Tin determination in canned foods

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Abstract The determination of tin in canned food became very important in the last decades since it gives important information about the contamination process helping to increase canned food quality and safety.
The present work describes the validation of tin determination in canned foods by flame atomic absorption spectrometry (FAAS). Linearity domain of the concentration, limit of detection (LOD), limit of quantitation (LOQ), precision (by fidelity, repeatability and reproducibility), accuracy (by recovery tests) have been assessed as performance criteria. The obtained results indicate that the method is efficiently and properly implemented. The uncertainties for each concentration level have been also calculated and are considered as relevant ones for canned foods, drinks and baby food. The validated method was applied for tin concentration analysis in a wide range of canned foods from the local market. In all analysed samples tin concentrations were below the imposed limits, most of them being under the LOD.

Keywords: tin, flame atomic absorption spectrometry, method validation, uncertainty, canned foods

1. Introduction

Tinplate is widely used in food industry as a robust form of packaging, allowing minimization of headspace oxygen and sterilization of foodstuff within the hermetically sealed can, giving a long, safe, ambient shelf life with no or minimal use of preservatives. It is also extensively used for the production of beverage cans. The use of tinplate for food and beverage packaging will result in some tin dissolving into the food content [1]. Although tin is not a toxic element, there are studies reporting gastrointestinal perturbations when it is present in concentrations above 200 mg/kg [2, 3]. Moreover, when the contamination reaches at this level the organoleptic properties of the food can be seriously affected.

According to EC 1881/2006 maximum limit for tin (in mg/kg wet weight) are: (i) 200 in canned foods other than beverages (ii) 100 in canned beverages including fruit and vegetable juices and (iii) 50 in baby food [4]. Due to all this, the determination of tin in canned food became very important in the last decades since it gives important information about the contamination process helping to increase canned food quality and safety.

Several methods have been used to evaluate tin concentration in canned food and beverages: molecular spectrometry of absorption (spectrophotometry) [5] or emission (fluorimetry) [1, 2] most of them using surfactants to increase the sensitivity of the determinations; atomic absorption [6-8] or emission [9-12] spectrometry but also electrometric techniques like stripping potentiometry [13], polarography [14] and stripping voltammetry [15]. In last years important analytical studies have been performed in order to assess the food exposure to package materials [16, 17].

The present work describes the validation of tin determination in canned foods by flame atomic absorption spectrometry (FAAS). Linearity domain of the concentration, limit of detection (LOD), limit of quantitation (LOQ), precision (by fidelity, repeatability and reproducibility), accuracy (by recovery tests) have been assessed as performance criteria. The uncertainties for each concentration level have been also calculated. The method was

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applied for tin determination in canned foods, drinks and baby food from the local market.

2. Experimental

2.1. Materials and reagents

Analytical grade chemicals (HCl 37%, hydrogen peroxide 30%, Sn certified analytical standard solution 1000mg/L purchased from Merck) and certified reference material MRC T0772 tomato puree have been used.

2.2. Sampling

Different canned food samples have been collected in 2008-2010 from the local market: (i) solid and semisolid: tomato paste, peeled tomatoes, green beans, black olives, mushrooms, pineapple compote, baby food (fruit purees, cereals with apples and bananas, rice with carrots) and (ii) liquid: grape, tomato and orange juices, soft drinks.

The solid and semisolid samples (including the reference material) have been chopped, mixed, then 50 g weighed and dried. The liquid samples have been homogenized by repeated twists and quantities between 100-200 g have been dried at 100-150^{0}C in porcelain dishes.

All samples have been processed in calcination furnace using the next temperature program: 2 hour at 100^{0}C, slowly increase to 350^{0}C (50^0/hour) maintain at this temperature until complete carbonization (no longer emit smoke), increase to 450^{0}C and 24-48 hours keep at 450^{0}C.

The white ashes have been dissolved after cooling in 5 mL HCl 1:1 (v/v); the mixture was heated 15 minutes to dissolve, cooled, filtered in 25 mL calibrated flask and brought to volume with deionised water.

To obtain fortified samples, certified material has been enriched with different Sn standard solution before sample dissolution, and the same procedure has been applied.

2.3. Apparatus

For the development and evaluation of the method, a GBC Avanta flame atomic absorption spectrometer with tin hollow cathode lamp has been used.

The main characteristics of the equipment for Sn determination are: wavelength - 286.3nm, flame: air (10L/min) - acetylene 99.9% (1.7L/min), linear concentration range 25-200 mg/L.

2.4. Measurements

Appropriate quality assurance procedures and precautions were carried out to ensure the reliability of the results [18].

The Sn concentrations to plot calibration curve were (in μg/mL): 25, 50, 75, 100, 150, 200. A witness solution containing all reagents used in sample preparation step has been prepared.

The metal concentration in samples has been calculated using the formula:

$$E,\ mg/kg = (C_{sample}-C_{witness}) \times V \times dilution / m$$

where:

- C_{sample} and $C_{witness}$ – metal concentration from calibration curve in the sample solution respectively in the witness (mg/L);
- V – total volume of the sample' solution (25 mL);
- m – sample's weight (g).

2.5. Internal validation procedure

Linearity domain of the concentration, limit of detection (LOD), limit of quantitation (LOQ), precision (by equipment precision, repeatability and reproducibility), accuracy (by recovery tests) and the uncertainties of the assigned values.have been assessed as performance criteria.

