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**Comparison of four analytical techniques based on atomic spectrometry for the determination of total tin in canned foodstuffs**

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**Abstract**

Different techniques for the determination of total tin in beverages and canned foods by atomic spectrometry were compared. The performance characteristics of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Hydride Generation-Inductively Coupled Plasma - Atomic Emission Spectrometry (HG-ICP-AES), Electrothermal Atomization - Atomic Absorption Spectrometry (ETA-AAS) and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) were determined in term of linearity, precision, recovery, limit of detection, decision limit (CC $\alpha$ ) and detection capability (CC $\beta$ ) (Decision 2002/657/EC). Calibration ranges were covered from ng/L to mg/L level. Limits of detection ranged from 0.01; 0.05; 2.0; 200  $\mu$ g/L were respectively reached for ICP-MS; HG-ICP-AES; ETA-AAS and ICP-AES. Precision, calculated according to ISO 5725-2 for repeatability and within lab-reproducibility and expressed as relative standard deviation (RSD), ranged from 1.6 to 4.9% and recovery, based on the decision 2002/657/EC, was found between 95 to 110%. Procedures for the mineralization or extraction of total tin were compared. Wet digestion, sequentially, with nitric acid and hydrogen peroxide provided the best results. The influence of possible interferences present in canned food and in beverage was studied but no interference in the determination of tin was observed. Since maximum levels for tin established by EU legislation vary from 50 mg/kg in canned baby foods and infant foods up to 200 mg/kg in canned food, ICP-AES was chosen as the preferred technique for routine analysis thanks to its good precision, reliability and easy-to-use. The accuracy of this routine method was confirmed by participating in 6 proficiency test schemes with z-scores ranging from -1.9 to 0.6. Several canned foodstuffs and beverage samples from local market were analysed with this technique.

**Keywords:** Canned food, tin determination, wet digestion, atomic spectrometry

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## INTRODUCTION

For a very long time, precisely since two centuries, tin was the only material for holding foods because it did not influence the taste and flavour of meat and drinks. Today it is well known that canned food contains more or less dissolved tin depending on the pH of the content, storage temperature, time and presence of nitrates used as fertilizers (Blunden et al. 2003). The exposure of the general population to tin is essentially dietary in origin, coming particularly from the consumption of food stored in cans.

The Expert committee of the FAO and the WHO (JECFA) has established a provisional tolerable weekly intake (PTWI) of 14 mg/kg b.w. (JECFA 2005) because they noted that inorganic tin compounds generally have low systemic toxicity due to limited absorption from the gastrointestinal tract and the low accumulation tin in tissues.

The ingestion of canned food highly contaminated with soluble tin compound results in various symptoms: nausea, abdominal cramps, vomiting, headache, diarrhoea and fever (Schäfer et al. 1984). Due to its moderate toxicity, the maximum permissible levels enforced by the European regulation are 50 mg/kg for infant food, 100 mg/kg for beverages and 200 mg/kg for canned solid food (European Commission Regulatory (EC) 2006).

Several analytical methods have been used for the determination of tin in various food matrices. Among these includes X-Ray fluorescence (Yoshiki et al. 2006), spectrophotometry (Gutierrez et al. 1985; Capitán-Vallvey et al. 1994; Huang et al. 1997), neutron activation analysis (NAA) (Vermaercke et al. 2009; Chiba et al. 1994), spectrofluorimetry (Manzoori et al. 2006; Rubio et al. 1985), atomic absorption spectrometry (Knápek et al. 2009; Dogan et al. 1980; Martin et al. 1994), atomic emission spectrometry (Perring et al. 2002; Sumitani et al. 1993; Ribeiro et al. 2003),

hydride generation (Hanwen et al. 2003; Fang et al. 1992), and electrochemical methods (Ekmekci et al. 2000; Qiong et al. 1999; Clinio et al. 2004).

In this work, we introduce, optimised and validated some atomic spectrometric techniques and we have compared their analytical performance in order to select the most appropriate and reliable technique for routine analysis of tin in canned foodstuffs.

