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Sequential injection fluorimetric determination of Sn in juices of canned fruits

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ABSTRACT

The present work describes the development of a fast and robust sequential injection fluorimetric procedure for the determination of Sn in juices of canned fruits. The developed automatic methodology is based on the complexation of Sn with 8-hydroxyquinoline-5-sulfonic acid (HQSA) to form a fluorimetric product (λ_{exc} = 354 nm; λ_{em} = 510 nm). The influence of dimethylsulfoxide (DMSO) and cetylpyridinium bromide (CPB) on the sensitivity of the fluorimetric determination was evaluated.

Linear calibration plots were obtained for Sn concentrations between 1 and 10 mg L^{-1}, with a detection limit of 0.38 mg L^{-1}. In each analytical cycle 0.006 mg of HQSA and 0.47 mg of CPB were consumed and 1.5 mL of effluent was generated.

The developed methodology was applied to the determination of Sn in juices of canned fruits and the results complied with those furnished by an electrothermal atomic absorption spectrometry comparison procedure, with relative deviations lower than 5.2%.

The automatic procedure exhibited good precision (R.S.D. < 1.4%) and the sampling rate was about 70 determinations per hour.

1. Introduction

Tin, namely tinplate, is widely used in the manufacture of food and beverage packaging providing a hermetic environment that demands minimal use of preservatives [1]. However, it has been proved that some tin will dissolve into the food content and this fact can result in changes in the organoleptic properties of the food. Although tin is not a toxic element, there are studies reporting gastrointestinal perturbations when it is present in concentrations above 200 mg kg^{-1} [2]. According to Food and Agriculture Organization (FAO) the maximum permissible levels of tin in food are 250 mg kg^{-1} in solid foods and 150 mg kg^{-1} in beverages [3].

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 namely: spectrophotometric [4–9] and fluorimetric [10,11] most of them using surfactants to increase the sensitivity of the determinations. There are some reports of the determination of tin by potentiometry [12], voltammetry [13] and atomic absorption spectrometry [14] and ICP-AES [15]. Even though these techniques can represent simple and sensitive alternatives for the determination of tin they are time-consuming and must be performed in batchwise, requiring the constant presence of a trained operator.

It is also possible to find two flow injection analysis (FIA) methodologies for the determination of tin in canned foods [5,16]. Fang et al. developed a hydride generation atomic-absorption spectrophotometric flow injection method for the determination of tin in canned food digests [16]. More recently a FIA methodology with diode array detection for the simultaneous determination of tin, molybdenum and germanium in food samples was proposed [5]. These methodologies represent a step forward in the automatization of this kind of procedure but involve the consumption of considerable amounts of solutions due to their continuous operation mode.

In an attempt to provide a fast, robust and automatic method for the analysis of tin in juices of canned fruits the determination was implemented in a sequential injection analysis (SIA) system, in agreement with the actual concerns of Green Chemistry. This flow technique [17] has already proved to be a simple and versatile sample handling approach that minimizes the consumption of sample and reagent solutions and the generation of effluents. Furthermore, the computer controlled operational mode of a SIA system makes it a very reliable option in routine analysis.

The main goal of this work was the development of an automated methodology for the determination of Sn that could constitute an advantageous alternative to the existing procedures, supported by

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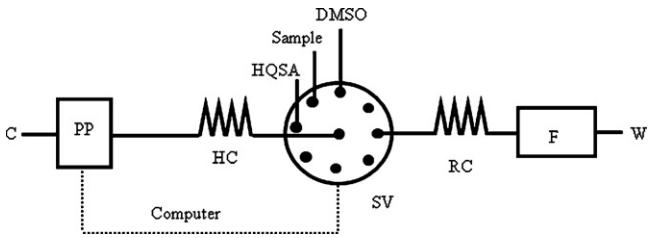

Fig. 1. SIA system used for the determination of Sn in juices of canned fruits. C: carrier solution, acetate buffer 5×10^{-2} mol L^{-1}, pH 5.2; PP: peristaltic pump; SV: selection valve; HC: holding coil (4 m, straight); RC: reaction coil (0.5 m, figure eight); F: fluorimetric detector; W: waste.

its simplicity, versatility, low reagent consumption, robustness and easy of operation.

