Electrochemical hydride generation atomic fluorescence spectrometry for detection of tin in canned foods using polyaniline-modified lead cathode

Xianjuan Jiang, Wuer Gan*, Lingzhong Wan, Yun Deng, Qinghua Yang, Youzhao He

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

An electrochemical hydride generation system with polyaniline-modified lead cathode was developed for tin determination by coupling with atomic fluorescence spectrometry. The tin fluorescence signal intensity was improved evidently as the polyaniline membrane could facilitate the transformation process from atomic tin to the SnH_4 and prevent the aggradation of Sn atom on Pb electrode surface. The effects of experimental parameters and interferences have been studied. The limit of detection (LOD) was $1.5\,ng\,mL^{-1}$ (3σ) and the relative standard deviation (RSD) was 3.3% for 11 consecutive measurements of $50\,ng\,mL^{-1}$ Sn(IV) standard solution.

1. Introduction

The wide usage of tinplate in food and beverage packaging will result in some tin dissolving into the food content [1–3]. Although inorganic tin has been described as "essentially non-toxic" [2] due to its poor absorption and retention in tissues, high levels of inorganic tin over concentrations of $200\,\mu g\,g^{-1}$ in food may cause gastrointestinal symptoms provoking nausea, vomiting, diarrhea, abdominal cramps, bloating, fever and headache. To reduce corrosion and dissolution of tin, cans are usually resin coated, which gives a marked reduction of tin migration into the food product [1,3].

Several techniques have been available to the analyst for total tin analysis including spectrophotometry [4,5], atomic absorption spectrometry (AAS) [6–9], spectrofluorimetric method [10], X-ray fluorescence spectrometry (XFS) [2] and inductively coupled plasma atomic emission spectroscopy (ICP-AES) [3]. Electrochemical hydride generation (EC-HG) of SnH_4 has also been used for tin determination by coupling with AAS [11] and ICP-AES [12].

In general, the cathode material of EC-HG cell should have the characteristics of both higher hydride generating efficiency and better stability in acidic solution. The Pb and carbon materials in its different forms, which have higher hydrogen overpotential and could bring higher hydride generating efficiency under same conditions, were often used for generation of SnH_4 [12]. However, the frangibility of carbon and the instability of Pb in acidic solution are against their applications in EC-HG cell. What is more, is that sub-sequent transformation of atomic tin in cathode surface to SnH_4 is not as efficient as Sn(IV) reduction on these cathodes [12].

In order to enhance the stability of Pb electrode in acidic solution and improve the hydride generating efficiency, considering the fact that the analytical performances of the EC-HG was directly related to the cathode material [13], an effort was made in this work to modify the physico-chemical properties of cathode for EC-HG determination of tin.

The utilization of polyaniline (PANI) to modify electrodes is particularly attractive as it is very stable mechanically, chemically and electrochemically and its preparation avoids the use of organic solvents [14]. The nitrogen atoms in PANI film might provide sorption sites for positively charged ions [15–19]. Moreover, the nitrogen atoms could adsorb hydronium ion and be protonated at higher acidities [18]. In addition, the PANI film could keep Pb cathode from dissolution in acidic solution dramatically [20].

In the present work, PANI on Pb electrode was synthesized electrochemically and this PANI/Pb electrode was used as cathode material in the EC-HG-AFS system for the determination of tin. Attributing to the superior reduction activity of the PANI film for Sn(IV), this proposed method had the virtues of higher sensitivity, excellent stability and lower memory effect. This developed method was successfully applied for analyzing total tin in canned foods.

2. Experimental

2.1. Instrumentation

An AFS-230 double channel nondispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was

* Corresponding author. Tel.: +86 551 3600021; fax: +86 551 363 17 60.
  E-mail address: wgan@ustc.edu.cn (W. Gan).

Table 1
Operating parameters of the atomic fluorescence spectrometry system.

