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TIN COMPOUNDS IN FOOD – THEIR DISTRIBUTION AND DETERMINATION

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ABSTRACT

The aim of this work was optimization of the methods of trace- and ultratrace analysis, such as ICP-OES, ETA-AAS for charting the resources of individual forms of tin in foodstuffs. Increase of the sensitivity of the method of ICP-OES was achieved using the techniques of generation of hydrides, which was also optimized. Based on the information available on the occurrence of the different forms of tin, it appears that many of these organometallic compounds are contained in marine animals; attention has mainly focused on organisms such as marine fish, crustaceans, molluscs and algae. Tin compounds of predominantly inorganic origin can be found in foods and beverages which are packed in cans with a protective tin coating, too. The above mentioned methods have been applied to the analysis of selected beverages with low content of tin such as Coca Cola, Sprite, Fanta, Gambrinus 10°, PowerKing, and milk in the cans. Furthermore samples of animal origin as Sardines in oil, and Hunter's salami were examined, too. Prior to the determination of tin, samples need to be appropriately modified or analysed. Decomposition of the samples was done in the microwave system. Low pressure ion exchange chromatography with on-line detection of ICP-OES was used for separation of inorganic tin compounds. Separation of organically bound tin compounds was performed by HPLC on a column of ACE C-18, 3 µm, 15 cm × 1.0 mm with off-line detection by ETA-AAS. All of the above forms of tin compounds can be separated with this column. Due to the improvement in the detection of organically bounded tin, HPLC with identical ACE C-18 column coupled online for example with ICP-MS or spectrofluorimetry could be recommended.

Keywords: foods; tin; speciation of organotin; HG-ICP-OES; HPLC-ETA-AAS

INTRODUCTION

One of the indicators of the toxicological quality of food is the content of toxic mineral compounds. Lead, cadmium, mercury and arsenic belong among the most toxic elements. In higher concentrations trace elements such as, tin, chromium, cobalt, copper, molybdenum, nickel, selenium, vanadium, and others may show toxic effects. For these elements, the maximum allowed quantity, the permissible maximum quantity or special dose are specified in food legislation in the Czech Republic.

For humans or for other animals, tin is an essential element, but in larger quantities it appears as toxic. Its biological importance for humans has not yet been fully elucidated; it is assumed that it is indispensable for optimal growth and the formation of blood. Tin compounds are primarily located in the Earth's crust and also due to the human activities in the air and water flow.

The most dangerous form of tin are the compounds where tin is organically bounded in organometallic compounds. In spite of its potential toxicity, tin is used in large quantities in plastic and canning industry and for destruction of pests in agriculture, where it gets into agricultural products and from there into the food. Toxic effects of tin are known, but its use is increasing.

Humans can absorb tin from food, during breathing, and through the skin. Absorption of tin can enter human organism in the digestive system, thus food control has been emphasized quite intensively recently.

The average content of tin in the Earth's crust is about 3.0 mg.kg^{-1}. In nature, tin occurs as the mineral cassiterite (stannic oxide SnO_2,) and as an ingredient in some sulphides.

Metal tin is an important component of common alloys (bronze). The tinplate cans are made of steel sheets used in the food industry. Consumption of tinplate in food packaging is still growing and the largest share goes to the production of cans for the distribution of beer and other beverages **(Greenwood and Earnshaw, 1993)**.

A large quantity of tin is consumed for the production of organometallic compounds. Tin is used as a component of special paints for ships and other bodies subjected to the long-term effects of the sea water. Tributyltin compounds are used for the preservation of wood. Tributyltin oxide

$O(SnBu_3)_2$ is an excellent agent for protection of the wood. R_3SnX is also used as an antimicrobial agent to exterminate of slime mould in the paper and pulp.

Triphenyltinacetate and triphenyltinhydroxide are applied in agriculture as fungicides. For example, Bu_2SnOH and Ph_3SnOAc inhibit the growth of fungi, such as potato blight and similar infections, in sugar beet, peanuts and rice. Tin also serves as a mite-killer on apple and pear trees. Other R3SnX compounds are effective at killing insects as chemosterilant or by killing of larves **(Velíšek, 1999)**.

Dibutyldilaurate and analogue octyltin compounds are used as stabilizers for plastics (PVC). The most effective stabilizer compounds (R_2SnX_2 – R = octyl-, X = laurate, maleate). For the packaging of food products, the polymeric cis-butenedioic and ($Oct_2SnOCOCH$ = CHCOO)n and $Oct_2Sn(SCH_2COO\ Oct)_2$, with S,S´-bis (isooctyl-mercaptoethanolate), which is used in cases where a colorless, non-toxic, highly transparent material is essential, were approved.

