			
			50	94.1	5.70
			250	99.8	2.95
Pineapple[b]	56.5	1.76			
			50	105.2	9.44
			250	98.6	4.48
Apple juice[b]	33.4	0.91			
			50	102.2	8.40
			250	98.2	1.77
Mushroom[b]	19.8	10.3			
			50	109.4	3.99
			250	95.8	8.54
Asparagus[c]	81.2	3.25			
			50	101.4	3.56
			250	97.1	4.20
Evaporated milk[d]	19.3	7.48			
			50	93.9	4.88
			250	101.1	4.54
Short-necked clam[e]	8.9	4.59			
			50	95.3	8.14
			250	100.0	4.44
Spinach[e]	ND[f]				
			50	98.4	4.27
			250	101.8	3.69
Whole tomato[e]	ND				
			50	100.3	6.15
			250	95.4	5.52
Meat[e]	ND				
			50	95.3	5.04
			250	94.4	8.63
Salmon[e]	ND				
			50	107.1	4.32
			250	102.3	1.66

[a] Five replicates per food. RCV, repeatability coefficient of variation. Mean recovery, 99.2%.
[b] Food packed in tin plate can.
[c] Food packed in high-tin fillet can.
[d] Food packed in tin plate can with inside lacquered ends.
[e] Food packed in inside lacquered can.
[f] ND, not detected.

lacquered can, such as spinach, whole tomato, meat, and salmon, except for shortnecked clam. Tin concentration detected in canned shortnecked clam was 8.9 μg/g. Internal corrosion was found at the side seam of the lacquered can. Tin detected in the sample is assumed to originate from the tin plate exposed by corrosion.

The large dynamic range of ICP/AES, compared with AAS, generally permits calibration over a very wide concentration range. The time-consuming dilutions are, therefore, not required.

Conclusion

The purpose of the study was to establish a rapid and accurate method of quantifying tin in canned foods by ICP/AES. Results from wet digestion by HNO_3 and HCl followed by ICP/AES were obtained rapidly and were moderately accurate. Sample preparation was easy; however, it was difficult to digest fat and oil. Nevertheless, it was possible to determine tin in fatty foods. The standard addition method is the most preferable method for tin determination by ICP/AES.

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