Parameter	Setting
Peak current of high intensity tin hollow cathode lamp (mA)	85
Negative high voltage of PMT (V)	310
Atomizer height (mm)	8
Delay time (s)	1
Read time (s)	20
Read mode	Peak area

employed throughout. A high intensity tin hollow cathode lamp (General Research Institute for Nonferrous Metals, Beijing, China) was used as a radiation source. Quartz tube (7 mm I.D. × 14 mm length) was used as atomizer. The operating parameters of the atomic fluorescence spectrometry system were listed in Table 1.

A homemade thin-layer electrolysis cell similar to that described in our previous work [21] was applied as the ECVG cell for tin hydride generation, in which, a Pt foil and a piece of PANI/Pb electrode (58 mm × 9 mm) were used as anode and cathode, respectively. The interelectrode gap was about 6 mm and a homogeneous anion exchange membrane was used for the separation of the two compartments. A direct current (DC) constant current and voltage unit (Type DH1719A-3, Beijing Da Hua Wireless instrument Co., Beijing, China) operating at constant current mode was used. MDS-6 Microwave Digestion System (Shanghai sineo microwave chemistry technology Co. Ltd., Shanghai, China) was used for sample digestion.

A WFX-120 atomic absorption spectrometry with a WF-4C graphite furnace (Beijing Ruili Instrument Co., Beijing, China) was employed for the validation of the proposed method. The graphite furnace atomic absorption spectrometry (GF-AAS) operating conditions were as follows: (1) the wavelength was set at 224.6 nm, (2) the signals were evaluated from the peak area yielding an integration time of 6 s, (3) the pyrolysis temperature and atomization temperature were 800 and 2100 °C, respectively.

2.2. X-ray photoemission spectra (XPS)

All X-ray photoemission spectra (XPS) measurements were recorded in an ESCALAB 250 spectrometer (Thermo-VG Scientific), which incorporated an Al Ka ($h\nu$ = 1486.6 eV) X-ray source and operated in the CAE mode. The pass energy was set to 20.0 eV and the energy step size was 50 meV. Before recording the spectra, the samples were stored in a vacuum of better than 5×10^{-10} mbar in order to degas. During the measurement the vacuum in the spectrometer was better than 1×10^{-10} mbar. Measurements were taken to examine tin content in the PANI/Pb and Pb cathode surface before and after hydride generation process.

2.3. Reagents and materials

A series of standard solutions were prepared daily by stepwise dilution of Sn(IV) stock solution (1 g L^{-1}, Tianjin Guangfu fine Chemical Research Institute) with 0.5 mol L^{-1} HCl just before use. Unless otherwise stated all reagents were at least of analytical grade. Ultrapure water (resistivity 18 MΩ cm) used throughout the experiment was obtained from a Milli-Q water-purification system of Millipore (Bedford, MA, USA).

Commercial canned foods including resin-coated cans (crab, meat and conjee) and plain cans (tomato sauce and orange juice) were bought at local public markets.

2.4. Sample preparation

Approximately 0.5 g of spoon meat was weighed into polytetrafluoroethylene microwave digestion vessels; for solid samples,

50 g (fresh weight) of sample were firstly homogenized with blender and then 0.5 g of it was weighed.

After adding 5 mL concentrated HNO$_3$ and 1 mL H$_2$O$_2$, the vessels were sealed and placed in the microwave digestion oven. The digestion program consisted of five stages, stage 1 (0.2 MPa, 6 min, 600 W); stage 2 (0.5 MPa, 4 min, 800 W); stage 3 (1.0 MPa, 4 min, 800 W); stage 4 (1.5 MPa, 6 min, 800 W); stage 5 (2.0 MPa, 10 min, 600 W). After being digested and cooled to room temperature, the solution in the vessels was transferred to a 50 mL beaker and gently heated to remove the residual HNO$_3$. Then, it was transferred to a 25 mL calibrated flask and brought up to volume with 0.5 M HCl. The sample solutions of plain cans need to be diluted once again prior to determination due to its higher tin content.