Another no less important application of organotin compounds is their use as curing agents in vulcanization of silicone under normal temperature **(Greenwood and Earnshaw, 1993)**.

On other hand, the inorganic forms of tin are less toxic for human organism. Inorganic tin is just difficult to be absorbed by the organism and is usually excreted in the urine. According to the study from 1997, tin (II) is more toxic than tin (IV). Due to the presence of humic acids in the ground waters that reduce tin (IV) on tin (II) its concentration is increasing **(Pawlik-Skowronska, Kaczorowska and Skowronski, 1997; Rüdel, 2003)**. Inorganic tin is not carcinogenic or teratogenic.

Tin in all organic industrial compounds is tetravalent. Organic alkyl or aryl groups are groups that are covalently bonded with the central atom of tin. Mono-, di- and trisubstituted butyltin, phenyltin, and their derivatives are considered its most important compounds. The solubility of organically bounded tin compounds depends on pH, ionic strength and temperature of environment.

Degradation of organotin compounds occurs in biotic or abiotic processes. The transformation is similar for both cases **(Rüdel, 2003)** it leads through the dealkylation or dearylation on inorganic tin compounds **(Hoch, 2001)**.

The European Union (EU) limits maximum levels for certain contaminants with a view to reduce the content of these substances in foods at such a low level, which is yet to be achieved in compliance with the good manufacturing or agricultural practices. The aim is to achieve a high level of public health protection, especially for vulnerable groups of the population: children, allergies, etc. **(Commission Regulation (EC), 2006)**.

Tin gets into tinned food via further decomposition of the inner walls of tinned food cans. The decomposition of tinplate is dependent on the food matrix, pH, the presence of oxidizing substances (anthocyanines, nitrates, ions of iron and copper), and the presence of air (oxygen) in the area of food, time and storage temperature.

Nowadays, corrosion and dissolution of tin cans will be suppressed by a varnish, which greatly reduces the penetration of tin in food products.

Tin cans contain mainly canned vegetables, fruits, juices and other beverages, fruits in sweet pickle, mixed fruits in brine, canned milk and pickled mushrooms (Figure1).

For the determination of trace elements as well as for detection of tin in foodstuffs, it is necessary to choose the analytical methods, which are able to detect very low, trace amounts of analyte. Atomic Spectrometry methods – atomic absorption, emission and mass spectrometry are suggested for analyses of tin in food.

The most common method is atomic absorption spectrometry (AAS). When you use flame atomization the limit of detection is on the level of 0.1 $mg.L^{-1}$; using the electrothermal atomization even decreases this limit. Additional options for the determination are represented by different extractants (e.g. with hexane, toluene, chloroform r methanol), conversion of the compounds into volatile derivatives (by reaction with Grignard´s reagents or reaction with $NaBH_4$ result in volatile hydrides usable for atomic absorption spectrometry determination) and separation by gas chromatography. It is also possible to use liquid chromatography with mass spectrometer with ICP (inductively coupled plasma).

These methods offer for many elements excellent limit of detection, so they are suitable for the determination of trace amounts of elements in biological materials. Comparable results are achieved using sensitive electroanalytical methods, mainly a modification of polarography and voltamperometry, electrogravimetry or fluorescence.

For the determination of organically bounded forms of tin, in particular of tributyltin compounds (including degradation products – di- and monobutyl derivatives) are also used the above methods (AAS, ICP-OES and ICP-MS), in connection with sepraing in on-line or off-line arrangement (Figure 4).

To determine total tin detection of different forms (separation of inorganic and organically bound forms of tin) is performed both via complete mineralization of samples and in dry (combustion and subsequent dissolution in acid) or wet way (oxidation reactions in the strongly acidic environment). Mineralization by the wet way can be further performed under the hood in an open or closed system. Mineralization in a closed system can be done under high or low pressure and either common or

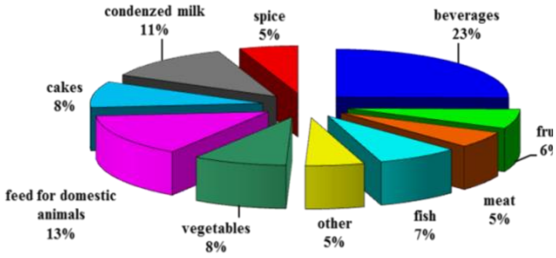

Figure 1 The most frequently observed types of canned food on the tin content **(Perring and Basic-Dvorzak, 2002)**.

microwave heating can be employed **(Mader and Čurdová, 1997)**.

