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Spectrofluorimetric determination of tin in canned foods

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Abstract

A simple and sensitive spectrofluorimetric method for the determination of tin as its complex with 1-(2-pyridylazo)-2-naphtol (PAN) in a mixed micellar medium was developed. The mixture of a non-ionic surfactant, Triton X-100 and an anionic surfactant, bis(2-ethylhexyl) sulfosuccinate (AOT) was used as a suitable micellar medium for solubilizing of complex and ligand and also for enhancing the fluorescence intensity of complex. In the optimum experimental conditions the maximum excitation and emission wavelengths of Sn–PAN complex were 300 and 360 nm, respectively. The calibration graph was linear in the range of 0.01–0.8 $\mu g\,ml^{-1}$ with a correlation coefficient of 0.9991. The detection limit was found to be $2\,ng\,ml^{-1}$. The relative standard deviation of the method for the determination of $0.1\,\mu g\,ml^{-1}$ tin was calculated to be 0.74%. The interferences caused by the presence of a number of common cations and anions were studied. Finally, the method was successfully applied to the determination of tin in various canned products.

Keywords: Spectrofluorimetry; Tin determination; PAN; Mixed micelles; Canned food

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 [1,2]. According to Food and Agriculture Organization of the UN/World Health Organization (FAO/WHO) the maximum limit for tin in canned foods is $250\,mg\,kg^{-1}$ [3]. On the other hand, there is some evidence suggesting that consumption of food or beverages containing tin above $200\,mg\,kg^{-1}$ has caused gastrointestinal effects [4]. Moreover, when the contamination reaches at this level the organoleptic properties of the food can be seriously affected. Consequently, the determination of tin in canned products is very important. Several analytical methods have been developed for the determination of tin including spectrophotometry [5–10], atomic absorption spectrometry [11–17], atomic emission spectrometry [18,19] and electrochemical methods [20–23]. A few spectrofluorimetric methods have also been proposed for the determination of tin [24–28] but most of them have not been applied to the analysis of real samples. Thus, further efforts to develop simple and sensitive methods appear to be worthwhile.

Micelles are dynamic aggregates of amphiphilic molecules (surfactants) formed at surfactant concentrations above the critical micelle concentration (cmc). It is well known that the use of micellar microheteregeneous systems in fluorescence spectrometry presents several advantages over conventional homogenous solutions including increased sensitivity, reduced interference and enhanced experimental convenience [29]. Several reports on the application of micelles to improve the performance of spectrofluorimetric methods have been appeared in literature [30–32]. However, precipitates may occur especially at room temperature. To overcome this drawback the use of mixed surfactants has been proposed.

In the present work a simple, sensitive and non-extractive spectrofluorimetric method for the determination of tin(II) is described. It is based on the formation of a fluorescent complex with 1-(2-pyridylazo)-2-naphtol (PAN) in a micellar medium. The mixture of Triton X-100 and bis(2-ethylhexyl) sulfosucci-

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nate (AOT) is used as a suitable micellar medium for solubilizing of complex and ligand and also for enhancing the fluorescence intensity of complex.

2. Experimental

2.1. Instrumentation

Spectrofluorimeter—a Shimadzu RF-540 was used for fluorescence spectra and intensity measurements. Spectrofluorimetere was equipped with a 150 W xenon lamp. A 1.0 cm quartz cell was used. Slit widths of both monochromator were set at 5 nm.

pH meter—a Metrohm model 654 was used for pH measurements.

2.2. Standard solution and reagents

All reagent used were of analytical-reagent grade. Triply distilled water was used throughout.

Tin(II) stock standard solution of 1000 μg ml^{-1} was prepared by dissolving 190.0 mg of $SnCl_2{\cdot}2H_2O$ in ca. 10 ml of concentrated HCl, adding 5 ml of 0.1 M hydrazine chloride and diluting to the mark in 100 ml volumetric flask with water. This solution was prepared daily and was stable during the day. Solutions of 2.5% (v/v) Triton X-100 and 0.02 M AOT were prepared in water. A 0.1% (m/v) stock solution of PAN was prepared in ethanol.