2.5. Cathode pretreatment

The PANI/Pb electrode was prepared by means of galvanostatic technique. The electro-polymerization process were as follows: introducing 0.5 mol L^{-1} H$_2$SO$_4$ + 0.1 mol L^{-1} aniline solution into the anode chamber and 0.5 mol L^{-1} H$_2$SO$_4$ into the cathode chamber, respectively, and then electrolyzing at current density of 0.022 A cm^{-2} for 6 min. In this process, the bare Pb electrode acted as the anode and Pt foil as the cathode. The prepared PANI/Pb electrode was rinsed by introducing DDW into the cathode chamber continuously for 2 min. It was observed that the fluorescence signal intensity decreased after the electrode operated more than 3 days. As a result, the electrode should be treated every 3 days with aforementioned method.

2.6. Analytical procedures

The blank catholyte (0.5 mol L^{-1} HCl) and anolyte (0.5 mol L^{-1} H$_2$SO$_4$) were continuously introduced into the cathode and anode chambers of the cell, respectively, at a flow rate of 6.0 mL min^{-1} by the peristaltic pump. After the anode and cathode chambers were filled, the power operating was opened at a constant current of 2.5 A and the sample solution was introduced into the cathode chamber at the same flow rate for 20 s. The generated hydrogen and SnH$_4$ were directed to the quartz tube by argon carrier gas for the atomic fluorescence measurements and peak area measurement with integration time of 20 s was used for quantification. While oxygen produced in the anode chamber was driven out along with the anolyte and then diffused to the surroundings at the outlet of the transferring tube. The anolyte was reclaimed and recycled. A bare Pb electrode of same dimension was used for comparison purposes.

CHG-AFS was adopted for validation of the proposed EC-HG-AFS method. Here, L-cysteine of 1% (m/V) was added to the sample solution and then the sample merged with a stream of 4% KBH$_4$ in 0.5% NaOH. The generated SnH$_4$ was introduced to the quartz atomizer by argon carrier gas for AFS determination.

3. Results and discussion

3.1. Performance of the PANI/Pb electrode

Firstly, we investigated the performance of the PANI/Pb-EC-HG system: according to the analytical procedures in 2.6, 50 ng mL^{-1} Sn(IV) standard solution was introduced into the EC-HG cell and determined for 6 runs [Fig. 1(1–6)]. In succession, introducing blank catholyte (0.5 mol L^{-1} HCl) and determined for 3 runs [Fig. 1(7–9)]. After 2 days' routine operation, 50 ng mL^{-1} Sn(IV) standard solution was once again introduced into the EC-HG cell and determined for 6 runs [Fig. 1(10–15)]. Bare Pb electrode EC-HG system was also evaluated for comparison.

From Fig. 1(1–6, 10–15), we could find that the application of PANI/Pb electrode in the proposed present system could increase
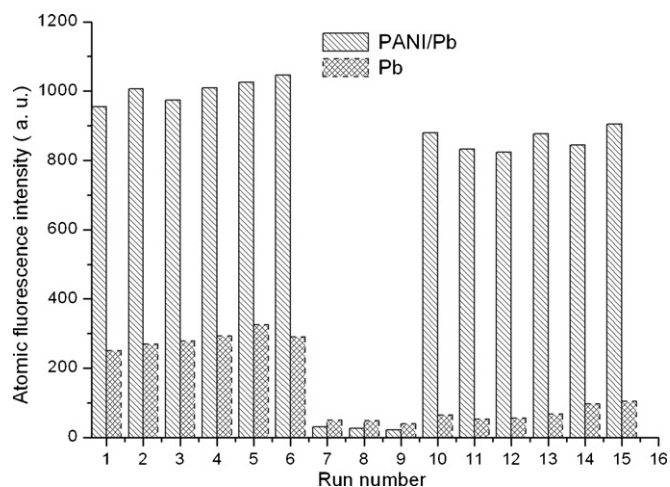
Fig. 1. The comparison of performances of EC-HG system for tin determination using the PANI/Pb electrode or bare Pb electrode as cathode material. Run numbers 1–6, 50 ng mL^{-1} Sn(IV) standard solutions; run numbers 7–9, blank catholyte (0.5 mol L^{-1} HCl); run numbers 9–15, after 2 days' routine analysis, 50 ng mL^{-1} Sn(IV) standard solutions was introduced into the EC-HG cell and determined.