At the beginning and on the basis of the existing methods (Perring et al. 2002; Chiba et al. 1987), we tried to adapt these methods to our objective which is the determination of tin in canned foods.

**MATERIALS AND METHODS**

**Instrumentation**

*ICP-AES and HG-ICP-AES*, a Perkin-Elmer (PE) (Norwalk, CT, USA) ICP Optima 4300 DV inductively coupled Ar plasma optical emission spectrometer equipped with an autosampler (AS93 plus, PE) and with a hydride generation (HG) system (FIAS 400 PE) with two peristaltic pumps and regulated gas supply. The gas flow rate was set to 40-250 ml/min.

*ETA-AAS*, a Perkin-Elmer (PE) (Überlingen, Germany) Simultaneous Multi-element atomic absorption spectrometer model SIMAA 6000 equipped with longitudinal Zeeman background correction and a transversely heated graphite atomizer (THGA). A Hallow cathode Lamp was used.

*ICP-MS*, a Perkin-Elmer (PE) (Ontario, Canada) ICP MS ELAN DRC II inductively coupled Ar plasma mass spectrometer.

Samples for total tin were digested in a drying oven (Binder FD 115, Tuttlingen, Germany), equipped with thermostatisation and an integrated timer.

**Chemicals and reagents**

Ultrapure water of 18 MΩ/cm specific resistivity was obtained from a Milli-Q® water system purification (Millipore, Milford, MA, USA). Chemicals for mineralization were Nitric acid (70% (w/w), J.T. Baker, USA), hydrogen peroxide (30% (w/w), J.T. Baker,

Deventer, Holland). Hydrochloric acid (37% (w/w), J.T. Baker, USA) was used to stabilize tin solutions.

*HG-ICP-AES*, for the flow injection system,  $\text{NaBH}_4$  0.3% (w/v) solutions were prepared daily by dissolving appropriate amounts of powdered  $\text{NaBH}_4$  (for cold vapor analysis, J.T. Baker, Holland) in 0.1% (w/v)  $\text{NaOH}$  (Pellets, Merck, Germany).

*ETA-AAS*, for chemicals modifier [ $5 \mu\text{g Ni} + 145 \mu\text{g H}_3\text{PO}_4$ ] was prepared by using Ni solutions of 1000 mg/L (atomic spectrometry standard, Perkin-Elmer, USA) and  $\text{H}_3\text{PO}_4$  (85% (w/w), Merck, Darmstadt, Germany).

A commercially available 1000 mg/L Sn standard solution purchased from Perkin-Elmer, Pure atomic spectrometry standard (Shelton, CT, USA).

Working solutions for Sn were prepared daily by serial dilutions of this stock solution in: 0.5% (v/v)  $\text{HNO}_3$  for ICP-MS; 0.1 mol/L  $\text{HCl}$  for HG-ICP-AES and 1 mol/L  $\text{HCl}$  for ETA-AAS and ICP-AES.

All solutions containing the potential interfering ions studied were prepared at the required concentrations by adding appropriate amounts of stock solutions (Perkin-Elmer, Shelton, CT, USA).

Canned food and beverages from proficiency testing exercise was used as: FAPAS S7R54, FAPAS S7R60, FAPAS S7R76, FAPAS S7R85, FAPAS S7R98

All canned foods were purchased from local markets.

### Digestion procedures

After opening the canned food, the contents were transferred into a clean beaker, then samples were homogenized by mechanical mixing with a high-speed blender. Approximately 1.0 g of canned food wet weight or 1 mL of canned beverage was taken then was placed in a PFA digestion tube, with 5 ml of concentrated nitric acid. Afterwards, digestion was carried out at temperature of  $180^\circ\text{C}$  in the oven. After cooling the tubes, 3 ml  $\text{H}_2\text{O}_2$  was added and evaporated to about 0.5 mL. Each digested sample was transferred quantitatively into a 10 ml calibrated tube and setting to volume with hydrochloric acid solution 1 mol/L. If analysis is carried out

later, sample solutions must be stored in 6 mol/L HCl to prevent hydrolysis of tin which forming a semi-colloidal suspension.