To be effective, a proposed method must permit a LOQ under the maximum residue limit (MRL) minus three times standard deviation of repetability/ reproductibility for a fortified sample to the MRL.

The samples enrichments have been done to reach 0.5, 1.0 and 1.5 times the MRL [4].

Samples of different food matrices and Sn MRLs have been processed and fortified for validations measurements: green beans and canned mushrooms for 200mg/kg, peach puree for children, canned tomatoes, apricot compote and tomato juice for 100 mg/kg and cereals for children for 50 mg/kg.

3. Results and Discussions

Multiple calibration curves for Sn have been plotted with excellent values of correlation coefficient. In **Fig. 1**. is presented one of them,

having the correlation coefficient 0.999, to demonstrate the linearity of the method.

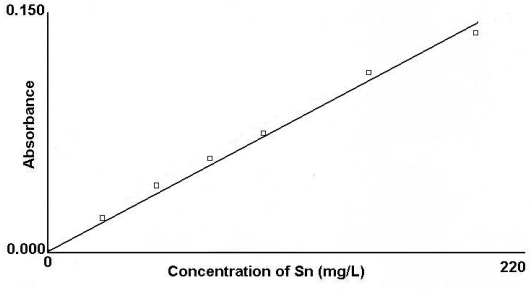

Fig.1. Sn calibration curve

The linearity for Sn determination using FAAS is respected in the range of 25-200 mg/kg dry weight.

The obtained LOD (3mg/kg) and LOQ (6mg/kg) are below the imposed values by regulations: LOD<5mg/kg and LOQ<10 mg/kg [19].

To assess the fidelity of the method the certified reference material has been analyzed and the obtained results are presented in **Table 1**.

Table 1 Calculated parameters describing the fidelity for Sn determination in canned foods by FAAS

Parameter	**Value**
Certified material	MRC T0772 tomato puree
Certified value	232.00mg/kg
Mean of determined concentrations	237.21 mg/kg
Standard deviation,	2.022325 mg/kg
RSD, %	0.852546
Repeatability	5.66251 mg/kg
$HORRAT_R$	0.118
Fidelity%	102.24

The other calculated parameters of the method performances have respected the recommended criteria and allow demonstrating that the method is adequate to the purpose (**Table 2**).

The uncertainties calculated from reproducibility have the mean value 4.56%, varying for different matrix and concentration levels. (**Table 3**).

Table 2. Quality parameters for Sn determination in canned foods by FAAS at different concentrations level

Sn concentration	100 mg/kg	200.0 mg/Kg
Mean of determined values	91.82 mg/Kg	186.95 mg/Kg
Recovery	91.82%	93.48%
Confidence interval	91.82 mg/Kg ±4.470864	186.95 mg/Kg ±18.848467
Standard deviation	1.739635mg/kg	7.334034 mg/kg
u reproducibility,	1.005569mg/kg	4.239326mg/kg
Reproducibility, R	4.870978mg/kg	20.535295mg/kg
RSD reproducibility	1.894615 %	3.922992 %
Extended uncertainty	3.479272 mg/kg	14.668068mg/kg
Uncertainty	3.48 %	7.33 %

Table 3. Uncertainties calculated from reproducibility for Sn analysis in different canned foods by FAAS

Matrix	Conc., mg/Kg	Standard uncertainty mg/Kg	Standard uncertainty, %
Green beans	200.0	14.668068	7.33
Tomato juice	100.0	3.827918	3.83
Children cereals	50.00	1.271094	2.54

Similarly, the combined relative standard uncertainties, having the mean value 4.13% depend on the same factors: matrix nature and Sn concentration level (**Table 4**).

Table 4. Combined relative standard uncertainties (Uc) for Sn determination in different canned foods

Matrix	Conc., mg/Kg	Uc, mg/Kg	Uc, %
Green beans	200.0	8.80	4.40
Tomato juice	100.0	3.08	3.08
Children cereals	50.00	2.46	4.92

The real samples analyses (**Table 5**) show results comparable with other reported values [12, 13].

In all analysed samples tin concentrations were below the imposed limits, most of them being under the LOD. The canned mushrooms and pineapple

compote were the only ones containing Sn, but in low concentrations.

Table 5. Sn concentration in canned foods from local market in 2008-2010 by FAAS

No	Sample	Sn, mg/kg
1	Green beans	ND
2	Rice with carrots for children	ND
3	Peaches puree for children	ND
4	Grape juice	ND
5	Mushrooms	55.00
6	Peeled tomatoes	ND
7	Pineapple compote	31.23
8	Tomato paste	ND
9	Tomato juice	ND
10	Tomato paste	ND
11	Soft drink	ND
12	Orange juice	ND
13	Green beens	ND
14	Tomato juice	ND
15	Green beens	ND
16	Pineapple compote	34.51
17	Fruits puree for children	ND
18	Fruits puree for children	ND
19	Fruits puree with cereals	ND
20	Baby food	ND
21	Cereals with apples and bananas	ND
22	Black olives	ND

ND- not detectable

4. Conclusions

The obtained results for method validation demonstrated that the studied method corresponds for the Sn concentrations determination in different canned foods using FAAS, the method being efficiently and properly implemented.

The uncertainties for each concentration level have been also calculated and are considered as relevant ones for canned foods, drinks and baby food.

In all analysed samples collected in 2008-2010 from the local market, tin concentrations were below the imposed limits, most of them being under the LOD.

5. References

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