tin fluorescence signal intensity. It may be ascribed to the fact that the PANI film on Pb electrode surface could prevent atomic tin from combining with Pb in electrode surface to avoid formation of PbSn$_x$ alloy. At the same time, the PANI film could catalyze and accelerate the atomic Sn transformation to the SnH$_4$. Comparatively, bare Pb electrode is prone to form alloys with analytes [22] and the active sites on its surface are easily blocked resulting to tin fluorescence signal intensity falling.

In present system, the stability of this PANI/Pb-EC-HG system (the RSD for 1–6 runs was 3.3%) was highly enhanced relative to bare Pb-EC-HG system (the RSD for 1–6 runs was 8.9%). Operating life of the PANI/Pb electrode is also prolonged. A satisfying result can yet be obtained after 2 days' routine operation in the proposed system. Whereas, the tin fluorescence signal intensity in bare Pb electrode was obviously falling after 2 days' routine operation [Fig. 1(10–15)].

3.2. Potential memory effect

As far as known, the bare Pb electrode could efficiently reduce Sn(IV) into atomic Sn, but their subsequent transformation to SnH$_4$ is insufficient, since the reduced analyte on bare Pb electrode is easily combined with Pb [21]. As a result, it will bring higher memory effect in determination procedure. This case can be found in Fig. 1(7–9) that fluorescence signal intensity of blank catholyte was as high as about 20% of that of 50 ng mL^{-1} Sn(IV) standard solution. In the present PANI/Pb-EC-HG system, it could not only reduce Sn(IV) on the PANI film but also efficiently transform atomic Sn to the SnH$_4$. The fluorescence signal intensity of blank solution decreased to less than 10% of that of 50 ng mL^{-1} Sn(IV) standard solution. Consequently, the memory effect in the proposed system was evidently cut down.

In order to testify aggradation of Sn atom on Pb electrode surface, X-ray photoelectron spectrum (XPS) was applied to examine the tin content on the PANI/Pb and Pb cathode surface after hydride generation. As illustrated in Fig. 2, there is a distinct Sn3d^5 peak on the Pb cathode surface and a weaker Sn3d^5 peak on the PANI/Pb cathode surface. Quantitative data indicated that the tin content on lead cathode surface was about 1.2‰ deduct from background response, while the tin content on PANI/Pb cathode surface was about 0.4‰. These results implied that the PANI film was capable of facilitating transformation of atomic Sn to the SnH$_4$ and lessen the conglomeration of Sn atom on electrode surface.

3.3. The potential PANI film electrochemical hydride generation mechanism

The basic form of the PANI film has the general formula as shown in Fig. 3(a), containing y reduced and $(1-y)$ oxidized repeat groups; y can in principle be varied continuously from one, the completely reduced material, to zero to give the completely oxidized polymer [23]. The completely reduced PANI film is nonconductor, however, doping with inorganic acid such as H$_2$SO$_4$ or HCl would lead to the conductivity increases as ten factors of ten 10^{10} [24]. In terms of the fact that the PANI/Pb electrode acted as cathode in the EC-HG cell, the structure of PANI film was considered as the completely reduced polymer ($y=1$) when describing the potential electrochemical hydride generation mechanism [Fig. 3(b)].

In light of PANI film having sorption sites of positively charged Sn^{4+} and H$^+$ [18], it is assumed that the first step of electrochemical hydride generation in PANI film is the diffusion of the Sn^{4+} and H$^+$ in the catholyte to the surface of the PANI film to form a weak bond between the analyte species and the nitrogen atoms. The adsorption processes could be characterized by (1)a and (1)b.