If the determination of the different forms of tin is required, treatment of samples keeping tin compounds in their original form is essential and also maintaining their initial relationship in the sample is crucial. For these purposes very gentle procedures must be employed. They are based on the extraction with helping of ultrasonic wave or with the support of many microwaves in pH buffered environments. If the separation or isolation of the individual forms in one step is impossible, it is necessary to use a multi-step extraction or specific extraction or the conversion of other forms, and then multi-step analysis must be carried out **(Simon et al., 2002)**.

Scientific hypothesis

Since the determination of the tin compounds in foods is of great importance, particularly in terms of the occurrence of organotin compounds that accumulate in human adipose tissue, many techniques have been used for this purpose. Studies using different techniques, such as graphite furnace atomic absorption spectrometry (GF AAS) and cold vapour atomic absorption spectrometry (CV AAS), have been reported.

The inductively coupled plasma optical emission spectrometry (ICP-OES), which makes it possible simultaneous determinations on more different wavelength and allows rapid an effective analysis, is also reported. The design of experiments is an important approach and has been successfully employed in sample preparation procedures to identify the optimum conditions and select the proportions between the reactants, allowing a faster acquiring of results, minimizing costs and time involved. The use of diluted reagents in decomposition or extraction procedures, which leads to media with reduced acidity and also decreases the amount of corrosive substances, is an example of the experimental design application. Chemometric tools were used to establish the appropriate experimental conditions for determination of total tin content by CV AAS or by hydride generation atomic emission spectrometry with inductive coupled plasma (HG ICP-OES) and combination of separation step (EC or HPLC) with the same methods of detection for determination of tin (II) and tin (IV) and organotin compounds in biological samples.

Thus, this paper purpose is a multivariate optimization of an analytical method through all parameters outside the device parameters conclude selection the most suitable wavelength, concentrations of reagent solutions, correction of interferences and inlet flows of gases and solutions to determine the individual species of tin employing ICP-OES.

MATERIAL AND METHODOLOGY

Material and reagents

All reagents used were analytical grade, and solutions were prepared with ultrapure deionized water obtained from a reverse osmosis water purification system and ultrapure system (Aqua Osmotic 02 Tisnov, CR and Purelab ULTRA, Elga, UK). The nitric acid (68%), hydrochloric acid (37%) and hydrogen peroxide (31%) used were of Analpure Ultra (Analytika, s.r.o., CR). External calibration was prepared from stock solution of tin of 1000 mg.L^{-1} (Astasol®). Also, 1000 mg.L^{-1} stock solutions organotin compounds were prepared from dibutyltin dichloride (97%), triphenyltin chloride (95%) and tributyltin chloride (95%), Sigma – Aldrich s.r.o. CR and diluted according to the working range required. The calibration curves were prepared in a suitable range of concentrations in accordance with the purpose.

Other reagents such as sodium tetrahydridoborate NaBH4, NaOH, KOH for hydride generation used and organic solvents and acids (methanol, acetonitrile, acetic acid and triethanolamine) were HPLC grade from Sigma – Aldrich s.r.o. CR.

The glassware used in the experiments was previously decontaminated with a nitric acid solution (10% v/v) for 24 h **(Dantas et al., 2013)**, subsequently washed with ultrapure water and dried at room temperature.

Instrumentation

For the analysis of the food samples an inductively coupled plasma optical emission spectrometer with axial view (ICP-OES, Thermo Jarrell Ash, IRIS/AP,USA) and an atomic absorption spectrometer with electrothermal atomisation (Thermo Elemental, Solaar M6, UK) were used, and the operating conditions are detailed in Table 1 and Table 2. For preparation of samples for total tin content analyses a microwave digestion system MLS 1200, Milestone it was used and for separation of organotin forms an HPLC system (Dionex RS 3000 Ultimate, USA) was used.

Optimization strategy and analysis of the data

In order to achieve the best working conditions providing the lowest detection limit were performed an optimization, which includes the choice of the best wavelength for tin and appropriate instrument settings. Sensitive wavelengths for tin have been selected from a database of TEVA^{TM} (Thermo Elemental Validated Analysis, ICP-OES software, v. 1.4.0. for controls the optical emission spectrometer with inductively coupled plasma). It was tested a total of six wavelengths, which is able for the tin determination. Of these six wavelengths were chosen two (Table 2), which was the signal for tin the best response (SBR).

Other parameters were setting the input of the plasma on 1150 W, auxiliary gas flow 1 L.min^{-1}, the uptake of the sample to the nebulizer 1.85 mL.min^{-1}.

Statistic analysis

Validation of analytical method

The precision of the method was evaluated via the repeatability and can be expressed as the relative standard deviation (RSD) of a set of measurements. Accuracy expresses the difference between the value found experimentally and a reference value. In this study, Trace elements in CRM material fish tissue (NIES-11) was used to establish the accuracy through the values calculated using the Eq. (1). This approach is directly related to international standards.