The sequential injection determination of Sn was based on the complexation of Sn with 8-hydroxyquinoline-5-sulfonic acid (HQSA) in the presence of dimethylsulfoxide (DMSO) and cetylpyridinium bromide (CPB) to form a fluorimetric product (λ_{exc} = 354 nm; λ_{em} = 510 nm) [18,19].

2. Experimental

2.1. Reagents

All solutions were prepared using chemicals of analytical reagent grade and high purity water, with a specific conductance < 0.1 μS cm^{-1}.

A solution of HQSA 1×10^{-3} mol L^{-1} was prepared daily in acetate buffer 5×10^{-2} mol L^{-1} and was protected from light after the preparation and during its utilization in the analytical experiments; DMSO was used without dilution.

A stock solution of Sn 50 mg L^{-1} was prepared by appropriate dilution of a Fluka concentrated standard solution (1000 mg L^{-1}, in HCl 1 mol L^{-1}), to guarantee the stability of the analyte. Standard solutions of Sn were prepared daily from the stock solution by suitable dilutions in a solution of CPB 1×10^{-3} mol L^{-1} and HCl 5×10^{-2} mol L^{-1}. In the study of the influence of surfactants on the fluorescence reaction solutions of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulphate (SDS) were also tested.

The samples of canned fruits (pineapple, lichies, pear, mushrooms, apricot, guava, fruit cocktail and mango) were kept in a dry and fresh place and analysed after suitable dilution in the same solution of the Sn standard solutions (CPB 1×10^{-3} mol L^{-1} and HCl 5×10^{-2} mol L^{-1}).

2.2. Materials

The SIA system (Fig. 1) consisted of a Gilson Minipuls 3 peristaltic pump equipped with a PVC pumping tube (1.2 mm i.d.) and an 8-port multi-position Vici Valco selection valve. Manifold components were connected by means of PTFE tubing, 0.8 mm i.d., which was also used for the holding and reaction coil (4 and 0.5 m, respectively).

The fluorescence measurements were performed in a LabAlliance Fluorescence detector, equipped with an 8 μL flow-cell. Analytical signals were recorded on a Kipp & Zonen BD 111 strip chart recorder or by computer equipped with a convenient interface.

Analytical system control, including operation of the peristaltic pump and selection valve was achieved by means of an Advantech PCL 711B interface card and a Pentium-I based microcomputer. Software was developed in Microsoft Quick-Basic and permitted control of flow rate, flow direction, valve position, sample and reagent volume as well as data acquisition and processing.

Table 1
Analytical cycle for the determination of Sn.

Selection valve inlet	Solution	Volume (μL)	Flow rate (mL min^{-1})	Direction
1	DMSO	25	1	Aspiration
2	Sample	150	1	Aspiration
3	HQSA	25	1	Aspiration
4	Carrier	1500	3	Propulsion

2.3. Sequential injection procedure

The analytical cycle for the determination of Sn is summarized in Table 1. It began with the sequential aspiration of 25 μL of DMSO, 150 μL of sample and 25 μL of HQSA to the holding coil. Then by flow reversal the aspirated zones were propelled to the fluorimetric detector at a flow rate of 3 mL min^{-1} and an analytical signal was obtained at approximately 15 s.

2.4. Comparison procedure

In the absence of a reference procedure for the determination of Sn in juices of canned fruits the assay of the comparison method was accomplished by electrothermal atomic absorption spectrometry (ETAAS). A Perkin Elmer Model 4100ZL electrothermal atomic absorption spectrophotometer (PerkinElmer Instruments, Shelton, CT, USA) with longitudinal Zeeman-effect background correction was used as detection system. End-capped transversely heated graphite tubes with L'vov platform were used throughout. The standard solutions were prepared in 2% HNO_3 from the Sn stock solution of Fluka. The samples were suitably diluted in the same solvent. In each analytical cycle an aliquot of 5 μL of a solution of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ was used as matrix modifier. The concentration of this solution guaranteed that, as demand by the protocol for the determination of Sn, in each analytical cycle 5 μg of Pd and 3 μg of $Mg(NO_3)_2$ were added to the sample.