The electron-transfer-process between basic Pb electrode and Sn^{4+} occurred through PANI film, which could reduce the reaction activation energy, and therefore facilitate the adsorbed Sn^{4+} and H$^+$ reduced to adsorbed Sn atom and H atom. The reduction steps were characterized by (2)a and (2)b.
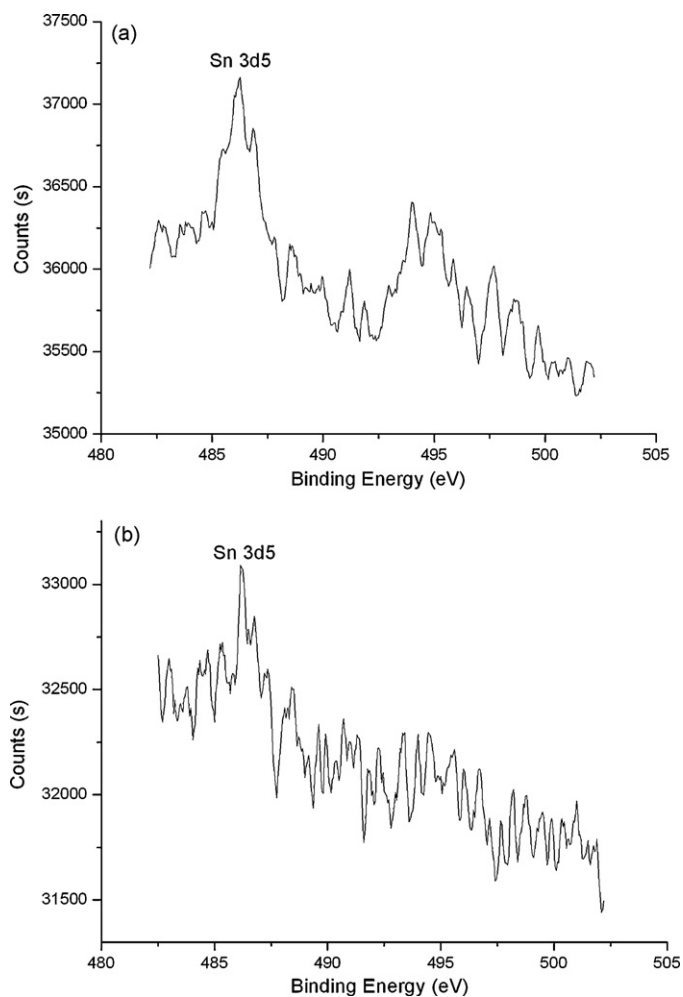
Fig. 2. Spectra of Sn(3d^5) on surface of electrode. (a) Bare Pb electrode, (b) PANI/ Pb electrode.
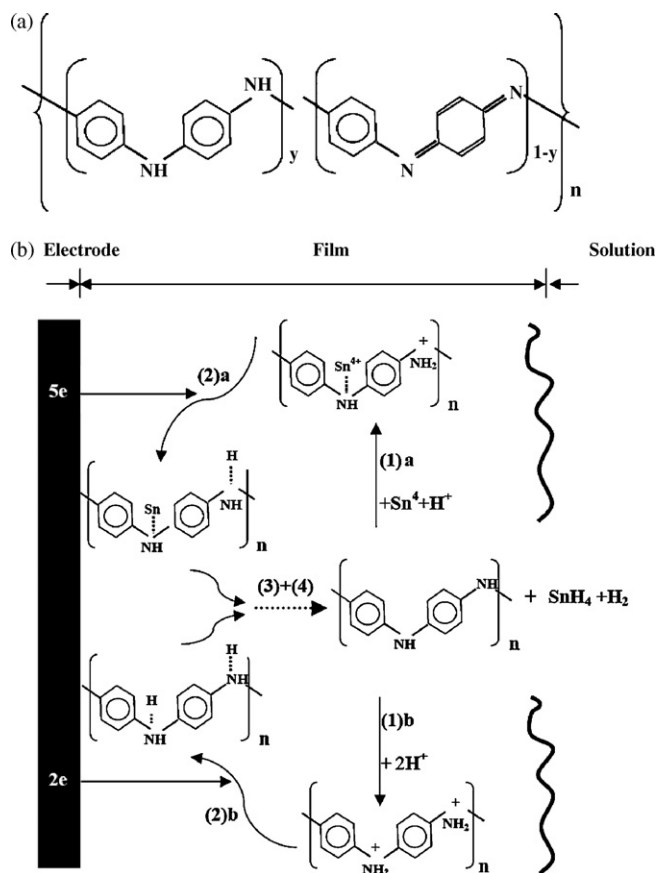
Fig. 3. (a) General structure of polyaniline. (b) Mechanism of the electrochemical hydride generation of Sn^{4+} on PANI film. The basic Pb electrode figured in black. Steps: (1a) the adsorption of Sn^{4+} on the PANI film; (1b) the adsorption of H^+ on the PANI film; (2a) the reduction of adsorbed Sn^{4+} into adsorbed Sn atom; (2b) the reduction of adsorbed H^+ into adsorbed H atom; (3), the recombination of adsorbed Sn atom and adsorbed H atom to formation of SnH_4; (4), the desorption of SnH_4 from the cathode surface.