The following reagents were used: $SnCl_2{\cdot}2H_2O$ (Merck, Darmstadt, Germany), Triton X-100 (Merck), sodium dodecyl sulfate (Merck), Brij-35 (Merck), *N*-cetyl-*N*,*N*,*N*-trimethylamonium bromide (Merck), bis(2-ethylhexyl) sulfosuccinate (Merck), 1-(2-pyridylazo)-2-naphtol (Fluka, Switzerland) and 37% HCl (Merck).

2.3. Test solutions

Aliquots of working standard solution, containing 10 μg ml^{-1} tin, were transferred into 25 ml volumetric flasks to produce solutions with concentrations in the range of 0.01–0.8 μg ml^{-1}. Then 0.25 ml of 2.5% Triton X-100 solution, 1 ml of 0.02 M AOT solution, 0.5 ml glycine buffer (pH 3.0) and 0.25 ml 0.1% PAN solution were added. After 20 min the solutions were diluted to the mark with water and their fluorescence intensities were measured at 360 nm using an excitation wavelength of 300 nm. A reagent blank was also prepared and its fluorescence intensity was measured in the same conditions.

2.4. Digestion procedures

2.4.1. Juice samples

Five millilitres of sample juice was transferred into a 250-ml Erlenmeyer flask and 10 ml concentrated sulfuric acid was added. The solution was diluted to about 75 ml by distilled water. Afterwards, it was cooled, filtered and washed with water and the filtrate was collected in a 100-ml calibrated flask and diluted to the volume with water. For the analysis, 0.5 ml of the obtained solution was transferred into a 25-ml calibrated flask and 0.02 g aluminum metal was added in order to reduce Sn(IV) to Sn(II). After adding the other reagents according to the general procedure, the fluorescence intensity was measured.

2.4.2. Fish sample

Approximately 2.0 g of the fish was dried and ashed at 600 °C. After that the ash was dissolved with 10 ml of concentrated HCl and diluted to 50 ml with distilled water and 1 mol l^{-1} NaOH so that the final pH was ca 1. For the analysis, 0.5 ml of the obtained solution was transferred into a 25-ml calibrated flask and 0.02 g aluminum metal was added in order to reduce Sn(IV) to Sn(II). After adding the other reagents according to the general procedure, the fluorescence intensity was measured.

The recovery assay was carried out using the same procedure but adding known amount of tin.

2.5. Calibration procedure

For spectrofluorimetric determination of tin in aqueous solution, a series of 13 standard solutions of tin were measured by following the procedure under Section 2.3. The calibration graph was found to be linear in the ranges of 0.01–0.8 μg ml^{-1}. The equation for calibration graph is $F = 2.12 + 128.33C$ ($r = 0.9991$), where F is the fluorescence intensity (in arbitrary units) and C is the concentration of tin expressed in μg ml^{-1}.

3. Results and discussion

3.1. Spectral characteristics of Sn(II)–PAN complex

Tin(II) ion reacts in acidic solution with PAN to give a fluorescent complex that is insoluble in water. Fig. 1 shows the excitation and emission spectra of the complex and also PAN in a mixed micellar medium. The excitation and emission maximum wavelengths are at 300 and 360 nm, respectively. The influence of time upon complex formation was investigated. The results indicated that the fluorescence signal is increased by increasing

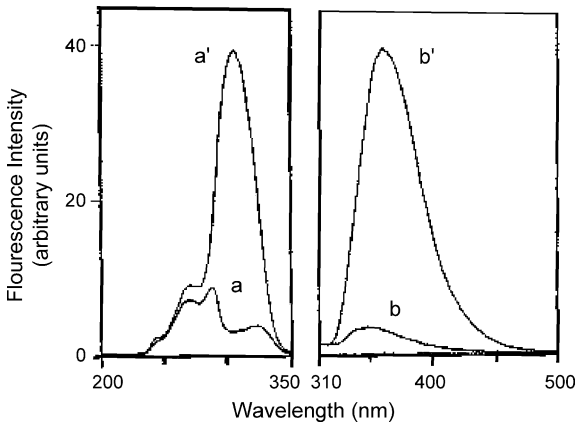

Fig. 1. Flouresence excitation (a and a′) and emission (b and b′) spectra of PAN (4×10^{-5} M) in the absence (a and b) and presence (a′ and b′) of 0.3 μg ml^{-1} Sn(II). Conditions: [AOT] = 8×10^{-4} M, [Triton X-100] = 0.025% (v/v), pH 3, λ_{ex} = 300 nm, λ_{em} = 360 nm.