**Analytical procedures**

All measurements were carried out in triplicate (instrument programmed). Detailed operating conditions of analytical set-up are summarised in Table 1 for all studied methods.

*HG-ICP-AES*, conversion into  $\text{SnH}_4$  resulted from transporting both the acidified sample solutions in 0.1 mol/L HCl and the reducing agent  $\text{NaBH}_4$  solution into the manifold block by two peristaltic pumps. Hydride was generated and separated from the gas-liquid mixture in the separator block added to the manifold, and swept with argon into the plasma for atomization and measurement of Sn.

*ETA-AAS*, autosampler volume of 20  $\mu\text{L}$  of sample or standard tin diluted with HCl 1 mol/L followed by 5  $\mu\text{L}$  of chemical modifier; [5  $\mu\text{g}$  Ni and 145  $\mu\text{g}$   $\text{H}_3\text{PO}_4$ ] were injected into a pyrolytically coated graphite tubes with inserted pyrolytic graphite L'vov platform. Then a programmed furnace temperature started to charring and atomizing the sample.

*ICP-MS*, the samples were diluted in 0.5% (v/v)  $\text{HNO}_3$ . Prior to measurement of tin, optimisation of the ICP-MS conditions was achieved by tuning for reduced oxide and doubly charged ion formation with a standard tuning solution.

*ICP-AES*, sample diluted in 1 mol/L HCl was pumped to the concentric nebulizer. After the sample aerosol is produced, a cyclonic spray chamber was used to allow only very fine droplets to pass to the plasma.

**RESULTS AND DISCUSSION**

**Optimisation of the ETA-AAS**

The optimum operating conditions for obtaining improved sensitivity for tin in acid digestion medium were determined. The effect of the ashing temperature, ashing time, atomizing temperature and the HCl concentration were studied. When the ashing was conducted at temperatures ranging from 400 to 1100 °C, we noticed that tin response was stable up to an ashing temperature of 1000 °C. Beyond this value, analyte loss was observed. The ashing time curve was carried out and the Sn signal

reaches a maximum plateau for time ashing from 30 sec, this period time was sufficient to ensure complete calcination of the sample. Similarly, the atomization temperature was investigated from 2000 to 2500 °C, an optimum signal with the best profile and reproducible results was found at 2200 °C. The concentration of HCl has a little effect on the tin signal in the range from 0.1 to 2 mol/L, a concentration of 1 mol/L HCl was selected to prevent hydrolysis of tin solution and to increase the lifetime of the graphite furnace tube. Several chemical modifiers were tested (Table. 2). The best one, given a well defined and sharp peak with negligible background absorbance, was composed of a mixture of Ni and H<sub>3</sub>PO<sub>4</sub>. The nickel solution stabilized the tin and prevented its loss during the charring step.

### Optimisation of the HG-ICP-AES

The efficiency of stannane (SnH<sub>4</sub>) production is a combined function of the used acid, its concentration and the sodium-tetrahydroborate (NaBH<sub>4</sub>) concentration. Different experiments were carried out to study the effect of NaBH<sub>4</sub> concentration on the tin signal. From 0.25% NaBH<sub>4</sub>, the signal reaches an optimum plateau. The concentration of 0.3% NaBH<sub>4</sub> was chosen as working condition.

The effect of HCl concentration was evaluated by varying the concentration from 0.05 to 0.4 mol/L. The concentration of Sn decreases constantly. The Sn signal was more or less stable within the range from 0.05 to 0.1 mol/L. Out of this range, the response decrease rapidly. Strict control should be required because small changes around the maximum value may produce a severe decrease in sensitivity. The effect of the argon gas flow used as the carrier gas on the tin signal was also studied. An argon flow of 225 mL/min was selected as optimum.