The instrumental conditions for the determination of Sn are summarized in Table 2.

Table 2
Instrumental conditions for the determination of Sn by ETAAS and respective furnace program.

Step	Furnace program				Instrumental conditions	
	Ramp (s)	Hold (s)	Temperature (°C)	Argon flow (mL min^{-1})		
Dry 1	1	20	110	250	Wavelength	286.3 nm
Dry 2	5	30	130	250	Integration time	5 s
Ash	10	20	1400	250	Slit width	0.7 nm
Atomize	0	5	2200	0	Background correction	Longitudinal Zeeman effect
Clean	1	4	2400	250	Inert gas	Argon
					Injection temperature	20 °C
					Sample volume	20 μL
					Measurement mode	Peak area

3. Results and discussion

All studies regarding the optimization of the physical and chemical parameters involved in the determination of Sn in the SIA automatic system, as well as the results of the determination of the analyte in the juice of canned fruits and their validation are described below.

3.1. Optimization of the physical and chemical parameters

Regarding the optimization of the analytical procedure, several studies were performed with the aim of investigating the influence of sample and reagents volume, reagent concentration, aspiration order, carrier flow rate and reaction coil length as well as configuration, on the formation of the complex and consequently on the respective fluorescence signal.

The developed methodology for the determination of Sn in the juice of canned fruits was based on the complexation of Sn with HQSA to form a fluorescence product [18,19]. Batch studies performed before the implementation of the reaction in the SIA system revealed that the wavelength of maximum excitation and emission were 354 and 510 nm, respectively.

The influence of sample solution volume on the fluorescence signal was studied between 50 and 200 μL and the results showed that the analytical signals increased, about 2.5 times, up to 150 μL. Furthermore, higher volumes led to irregular peaks, revealing mixing problems. Thus the optimization proceeded using 150 μL of sample.

Assessment of the influence of HQSA volume and concentration was carried out due to its importance in the formation of the metallic complex. The volume of HQSA was studied between 15 and 100 μL and it was observed that the fluorescence response increased up to 25 μL and above this volume there was a significant decrease of the sensitivity. Regarding the concentration of HQSA solution the optimization studies were performed in the range of 1×10^{-4} to 1×10^{-3} mol L^{-1}; above the latter concentration there were visible solubility problems so that it was not possible to use more concentrated solutions. In the studied range there was an enhancement of the fluorescence signal with the concentration up to 1×10^{-3} mol L^{-1}. The remaining studies were performed with 25 μL of HQSA 1×10^{-3} mol L^{-1}.

In order to guarantee the adequate pH for the complexation reaction, a solution of acetate buffer 0.5 mol L^{-1}, pH 5.2 was used as carrier solution. The pH of this solution was kept at 5.2 units in order to avoid sudden changes of the sensitivity due to small variations of pH above 6. Besides this, in alkaline media HQSA is fluorescent and at the same time the stability of Sn might be compromised.

Other important parameters affecting the magnitude of the analytical signal were flow rate and reaction coil length and configuration whose optimization allowed establishing the optimum residence time of the reaction zone inside the flow system allowing an adequate reaction development and avoiding excessive dilution of the formed complex. The propulsion flow rate was studied between 1.5 and 3 mL min^{-1} and the results showed that in the studied range there was an increase in the analytical signals of about 1.5 times. The excessive residence time for the lower tested flow rates led to an increased dispersion of the formed product and consequently to a decrease of the fluorescence signals. For all this the determination was performed with a propulsion flow rate of 3 mL min^{-1}.