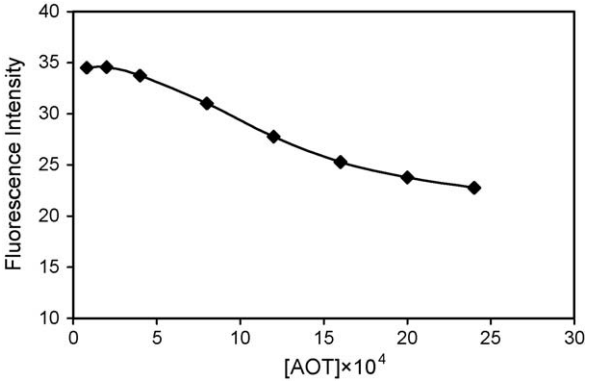

Fig. 2. The variation of fluorescence intensity of Sn–PAN complex with AOT concentration. Conditions: [Triton X-100] = 0.025% (v/v), pH 3, [Sn] = 0.2 μg ml^{-1}.

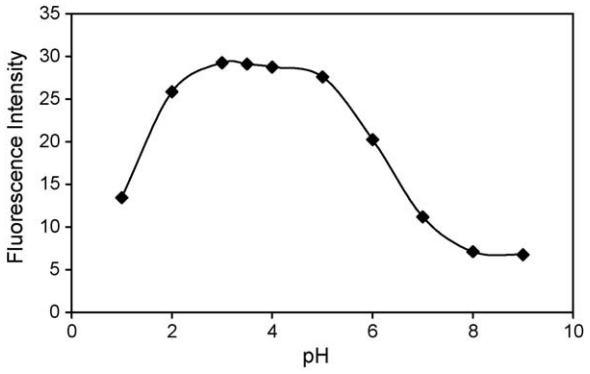

Fig. 4. The effect of pH on the fluorescence intensity of Sn–PAN complex. Conditions: [AOT] = 8×10^{-4} M, [Triton X-100] = 0.025% (v/v), [Sn] = 0.2 μg ml^{-1}.

time up to about 15 min and then remains constant for several hours. Therefore, in all experiments the fluorescence signal was measured after 20 min. It should be mentioned that tin(IV) ion does not react in this condition with PAN.

3.2. Influence of the operating conditions on the fluorescence intensity signal of Sn–PAN complex

3.2.1. Effect of type of surfactant

Several anionic (SDS and AOT), cationic (CTAB) and non-ionic (Triton X-100 and Brij-35) surfactants were tested in order to solubilize the complex and possibly enhance the fluorescence. All of the tested surfactants were able to solubilize the complex but the solutions became turbid after a few minutes. Among these surfactants, AOT gave the highest fluorescence intensity but this solution was also instable. Therefore, Triton-X100 was also added as an auxiliary surfactant. Under these conditions the solutions were stable at least for 24 h. Figs. 2 and 3 show the influence of concentrations of both surfactants on the fluorescence intensity of Sn–PAN complex. Based on these results, concentrations of 8×10^{-4} M and 0.025% (v/v) were selected as suitable concentration for AOT and Triton X-100, respectively. It should be mentioned that in lower concentrations of AOT, although the fluorescence intensity is slightly higher but the solubilization of complex is not complete and precipitation may occur.