Recovery (%) = [found value/certified value] x 100 (1)

Where found value is the analyte concentration determined by the proposed method and the certified value is the concentration value of the analyte reported in the SRM certification document. The precision and accuracy expressed as RSD (%) and recovery (%), respectively, obtained for the optimized analytical method calculated on the certified values and the found values for CRM. The recovery between the certified values and the found values ranged from (87.0 ±1.0) % (for tributyl tin) and about (92.0 ±5.0) % for total tin content, and the RSD values obtained were better than 5% (n = 3).

The tin content in different samples of foods was measured by HG-ICP-OES. Samples before the determination were decomposed in the microwave device by mineralization step. As samples were selected common beverages: Coca Cola, Sprite, Fanta, Gambrinus 10°, PowerKing and picnic in the cans. It was also determined a total content of the tin in caned Sardines in vegetable oil and in the hunter salami as a potential possible source of organotin compounds.

Samples of drinks before mineralisation step in the ultrasonic bath were degassed. For the decomposition of samples of beverages and foodstuffs was take up 10 mL or 1.0 g of samples and added 8 ml of HNO_3 and 2 mL of HCl. After this operation the sample was evaporated to near dryness, almost added to it 1 mL of HCl and volume was fill up on 10 mL. Values measured during both the wavelengths used are listed in Table 8.

The analysis of the data obtained from the experimental design was performed using Statistica® 12.0 software (StatSoft, USA). The measurements were performed in triplicate and the data are expressed as mean ±95% confidence interval (CI).

RESULTS AND DISCUSSION

Optimization of the hydride technique

The hydride generation technique was used for the reduction of the limit of detection. This technique based on reaction of $NaBH_4$ with acid to produce hydrogen, which generate volatile hydride with suitable ions of metal. These ions are then carried into the carrier gas stream into discharge of the ICP. If we compare the direct method of measuring tin and the hydride generation technique we can change measurement extent from the range ppm (mg.L^{-1}) to ppb (µg.L^{-1}) levels. The optimization of the concentration of sodium tetrahydroborate for the hydride generation for the correct determination was performed.

Optimization of the concentration range $NaBH_4$ was selected on the literature **(Hosick, Ingamells and Machemer, 2002)** where the optimum of concentration was about 2.4% of $NaBH_4$. Therefore, the optimization of reducing reagents at concentrations of 0.5; 1; 1.5; 2; 2.5; 3; 3.5; 4; 5% of the $NaBH_4$ dissolved in 0.1% KOH was performed.

Similarly for the acidification of the samples has been used 0.10; 0.25; 0.50; 0.75; 1.0 M hydrochloric acid.

As the most sensitive appeared wavelength of tin 189.989 nm (with the highest ratio of intensities (IR), which is the ratio of full intensity to the intensity of background or blank on the same selected wavelength), therefore the final optimization was carried out and the final results of processing of the content of tin was expressed only at this wavelength. The results of the optimization steps with a concentration of 100.0 ppb tin are presented in Table 3 and Table 4.

Calibration of hydride technique for the determination of different form of tin

The calibration solutions of standards of different forms of tin were measured at wavelengths 189.989 and 242.949 nm. The concentration of the calibration solutions was selected 50; 100; 150 µg.L^{-1} and as blank was used a 0.25 M solution of HCl. The calibration solutions of Sn (IV) species were prepared from standard calibration solution 1.0 g.L^{-1} in 0.25 M of HCl solution into the 100 mL flasks. Calibration solutions of Sn (II) were prepared by loading the appropriate amount of $SnCl_2.2H_2O$. This amount was transferred to 100 mL volumetric flask and fill up with deionised water. From this stock solutions have been further prepared calibration solutions of the above concentration.

Evaluation of the operating conditions obtained for the ICP-OES

This procedure made it possible to select the more sensitive lines, free of interference (Table 1), that were used to calculate the limits of detection (LOD) and the limits of quantification (LOQ) through the background equivalent concentration (BEC) and the signal-to-background ratio (SBR). The LOD and LOQ values were calculated using the BEC and the SBR, according to International Union of Pure and Applied Chemistry (IUPAC); BEC = $C_{standard}$ / SBR, where SBR = ($I_{standard}$ − I_{blank}) / I_{blank}; Cstandard is the reference element concentration in the solution; and Istandard and Iblank are the emission intensities for the reference element and blank solutions, respectively at the selected wavelength **(Da Costa et al., 2013, Schiavo et al., 2009)**.

The LOD was then calculated as (3 × RSD_{blank} × BEC / 100) and the LOQ as (3.3 × LOD), where RSDblank is the relative standard deviation of ten measurements of the emission intensity of the blank solution.