To produce SnH_4, the adsorbed Sn atoms were combined with the adsorbed H atom [Fig. 3(b): (3)]. The sorptive characteristic of the PANI film for both Sn atom and H atom increased the contiguity probability of Sn atom and H atom and facilitated the formation of SnH_4. The last step, tin hydride generation, was followed by the desorption of both the SnH_4 and H_2 from the cathode surface and diffusion into the solution [Fig. 3(b): step (4)].

3.4. Optimization of the experimental conditions

3.4.1. Polymerization conditions
The effect of polymerization conditions on the behavior of the modified electrode was studied in detail. It was found that larger current density would bring on larger bubbles on the electrode surface and make it against the polymerization process, whereas lower current density slow down the polymerization velocity. The current density of $0.022\,A\,cm^{-2}$ was selected in this work. Moreover, the EC-HG-AFS results revealed that the PANI film obtained after being electrolyzed at current density of $0.022\,A\,cm^{-2}$ for 6 min showed satisfying fluorescence signal intensity and preferable stability.

The stability of the obtained PANI/graphite electrode towards Sn(IV) reduction was tested by subjecting the PANI/Pb to the whole ranges of currents and potentials used in the EC-HG experiment. After these treatments the electrode showed the same behavior towards the Sn(IV) reduction as a fresh electrode. As a result, current density of $0.022\,A\,cm^{-2}$ with polymerization time of 6 min was adopted in our work.
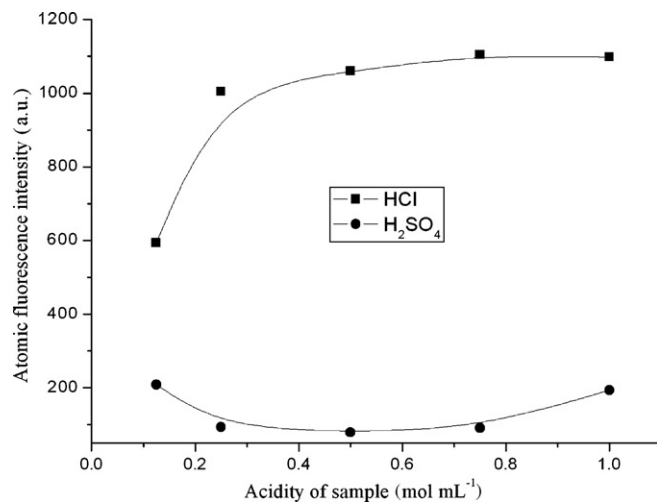

Fig. 4. Effect of catholyte acidity on fluorescence signal intensity of $50\,ng\,mL^{-1}$ Sn(IV).