### Optimization of the ICP-AES

The emission line wavelength 189.927 nm was selected because it gave the best signal to background ratio, compared to other emission lines, and was found to be robust enough with respect to interferences.

The stability of tin solution was tested versus time of storage and the variation of the slope was not significant during the time of study.

### Optimization of the ICP-MS



Determination of tin was carried out with the major isotope  $^{120}\text{Sn}$  which provides a high and sensitive signal and no interferences are present compared to other isotopes as 116; 117; 118 and 119 amu.

Standards and samples solutions were prepared in 0.5%  $\text{HNO}_3$  because there is no risk of tin hydrolysis at ng/L level.

**Analytical performance and validation**

The 4 techniques were evaluated on their analytical performances.

Calibrations curves

The experiments were carried out under the conditions described before. Five standards of Sn were used for each techniques ranging from ng/L level for ICP-MS,  $\mu\text{g/L}$  for HG-ICP-AES and ETA-AAS, mg/L level for ICP-AES. The calibration range, the slope, the correlation coefficient are summarised in table 3. All calibration lines were linear within their calibration range (correlation coefficient  $R^2 > 0.999$ ).

The detection limit

The detection limit (LOD) was calculated on the basis of the matrix blank mean concentration (fresh vegetables, beverages and baby food without the analyte), added to three times the standard deviation of 10 matrix blanks. The limit of quantification (LOQ) was calculated similar as the LOD except with six times the standard deviation. Corresponding methodological detection limits for tin in canned food as determined by ICP-MS, HG-ICP-AES, ETA-AAS and ICP-AES are 0.1  $\mu\text{g/kg}$ , 0.5  $\mu\text{g/kg}$ , 20  $\mu\text{g/kg}$  and 2 mg/kg respectively.

Precision

The precision of the methods, repeatability and within lab-reproducibility, were determined following the European decision 2002/657/EC (European Commission decision 2002) and were calculated according to the ISO 5725-2 (NBN ISO 5725-2). The repeatability and within lab-reproducibility results, expressed as relative standard deviation, are shown in table 3. The ICP-AES method provides a good precision since it is mainly due to ruggedness of the ICP system. The HG-ICP-AES and ETA-AAS give similar values of reproducibility. ICP-MS technique was less precise in comparison with the others techniques.

The uncertainty of the measurement was also determined by statistical analysis of data according to ISO 5725-2 and expressed in percentage. We noticed that ICP-MS method provides a more dispersed results than the other methods due partly to the high dilution of the samples.

#### Trueness and recovery

The trueness was also assessed by analysis of FAPAS S7R54 sample by these techniques, the assigned value is  $(227 \pm 16)$  mg/kg. The results obtained for all techniques, shown in table 3, are in good agreement with the reference value except for the ICP-MS which is less accurate compared to the other methods.

To complete the accuracy study, recoveries, based on the decision 2002/657/EC, were measured after spiking with tin at different concentrations. The obtained values (table 3) range from 95 to 110%. These results evidence the absence of matrix effect.

#### Decision limit and detection capability

The decision limit ( $CC\alpha$ ) and the detection capability ( $CC\beta$ ) were established according to ISO 11843 (ISO 11843-1). The obtained values, corresponding to the maximum limit (MRL) for each product, are shown in table 3. Both the ICP-MS and HG-ICP-AES techniques showed similar results of  $CC\alpha$  and  $CC\beta$  for all MRLs. ICP-AES technique, with the ETA-AAS, provide better results for all MRLs except for canned food where the values provided by ETA-AAS technique are higher.

Experiments were performed to check if the described techniques are susceptible to interferences from elements present in canned foodstuffs. The effect of major elements K and Na (500 mg/L), Ca and P (250 mg/L), Mg (100 mg/L) and minor elements (Co, Cr, Cu, Fe, Ni, Zn... at 50 mg/L) was evaluated and no interferences on the determination of tin was observed in any of the techniques under investigation.