Separation of inorganic forms of tin by ICP-OES method

Ion-exchange chromatography

Forms of tin were separated by ion-exchange chromatography with on-line detection of ICP-OES. The measurement was done by using the time scan module in the TEVA software. Before choosing a suitable sorbet is necessary to find out as much as possible information about samples, which considered the properties of the matrix and the analyte, and based on this knowledge, then choose the type of phase and size of columns. Offer of sorbents is similar as for filling for liquid chromatography. All sorbents, which were used, had to be activated at first. Activated sorbents under reduced pressure using the sorption apparatus were implemented in polypropylene columns. After filling the columns were washed up with deionised water.

Tin in the compounds occurs in the form cations Sn (II) and Sn (IV). Therefore ion changers were selected as cation exchangers. The most appropriate cation exchanger is like this the tin ions are relatively closely retained and they are not washed up with water. Another important parameter is the selection of appropriate eluent reagents.

Due to the stability of the plasma is not appropriate use of elution agents containing higher amount of organic compounds or high concentrations of salts.

In work were tested exchangers Amberlite IRC 50, Cellulose CM 23, Servacel CM 3, Dowex 50WX, Trisacryl M CM and Sephadex CM 50 with elution reagents 1 M HCl and 0,5 M NaOH. The most of them - Amberlite IRC 50, Cellulose CM 23, Trisacryl M CM and Sephadex CM 50 – were suitable for separation of Sn (IV). Perfect separation of Sn (II) and Sn (IV) ions is complicated how is describe in literature **(White et al., 1998)** that the solutions of salts of Sn (II) ions are very unstable, easily oxidized by air and especially on light. Therefore, the study was focused on time dependency of Sn (IV) conversion on Sn (II) species on the light. In the previous chapter, it was found that when using a column filled with exchanger Amberlite IRC 50, tin in the form Sn (II) is washed out at the sampling and Sn (IV) is retained on the exchanger and washed out with 1 M HCl. This phenomenon was used for determining the time conversion dependency Sn (II) on Sn (IV) species. The functional range of the pH for ion exchanger which was used Amberlite IRC 50 is 5-14, in order to the pH of the sample is not need regulate. Results of measuring dependences of peak areas on time in derivation and logarithmical modes are shown in Table 5 and Figures 2 and 3.

Determination of tin compounds by ETA–AAS method

Optimization of method

For the determination of tin in samples by electrothermal atomisation in graphite furnace an ELC (Extended Life Cuvette) and Sn hollow cathode lamp has been used. According to literature **(Chen et al., 1996)**, where it was performed by optimizing the working conditions for the determination of Sn by ETA AAS method. For background correction a Zeeman correction method has been selected and as matrix modifier a combination of Palladium and Ascorbic acid was used. The unit was setting to the basic working conditions recommended by the manufacturer (Table 6 and Table 7).

Application of optimized method to food samples

After settinµ the optimal conditions a calibration method for different forms of tin was performed. Calibration solutions were measured at a wavelength of 224.6 nm with calibration functions $y = 0.0073x + 0.0502$ and $R^2 = 0.9977$ for tributyltin chloride; $y = 0.006x + 0.0524$ and $R^2 = 0.9975$ for dibutyltin dichloride and $y = 0.004x + 0.0457$, $R^2 = 0.9962$ for triphenyltin chloride. The concentration of the calibration solutions 10, 30, 50 $\mu g.L^{-1}$ has been prepared. A solution of 50 $\mu g.L^{-1}$ of different forms of tin with the addition of 0.5 ml 65% HNO_3 into a 50 ml volumetric flask and added a mixture of MeOH: H_2O (40: 10) has been prepared from standard solutions **(Schiavo et al., 2009)**. As blank and dilution solution 0.65% HNO3 has been used. As a matrix modifier a solution of $Pd(NO_3)_2$ and 1% solution of ascorbic acid were used. This mixture with sample by autosampler was sampled to the ELC of ETA AAS.

Due to the improvement of the detection of organically bound tin and streamlining of analysis would be suitable HPLC with column ACE C-18 connect in on-line arrangement, for example with ICP-MS or fluorimeter (**Gonzáles-Toledo et al., 2001**).

Table 1 Characteristics and operating conditions used for analysis by ICP-OES with axial view.

Parameter	Characteristics
Radio frequency power (W)	1150
Plasma gas flow rate ($L.min^{-1}$)	15.0
Auxiliary gas flow rate ($L.min^{-1}$)	1.5
Sample uptake rate ($mL.min^{-1}$)	1.85
Nebulizer gas flow rate ($L.min^{-1}$)	1.00
Nebulizer type	Concentric
Spray chamber	Type cyclone
Replicates	3
Injector tube diameter (mm)	2.0
Signal integration time (s)	1.0
Wavelength (nm)	Tin 189.989 242.949

Table 2 Wavelengths suitable for determination of tin.