The better residence time was finally evaluated by determining the effect of the reaction coil on the analytical signals. Reaction coils above 0.5 m resulted in a decrease of the analytical signals as a result of an excessive dilution of the formed complex. Of the different tested configurations (straight, coiled, figure eight) figure eight reactors led to higher analytical signals in the studied concentration range confirming the fact that they originate lower dispersion of the reaction zone on its way to the fluorescence detector. For all this the optimization proceeded with a 0.5 m figure eight reaction coil.

After the optimization of the most important physical and chemical parameters the developed methodology exhibited a detection limit and sensitivity that were adequate for the determination of tin in the samples in which the contamination by Sn is considered problematic. However since the main goal of the work was to propose an alternative automatic methodology for the determination of tin it was important to decrease the detection limit in order to make it similar to those achieved by other existing techniques, allowing the determination in an extended concentration range.

Based on the known influence of organic solvents on the fluorescence of metallic complexes, DMSO was used with the aim of increasing the sensitivity of the determination [18]. This effect is complex and explained not only by the polarity of the solvent but also by the chemical interactions that can undergo with the solvent molecules [20]. The volume of DMSO was studied between 0 and 100 μL and an enhancement of sensitivity of about 20% until 25 μL was observed. Above this volume there was a significant decrease of the signal probably due to dilution of the formed complex related with the excessive volume.

In order to further increase the sensitivity and quality of the determination, several surfactants were tested, in concentrations above their CMC, as media for the preparation of Sn standard solutions, namely CTAB, CPB, Triton X-100 and SDS. The use of organized micellar media to increase the sensitivity of fluorescence measurements has become frequent in the last decades. Above their CMC surfactants have micelle forming ability, providing a microenvironment that favours both reaction development and fluorescence intensity of reaction products [21,22]. Cationic surfactants like CTAB and CPB showed to affect the sensitivity of the determination and were tested in concentrations between 1×10^{-5} and 1×10^{-3} mol L^{-1}. The results revealed that CPB exhibited higher hydrophobic medium effect than CTAB and that there was a fluorescence enhancement with its concentration up to 1×10^{-3} mol L^{-1}. Solutions of higher concentration were not tested because they were of difficult manipulation due to the formation of bubbles within the flow system. For all this the standard solutions were prepared in a solution of CPB 1×10^{-3} and HCl 0.05 mol L^{-1}. The presence of HCl was essential to guarantee the stability of the analyte. The association of DMSO and CPB to the reaction medium

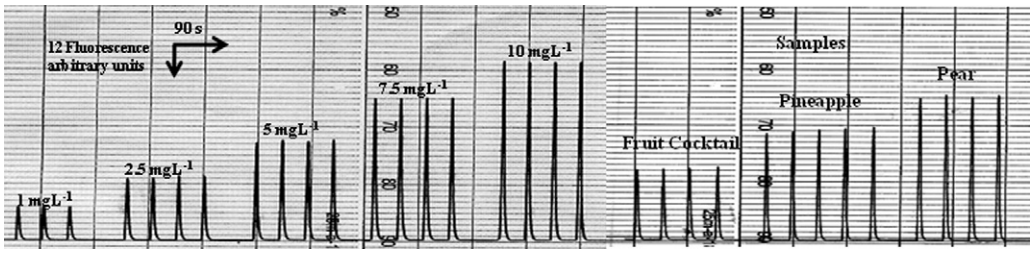

Fig. 2. Diagram of the developed methodology for the determination of Sn in juices of canned fruits.

Table 3
Results of the analysis of the determination of Sn in juices of canned fruits by SIA and ETAAS.