#### **Application to canned foodstuffs samples**

From the evaluation of the analytical performance of the techniques under investigation (precision, accuracy,  $CC\alpha$  &  $CC\beta$ ), ICP-AES is more suitable method for the determination of tin in canned foodstuffs in terms of robustness and financial cost of consumables. HG-ICP-AES technique has many inconvenient aspects; it required the optimisation of several parameters, a lot of reagents are used, it is also

cumbersome and required a well-qualified analyst. ETA-AAS can be used but also has some disadvantages comparing always to ICP-AES as the time of analysis and the life span of the graphite furnace which is reduced due to the use of hydrochloric acid and high atomization temperature. With regard to ICP-MS, this technique works at ppt level and in our case, samples must be diluted about  $10^6$  times. Therefore, an overestimation of the tin content is possible.

Several canned food and beverage matrices (fruit, vegetables, meat, fish, dairy product, baby food, beverages and juices) from local market were analyzed for total tin content by this method (ICP-AES) and none of its have exceed the MRL (table 4). High concentrations of tin were found mainly in canned fruit like pineapple, mango, fruit cocktail, peeled tomatoes and low content, less than LOD, was observed for the other categories of canned food.

Since maximum levels for tin established by European regulation is high and ranges from 50 to 200 mg/kg, ICP-AES is appropriate as well for this type of analysis and can be chosen as the preferred technique for routine analysis thanks to its good analytical performance, reliability and ease-of-use.

To confirm the reliability of this method, we have participated in many proficiency test schemes for the determination of tin, with the routine technique ICP-AES, in vegetables and fruit juices (from FAPAS), all the results were satisfactory with z-scores varying from -1.9 to 0.6 (table 5). From this study, we concluded that atomic spectrometry methods are reliable and still, up to this time, a good tool to determine tin in canned foodstuffs.

**CONCLUSIONS**

From the comparison between the four techniques it can be concluded that ICP-AES is the preferred technique for the analysis of Sn in canned foodstuffs. ICP-AES is an accurate technique showing good trueness and precision. The detection limits are significantly lower than the legal limits for Sn in canned foodstuffs. The method has several advantages compared to HG-ICP-AES, ICP-MS and ETA-AAS. The investment of the technique can be advantageous in the long-term since the costs of consumables are reduced.

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Methods	ICP-MS	HG-ICP-AES	ETA-AAS	ICP-AES
Instruments	ELAN DRC II, Perkin-Elmer	ICP Optima 4300 DV coupled to FIAS 400 Perkin-Elmer	SIMAA 6000, Perkin-Elmer	ICP Optima 4300 DV Perkin-Elmer
Experimental conditions	Isotope: $^{120}\text{Sn}$ Blank: 0.5% $\text{HNO}_3$ ultrapur Nebulizer gas flow: 940 mL/min Aux. Argon flow: 1200 mL/min Plasma gas flow: 15000 mL/min ICP RF Power: 1100 w	$\lambda = 189.927 \text{ nm}$ Blank: $\text{HCl}$ 0.1 mol/L 0.3% $\text{NaBH}_4$ in 0.1% $\text{NaOH}$ Argon carrier flow: 225 mL/min Sample Flow: 3.0 mL/min $\text{NaBH}_4$ flow: 2.6 mL/min	$\lambda = 286.3 \text{ nm}$ Blank: $\text{HCl}$ 1 mol/L $T^\circ$ drying: $130^\circ\text{C}$ t: 30 sec. $T^\circ$ ashing: $850^\circ\text{C}$ t: 30 sec. $T^\circ$ atomizing: $2200^\circ\text{C}$ t: 10sec. Tube cleaning $T^\circ$ : $2600^\circ\text{C}$ Modifiers: $5 \mu\text{g Ni} + 145 \mu\text{g H}_3\text{PO}_4$	$\lambda = 189.927 \text{ nm}$ Blank: $\text{HCl}$ 1 mol/L Nebulizer gas flow: 500 mL/min Aux. Argon flow: 200 mL/min Plasma gas flow: 15000 mL/min ICP RF Power: 1400 w