Wavelength λ [nm]	Spectral order	relative intensity
189.989	136	150,000
242.949	107	100,000

Table 3 Values obtained for BEC, LOD and LOQ in the analysis of liquid samples of beverages by ICP-OES[a].

Analytical parameter	Sn(II) 189.989 nm Direct method	Sn(IV) 242.949 nm Direct method	Sn(II) 189.989 nm Hydride generation	Sn(IV) 242.949 nm Hydride generation
BEC ($mg.L^{-1}$)	0.2185	0.9422	0.0298	0.0967
LOD ($mg.L^{-1}$)	0.0036	0.0232	0.0006	0.0011
LOQ ($mg.L^{-1}$)	0.0107	0.0697	0.0017	0.0033

Note: [a] For solid samples values of LOD and LQD is necessary multiplied with factor for mass of 1.00 g of samples and completed to 10.0 mL with deionised water and expressed in $mg.kg^{-1}$.

Table 4 Dependency of intensity ratios (IR) on the concentration of $NaBH_4$ in the solution.

% $NaBH_4$	IR	% RSD
0.5	13.57	0.6973
1.0	32.95	0.8726
1.5	49.96	0.8841
2.0	64.77	1.3630
2.5	80.50	0.7996
3.0	90.37	0.6808
3.5	78.21	0.7758
4.0	73.77	1.6490
5.0	18.40	5.5600

Table 5 Dependence of the peak area at the time by ICP-OES method in time scan model.

	Peak area	
t [s]	**Sn (II)**	**Sn (IV)**
20	6659.5	10211.0
420	2929.5	13678.0
780	1720.5	14204.0
1140	620.5	15217.0
1560	417.0	15450.0
1920	145.5	16006.5

Table 6 Working conditions for determination of tin by ETA-AAS method.

Parameter	Setting
Wavelength	224.6 nm
Background correction	Zeeman effect
Time of measurement	3 s
Slit	0.5 nm
HCL current	75% I_{max}

Table 7 Temperature – time programme for ETA AAS.

Phase	Temperature [ºC]	Time [s]	Ramp [ºC.s^{-1}]	Flow of Ar [L.min^{-1}]
1	100	30	10	0.2
2	120	10	50	0.2
3	800	20	150	0.2
4	2300	3	0	0
5	2600	3	0	0.2

Table 8 Content of tin in food samples obtained HG-ICP-OES method.

Sample	c [mg.L^{-1}] 189.989 nm
Coca Cola	0.1766 ±0.0629
Sprite	0.0903 ±0.1159
Fanta	0.0275 ±0.0390
Gambrinus 10° − beer	0.0360 ±0.0100
PowerKing	0.0227 ±0.0015
Piknik	0.3758 ±0.0078
Sardines in vegetable oil	1.0791 ±0.0892
Hunter salami	0.7016 ±0.1250