Sample (dilution factor)	SIA ($mg\,L^{-1}$) ± S.D.[a]	SIA dilution factor	ETAAS ($mg\,L^{-1}$) ± S.D.[b]	ETAAS dilution factor	Relative deviation (%)
Mango	<DL	–	0.46 ± 0.07	25	–
Pineapple 1	42.6 ± 0.3	8	44.2 ± 1.8	400	−3.8
Pineapple 2	74.1 ± 1.2	8	76.7 ± 0.8	500	−3.4
Fruit cocktail	26.3 ± 0.7	8	26.5 ± 1.5	400	−0.8
Papaya	269.8 ± 2.5	32	256.5 ± 2.5	5000	+5.2
Apricot	153.4 ± 0.8	16	157.0 ± 1.4	2500	−2.3
Guava	<DL	–	0.08 ± 0.02	25	–
Lichees	25.7 ± 0.6	8	26.7 ± 0.1	400	−3.7
Mushrooms	<DL	–	0.23 ± 0.12	10	–
Pear	58.5 ± 0.3	8	57.5 ± 0.2	400	+1.7

[a] Standard deviation of four replicates.
[b] Standard deviation of two replicates.

resulted in an increment of about 65% in the sensitivity of the determination that allowed the determination of Sn in the majority of the samples of juices of canned fruits.

3.2. Figures of merit

After the optimization of all the parameters affecting Sn–HQSA complex formation, the developed methodology was evaluated for Sn concentrations between 1 and 10 $mg\,L^{-1}$ (Fig. 2) and a linear calibration plot was obtained: IF = 5.552 (±0.096) conc ($mg\,L^{-1}$) + 7.231 (±0.591) (IF—fluorescence intensity; conc—Sn concentration, $mg\,L^{-1}$). The detection and quantification limits [23] of the determination were 0.38 and 1.27 $mg\,L^{-1}$, respectively. The sampling rate was about 70 samples per hour.

3.3. Analysis of juices of canned fruits

The developed SIA methodology was applied to the determination of Sn in juices of canned fruits. Due to the composition of tinplate [1] it is unlikely that other metals, besides Sn, would be present in the analysed samples. The presence of iron, as main component of steel, is not a problem per se because this species does not typically form fluorescent complexes with HQSA. This statement applies also to other species like Cu and Mn. The adjustment of the pH of the carrier solution in 5.2 units as well as the change of the excitation and emission wavelengths to 354 and 510 nm respectively, allowed creating unfavourable conditions for the complexation of metals like Al and Zn [19].

In order to evaluate the accuracy of the automatic method, the results were compared with those furnished by a reference ETAAS procedure. No significant disparity was obtained between both methods with relative deviations, expressed in percentage, lower than 5.2% (Table 3). This resemblance was confirmed by a paired *t*-Student's test, which, for a 95% confidence level, showed no significant statistical differences the results furnished by both methods (t calculated = −0.39; t tabulated = 2.57).

Along with the evaluation of the correlation significance using the *t*-test a linear relationship between the two methods was established: SIA ($mg\,L^{-1}$) = 1.048 (±0.023) ETAAS ($mg\,L^{-1}$)–3.71 (±3.86), confirming the null hypothesis.

No significant differences (R.S.D. < 1.4%) were obtained in the repetitive analysis (n = 15) of samples with different concentrations of Sn (76.0 and 48.2 $mg\,L^{-1}$) confirming the repeatability of the developed procedure.

4. Conclusions

The developed methodology combines the well-known advantages of the SIA technique like robustness and simplicity with the promptness and sensitivity of the fluorescence measurements. Regarding the already existing methods for the determination of Sn in canned foods the automatic methodology showed to be very simple and fast, leading at the same time to a very low consumption of sample and reagents and effluent production. In each determination 0.006 mg of HQSA and 0.47 mg of CPB were consumed and 1.5 mL of effluent was generated.

Even though the detection limit of the developed procedure was not enough to evaluate the tin content of a reduced number of samples containing small amounts of Sn, the increase of sensitivity achieved by the utilization of DMSO and CPB was considerable and allowed the successful analysis of the majority of the samples.

The results of the analysis of the samples exhibited good precision and accuracy and were in good agreement with those furnished by an ETAAS comparison procedure. The developed SIA methodology for the determination of Sn in juices of canned food for all the exposed advantages is suitable for routine analysis and can be used as alternative to other existing methods.

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