**Table 1.** Optimized working conditions for the atomic spectrometric methods.



Matrix modifier	Absorbance
3 µg Mg+5 µg Pd	0,0555
100 µg NH <sub>4</sub> <sup>+</sup>	0,0987
10 µg Pd	0,1241
5 µg Ni+145 µg H <sub>3</sub> PO <sub>4</sub>	0,1300
5 µg Ni+145 µg H <sub>3</sub> PO <sub>4</sub> +25 µg ascorbic acid	0,1392

**Table 2.** Effect of different matrix modifiers on the peak absorbance of tin

Validation data	ICP-MS	HG-ICP-AES	ETA-AAS	ICP-AES
Calibration range (µg/L)	0.05 – 1.0	1.0 - 20	10 - 100	500 - 5000
Slope (count/µg/L)	7870	1154	0.00113 (Abs/µg/L)	141.22
Coefficient of Correlation (R <sup>2</sup> )	0.99988	0.99925	0.99987	0.99972
LOD & LOQ (µg/L)	0.01 & 0.02	0.05 & 0.1	2 & 5	200 & 300
Repeatability (%)	4.9	3.5	1.7	1.6
Reproducibility (%)	7.2	4	4.7	3
Uncertainty (%)	19.3	8	13.2	11.3
Recovery (%)	100 - 110	95 - 104	101 - 107	98 - 109
Trueness (%)	110.6	99.1	101.8	104.4
Obtained results (mg/kg)	(251 ± 48)	(225 ± 18)	(231 ± 30)	(237 ± 26)
CCα & CCβ for MRL:				
Baby food: 50	56 & 63	56 & 62	53 & 57	52 & 53
Beverages: 100	110 & 121	110 & 119	106 & 112	107 & 113
Canned food: 200	218 & 235	218 & 236	222 & 245	206 & 213

**Table 3.** Validation data of tin determination by atomic spectrometric methods. The trueness was assessed by analysis of FAPAS S7R54 sample, the assigned value is (227 ± 16) mg/kg.

Categories	Canned products	Tin content (mg/kg)	Range (mg/kg)
Fruits	Mango slices	148	41 - 148
	Fruit cocktail	103	
	Pineapple slices	63	
	Apricot halves	48	
	Pear halves	46	
	Peach halves	44	
	Peeled tomato pieces	41	
Vegetables	Mushroom	11	<2 - 11
	Asparagus	<2	
	Spinach	<2	
	Green bean	<2	
	Haricot bean	<2	
	Maize	<2	
	Potatoes	<2	
	Carrots	<2	
	Garden pea	<2	
Meat	Corned beef	<2	<2
	Sausages	<2	
Fishes	Tuna	<2	<2
	Sardines	<2	
	Mackerel	<2	
	Salmon	<2	
	Mussel	<2	
	Crab	<2	
	Octopus	<2	
	Squids	<2	
Beverages and juices	Tomato soup	<2	<2
	Vegetables juice	<2	
	Sparkling water	<2	
	Lemonades	<2	
	Iced tea	<2	
	Energy drinks	<2	
	Orange juices	<2	
	Beers	<2	
Dairy products	Concentrated milk	<2	<2
	Rice pudding	<2	
Baby foods	Baby foods	<2	<2

**Table 4.** Tin levels in canned food from local market determined by ICP-AES.

Test materials	Matrices	Assigned value (mg/kg)	Found value	z-score
FAPAS S7R54	Tomato puree	227	237	0.6
LGC 7161	Tomato puree	225	225	Not given
FAPAS S7R60	Fruit juice	120	122	0.3
FAPAS S7R76	Fruit juice	100.7	85.2	-1.9
FAPAS S7R85	Vegetable puree	112	109.7	-0.3
FAPAS S7R98	Vegetable puree	214	190	-1.6

**Table 5.** Results of the proficiency test scheme for total tin determined by ICP-AES.

For Peer Review Only