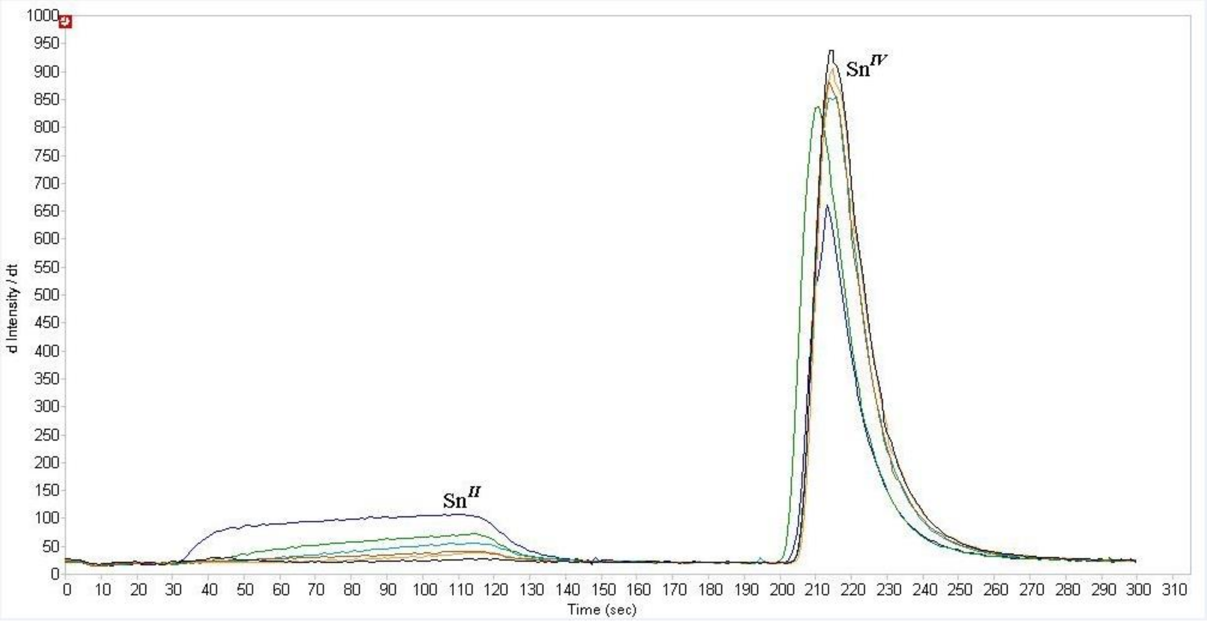

Figure 2 Time dependence of conversion Sn (II) on Sn (IV) – time scan model.

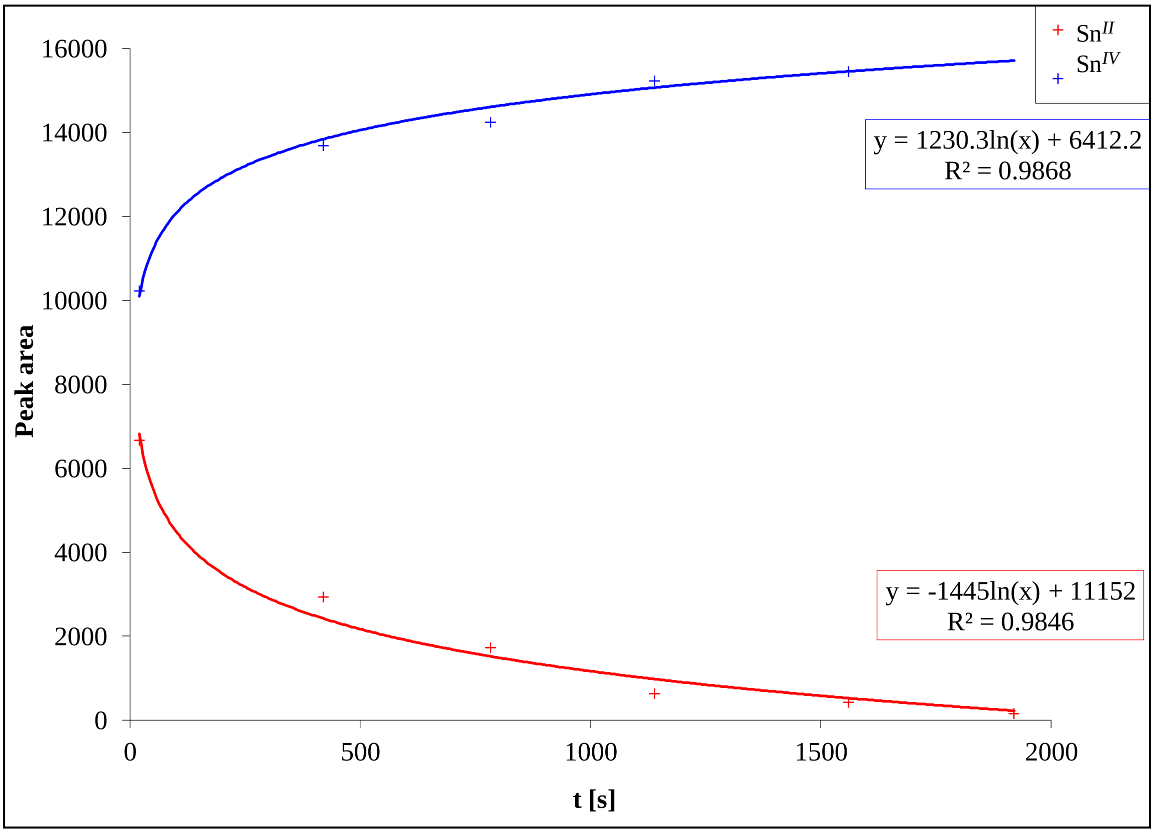

Figure 3 Logarithmical dependence of conversion of Sn (II) on Sn (IV).