3.4.2. Electrolytes
Diluted H_2SO_4 of $0.5\,mol\,L^{-1}$ was selected as the anolyte and the effects of different concentrations of H_2SO_4 or HCl catholyte on the atomic fluorescence intensity of $50\,ng\,mL^{-1}$ Sn(IV) were studied. It was found [Fig. 4] that the optimum catholyte was HCl and the fluorescence signal responses increased along with the HCl acidity from 0.1 to $0.5\,mol\,L^{-1}$, and then leveled off from 0.5 to $1.0\,mol\,L^{-1}$. This implies that some processes involved in tin hydride generation are affected by the solution pH. Since higher concentration of the electrolyte might introduce higher interferences, $0.5\,mol\,L^{-1}$ HCl was chosen as catholyte in this work.

3.4.3. Electrical current
The influence of applied current on the fluorescence signal intensity of $50\,ng\,mL^{-1}$ Sn(IV) was investigated within the range of 1.0–2.5 A. In general, signal intensity increased with electrolytic current and this corresponds to higher hydride generation efficiency at high electrolytic currents. At the same time, an increment in the electrolysis current implies an increase in the amount of hydrogen formed. From Fig. 5, we can find that the fluorescence signal intensity increased significantly along with the increasing electrolysis current up to 2.5 A and then levelled off. As a result,
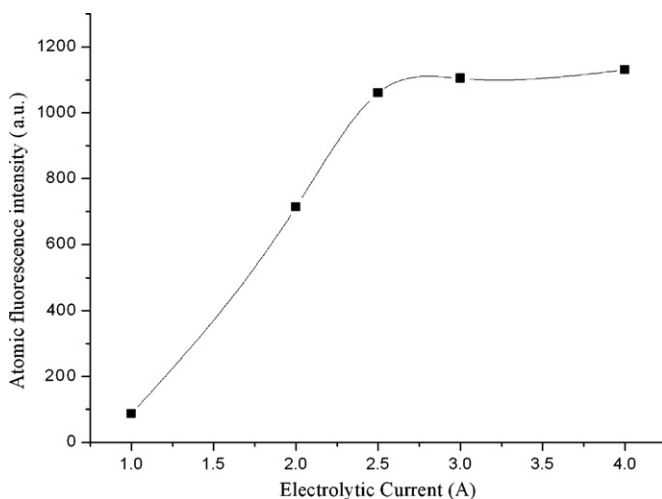
Fig. 5. Effect of electrolytic current on fluorescence signal intensity of $50\,ng\,mL^{-1}$ Sn(IV).

Table 2
Sample analysis and recovery experiment.

Sample	EC-HG-AFS		CHG-AFS	GF-AAS
	Determined ($\mu g\,g^{-1}$)[a]	Recovery (%)[b]	Determined ($\mu g\,g^{-1}$)[a]	Determined ($\mu g\,g^{-1}$)[a]
Crab	1.34 ± 0.05	107	1.30 ± 0.04	1.37 ± 0.05
Meat	2.33 ± 0.08	98	2.38 ± 0.08	2.30 ± 0.07
Conjee	1.85 ± 0.07	103	1.80 ± 0.05	1.91 ± 0.07
Orange juice	170.7 ± 6.3	–	176.5 ± 5.8	178.3 ± 6.2
Tomato sauce	60.3 ± 2.1	–	63.2 ± 2.0	57.9 ± 2.0

[a] Mean value ± standard deviation (n = 3).
[b] 1 $\mu g\,mL^{-1}$ Sn(IV) standard solution spiked in the sample.

electrolysis current of 2.5 A (0.48A cm^{-2} of current density) was used throughout this work.

3.4.4. Flow rate of carrier gas Ar

The influence of carrier gas (Ar) flow rate on the fluorescence signal intensity was studied in the range of 300–900 mL min^{-1}. The fluorescence signal intensity reached to maximum value at 500 mL min^{-1} and then decreased. Carrier gas (Ar) flow rate of 500 mL min^{-1} was selected as optimal for further experiments.