3.2.2. Effect of type of buffer and pH of the solution

The effect of pH on the fluorescence intensity of Sn–PAN complex was investigated. The results are graphically shown in Fig. 4. According to this figure, the fluorescence intensity is relatively constant in the pH range of 3–5. Therefore, pH 3 was chosen for the rest of experiments. Several buffers including tartarate, phthalate, oxalate, citrate and glycine were tested for pH adjustments. It was found that by using glycine buffer highest fluorescence intensity is obtained. The effect of glycine concentration was also studied. Fluorescence intensity is increased by increasing buffer concentration up to 0.01 M and then decreased. Therefore, 0.01 M was chosen as optimum concentration of buffer.

3.2.3. Effect of PAN concentration

The variation of fluorescence intensity of the complex with PAN concentration in the 8×10^{-6} to 2×10^{-4} M range is shown in Fig. 5. A 4×10^{-5} M PAN concentration was used thereafter. Since PAN was dissolved in ethanol, the effect of

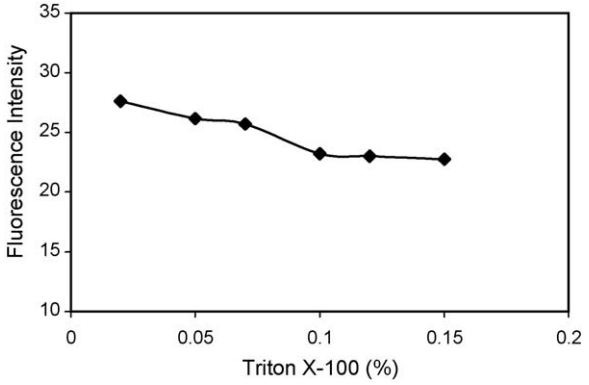

Fig. 3. The variation of fluorescence intensity of Sn–PAN complex with Triton X-100 concentration. Conditions: [AOT] = 8×10^{-4} M, pH 3, [Sn] = 0.2 μg ml^{-1}.

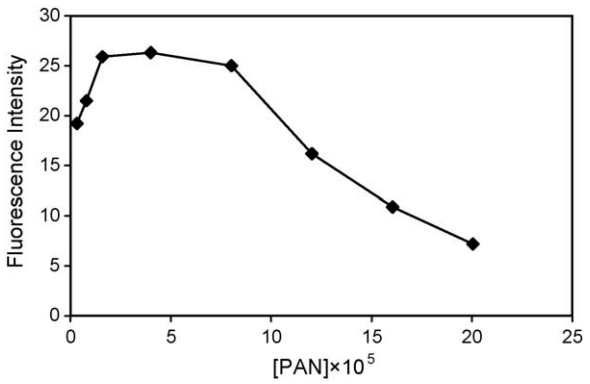

Fig. 5. The variation of fluorescence intensity of Sn–PAN complex with PAN concentration. Conditions: [AOT] = 8×10^{-4} M, [Triton X-100] = 0.025% (v/v), pH 3, [Sn] = 0.2 μg ml^{-1}.

Table 1
Recovery of tin from spiked products before digestion

Sample	Added (mg kg^{-1})	Found (mg kg^{-1})[a]	Recovery (%)
Pear nectar	48.2	47.2 ± 1.2	97.9 ± 2.5
	96.4	93.8 ± 2.2	97.3 ± 2.1
	144.6	143.3 ± 1.9	99.1 ± 1.3
	192.8	186.1 ± 1.6	96.5 ± 0.8
Mango juice	46.9	48.2 ± 1.8	102.8 ± 3.8
	93.8	93.7 ± 1	99.8 ± 1.1
	140.7	140.2 ± 1.1	99.6 ± 0.8
	187.6	184.3 ± 2.8	98.2 ± 1.5
Orange juice	47.8	46.6 ± 2.2	97.5 ± 4.6
	95.6	93.8 ± 2.8	98.1 ± 2.9
	143.3	142.3 ± 1.9	99.3 ± 1.3
	191.2	182.0 ± 1.8	95.2 ± 0.9
Pineapple juice	46.6	45.9 ± 1.1	98.5 ± 2.4
	92.3	89.9 ± 1	97.4 ± 1.1
	139.9	140.6 ± 1.8	100.5 ± 1.3
	186.5	183.7 ± 1.9	98.5 ± 1
Canned fish	125	128.4 ± 4.1	102.7 ± 3.3
	250	246.8 ± 4.5	98.7 ± 1.8
	375	362.3 ± 7.5	96.6 ± 2
	500	497.3 ± 7.8	99.4 ± 1.6