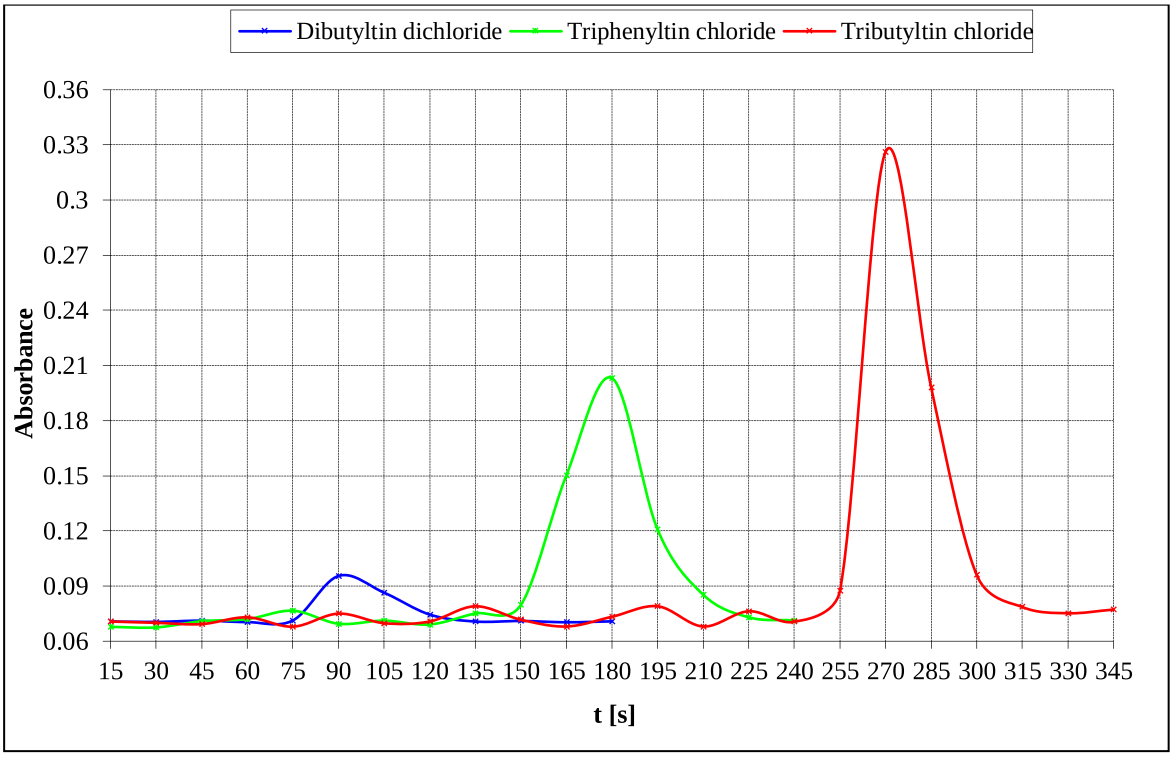

Figure 4 Dependence of absorbance on time for the separation of organotin compounds in the mixture by off-line ETA-AAS method.

CONCLUSION

In this work were simultaneously developed and tuned the three parts of the methodology on the determination of different forms of tin in food and beverages. The method for determination of total tin content in food materials by ICP-OES has been tuned. Increase the sensitivity of the method of ICP-OES was achieved using the techniques of generation of hydrides, which was also optimized. Hydride generation technique reduces the limit of detection, so it can be used for samples with low content of tin. This method has been applied to the analysis of real samples. Selected samples with low content of tin were drinks Coca Cola, Sprite, Fanta, Gambrinus 10°, PowerKing and picnic in the cans. Furthermore, Sardines in vegetable oil, and Hunter salami.

Simultaneously the method for separation of inorganic forms of tin was developed and at optimisation has been used low pressure ion exchange chromatography with on-line detection with ICP-OES. As appropriate ion exchangers shown cation exchangers Amberlite IRC 50, Cellulose CM 23, where elution reagent was 1 M solution of HCl and Trisacryl M CM, 50 CM-Sephadex, where elution reagent was 0.5 M NaOH solution. The best response was on Sephadex ion CM 50. The peak was detected during 40 seconds, and was sufficiently narrow and tall.

Similarly separation of organically bound tin was performed by HPLC on a column of ACE C-18 3 mm 15 cm × 1.0 mm with off-line detection by ETA AAS. Elution reagent was degassed mixture of acetonitrile-water-glacial acetic acid with 0.05% triethylamine (65: 23: 12) about pH 5. All of the above forms of tin can are with this column separated.

Since the performed analyses (inorganic forms of tin and organically bound tin) and information available on the occurrence of the forms of tin, it appears that many of these organometallic compounds are contained in marine animals, attention was necessary mainly focused on organisms such as marine fish, crustaceans, molluscs and algae. Based on these findings and the results of this work on the optimization of analytical procedures and the preparation of samples for analysis (homogenization, the selection of reagents and techniques for the extraction of individual forms, other modifications, such as pH adjustment, adding specific reagents, etc.) it will be possible to measure samples of the food and beverages by using this methodology that are created and optimized for the determination of the different forms of tin.

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