3.4.5. Flow rate of auxiliary H$_2$

As reported in previous work [25], only a small amount of hydrogen was produced in the electrolysis process, which is insufficient for maintaining the hydrogen–argon–air entrained flame. Auxiliary H$_2$ should be added into the Ar flow. The fluorescence signal intensity increased remarkably along with the auxiliary H$_2$ flow rate varying from 100 to 300 mL min^{-1}, and decreased afterward. In this work, 300 mL min^{-1} H$_2$ flow rate was chosen.

3.4.6. Sample flow rate

The dependence of the fluorescence signal intensity on the sample flow rate was tested in the range of 4–10 mL min^{-1}. Fluorescence signal intensity was maximum at the sample flow rate of 6.0 mL min^{-1} and then it decreased slowly. In this work, sample flow rate of 6.0 mL min^{-1} was suitable and applied throughout.

3.5. Effect of coexisting ions

The effects of some representative potential interference ions on the determination of Sn(IV) were examined by EC-HG-AFS, which were expressed as the relative response in the cases with and without interference ions. Variations less than 5% of relative response may be believed insignificant. An increase in the Sn(IV) fluorescence signal intensity were brought about by the addition of 20 $\mu g\,mL^{-1}$ of Pb(II), Al(III), 10 $\mu g\,mL^{-1}$ of Se(IV), Zn(II); while the fluorescence signal intensity decreases by adding 100 $\mu g\,mL^{-1}$ for Fe(III), 10 $\mu g\,mL^{-1}$ for Ni(II), Cu(II), Co(II), Cr(VI), Mn(II), Mo(II). There was no significant interference for ion concentrations as high as 2 $\mu g\,mL^{-1}$ for Fe (III); 100 ng mL^{-1} for Pb(II), Al(III), Se(IV), Zn(II), Ni(II), Cu(II), Co(II), Cr(VI), Mn(II), Mo(II). Moreover, 0.1% HNO$_3$ also did not interfere with the detection of Sn(IV). The levels of coexisting ions in the sample solutions of ordinary canned foods are below the tolerance levels, which permit the proposed method to be used for the determination of tin in the canned foods.

3.6. Analytical figures of merit

Under the optimal experimental conditions and procedure described above, the sensitivity and precision were evaluated for the determination of tin by EC-HG-AFS. The best line equation for the calibration plot is $I_f = -38.9 + 22.3C_{Sn}$ with the regression coefficients R of 0.9996, where I_f and C_{Sn} represented the peak area of the fluorescence signal and the concentration of Sn (ng mL^{-1}),

respectively. The detection limit based on three times the standard deviation of 11 measurements of the sample blank and the slope of the calibration curves was 1.5ng mL^{-1} (3σ). The relative standard deviation (RSD) was 3.3% (50 ng mL^{-1}, n = 11).

3.7. Analytical results of samples

The proposed method was applied to the analysis of three common food contained in resin-coated cans and two in plain cans and the results were listed in Table 2. The recoveries were in the region of 98–107%. The analytical results indicated that tin content of foods in resin-coated cans (<5 $\mu g\,g^{-1}$) were much less than those (60–08 $\mu g\,g^{-1}$) in plain cans. Since tin in canned foods is known to have dissolved from the tinplate surface of the inside of the can, resin coating on the surface was needed to inhibit the dissolving of tin.

The validation of this method was carried out by comparison of the data found by EC-HG-AFS with those obtained by CHG-AFS and GF-AAS and the results are also listed in Table 2. A t-test (95% confidence level) was performed and no significant difference was found between the results of the EC-HG-AFS and that of CHG-AFS and GF-AAS.

4. Conclusion

An EC-HG-AFS system with PANI-modified Pb electrode as cathode material was developed for the determination of tin. The EC-HG efficiency for Sn(IV) was improved evidently as the PANI membrane could facilitate the transformation process from atomic Sn to SnH$_4$ and avoid the aggradation of Sn atom on Pb electrode surface. Attributing to this superior reduction activity of Sn(IV) on polyaniline film, this proposed method had the virtues of higher sensitivity, excellent stability and low memory effect.

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