[a] Averages of three determinations ± standard deviation.

this solvent on the fluorescence intensity was also studied. Using ethanol up to 12% (v/v) has not a significant effect on the fluorescence but at higher percentages the intensity was lower. Since the ethanol content of calibration solutions does not exceed 1%, therefore there is no need for adjusting its concentration.

3.3. Accuracy

In order to check the accuracy of the proposed method, recovery experiments on various samples spiked with different amounts of tin were carried out (Table 1). As can be seen, the obtained recoveries are between 95.2 and 102.8%, which confirm the accuracy of the method.

3.4. Precision

According to the IUPAC recommendations [33] the random uncertainty in the value for measure is expressed in terms of relative standard deviation (R.S.D.). In order to study the precision of the method, a series of five solutions containing 0.1 μg ml^{-1} tin were measured on the same day. R.S.D. was found to be 0.74%.

3.5. Detection limit

The detection and quantification limits as defined by IUPAC [34], $C_{LOD} = 3S_b/m$ and $C_{LOQ} = 10S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration graph) were found to be 2.0 and 6.6 ng ml^{-1}, respectively. The slope of the calibration graph (m) is the calibration sensitivity according to IUPAC definition.

Table 2
Tolerance limit of diverse ions in the determination of 0.1 μg ml^{-1} tin

Ions	Tolerance limit (mass ratio)
Mg^{2+}, Na^+, K^+, Ca^{2+}, Al^{3+}, Mn^{2+}, Pb^{2+}	1000
$S_2O_3^{2-}$, SO_4^{2-}, Cd^{2+}, SCN^-, $CH_3CO_2^-$, F^-, NH_4^+, Br^-, Cl^-	500
$P_2O_7^{2-}$, I^-, Ag^+, Cr^{3+}	250
MoO_4^{2-}, WO_4^{2-}, EDTA	100
Bi^{3+}, Ni^{2+}	10
Cu^{2+}, Co^{2+}, Fe^{2+}	1
VO_3^-, Fe^{3+}	0.1

Table 3
The total tin content of canned products

Type of sample	Content of tin (mg kg^{-1})[a]
Pear nectar	69.9 ± 1.3
Mango juice	56.0 ± 2.1
Orange juice	60.2 ± 1.1
Pineapple juice	77.8 ± 2.2
Canned fish	109.7 ± 4.1

[a] Averages of three determinations ± standard deviation.

3.6. Study of interferences

The effects of 30 foreign ions on the determination of 0.1 μg ml^{-1} tin by the proposed method were examined. The tolerance limits for these ions are given in Table 2. A foreign ion was considered to interfere seriously when it caused an error of 5% in fluorescence signal. As can be seen, most of the ions do not interfere when they are present in 100-fold excess. Only Cu(II), Co(II), Fe(II), Fe(III) and V(V) interfered when present at the same level as tin. But the concentrations of these ions in canned products are very low and therefore they do not cause any interference in real sample analysis. However, the interferences of the most of these ions might be eliminated, if necessary, by using hydroxyethyle ethylenediamine triacetic acid (HEDTA) as masking agent [8] and ion exchange resin (for vanadate ion).

3.7. Analysis of samples

The proposed method was applied to the determination of tin in different canned products (beverages and foods). Prior to the determination, samples were digested according to Section 2.4. It should be mentioned that acid matrices of digested samples do not have any effect on fluorescence signal as long as the pH of final solutions are adjusted in optimum amount by adding buffer solution. The obtained results are shown in Table 3.

4. Conclusion

A simple and non-extractive spectrofluorimetric method was developed for the determination of traces of tin based on complex formation with PAN in a mixed micellar medium. The method is sensitive and has low detection limit and can be applied to the monitoring of tin in various canned foods and beverages.

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