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Abrasively Immobilized Multiwall Carbon Nanotubes Bismuth Film Electrode for Chronopotentiometric Stripping Analysis of Tin

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A sensitive chronopotentiometric stripping method for determination of trace tin was first developed using the novel abrasive immobilized MWCNTs and in-situ plated bismuth film electrode. The result showed that this environment-friendly electrode was stability and much easy to prepare. The effects of pH of acetate buffer, concentration of Bi(Ⅲ) and cetyltrimethyl ammonium bromide, deposition potential, accumulation time, stripping current and possible interferences were investigated in detail. Through the synergistic sensitization effect of MWCNTs and bismuth film, the fabricated electrode showed sensitive response with a well-defined peak to Sn(IV). Under the optimal conditions, the electrode exhibited linear ranges from 2.0 to 100.0 μg/L with a detection limit as low as 0.06 μg/L for tin. Good resolution between neighbouring Sn(IV) and Pb(II) signals was obtained in the presence of oxalic acid. The electrode was applied to detect trace tin in canned food with an average recovery between 94.6 and 106.6%.

Keywords: Bismuth film electrode; Multiwall carbon nanotubes; Response characteristics; Chronopotentiometric stripping analysis; Tin determination

1. INTRODUCTION

Tinplate is expensively used in food and beverage industry as a robust form of packaging [1]. Although tin is not a highly toxic element, there is a possibility that inorganic tin would turn into toxic organic tin compound in food stuff. Several analytical techniques have been introduced for the determination of trace tin, including electrothermal atomic absorption spectrometry (ETAAS) [2], electrochemical hydride generation atomic fluorescence spectrometry [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5] and X-ray fluorescence spectrometry [6], *etc*. Stripping voltammetric method (SV) [7-10] has proven useful for trace tin detection since they are sensitivity and accuracy, specifically, far less expensive and more portable than the aforementioned techniques. Chronopotentiometric stripping analysis (CPSA) is the most potential SV methods [11-12] for its notable advantages, such as much less affected by ionic strength and adsorbed organic compounds, lower background contributions. However, chronopotentiometric stripping analysis of tin has not been reported so far. Mercury-based electrode [13] has traditionally been used in stripping voltammetry due to the unique ability of mercury to preconcentrate heavy metal. In 2000, environment friendly bismuth has been introduced [14] as a new material to replace toxic mercury. Nowadays, bismuth based electrode has been introduced for stripping voltammetric analysis of tin [15-18].

Recently, carbon nanotubes bismuth film composition electrode (CNTs/BiE) [19-21] was introduced to improve the electrochemical performances of bismuth based electrode. CNT electrode is generally prepared by CNT paste (CNTP) [20], surface coating of CNT dispersion solutions on an electrode (SCCNT) [19] and screen-printed CNT [21]. However, CNTP, SCCNT and screen-printed CNT electrodes are time-consuming to prepare and always suffer from mechanical instability during measurement. Hence, the simple and reliable methods to prepare CNTs/BiE are highly desired. Salimi *et al* [22-23] produced an abrasively immobilized multiwall carbon nanotubes (MWCNTs) electrode by gentle rubbing of a preheated electrode surface on a filter paper supporting MWCNTs. This abrasively immobilized CNT electrode exhibited excellent catalytic activity, inherent stability, and much easy to prepare.

In this work, we expanded the analytical utility of abrasively immobilized MWCNTs (AIMWCNTs) electrode to develop a simple and fast method for the preparation of CNTs/BiE. A method for the measurement of trace tin using CPSA was proposed based on the abrasively immobilized MWCNTs bismuth film graphite electrode (AIMWCNTs/BiF/GE). The proposed method was used in the detecting traces tin in canned food.

2. EXPERIMENTAL

2.1. Reagents and chemicals

$TNMH_3$ carboxyl functionalized multiwalled carbon nanotubes (MWCNTs, 10-20 nm, CNT>wt 95%, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences). A stock solution of Sn(IV) (0.10 mg/mL) was prepared using 1.0 mol/L hydrochloric acid and was diluted to 0.01 mg/mL with 1.0 mol/L HCl when used. Bi(Ⅲ) plating solution of 0.25 g/L was prepared using 1.0 mol/L HNO_3 1.0 mol/L oxalic acid solution, 2.0×10^{-3} mol/L cetyltrimethylammonium bromide（CTMAB）solution, 0.4 mol/L acetate-sodium acetate buffer. All reagents were analytical reagent grade or guarantee reagent grade chemicals. The water used was double-distilled.

The canned foods were obtained from the local market and chopped and mixed then weighed and dried at 100-150 °C in porcelain dish.

2.2. Apparatus

The chronopotentiometric stripping analysis was performed by a MP-2A stripping analyzer with a MCP-2T polar graphic workbench (Shandong 7 Telecommunications Factory, China). Three-electrode system: an abrasively immobilized MWCNTs graphite electrode (GE, 4 mm diameter) was used as the working electrode, an saturated calomel electrode (SCE) and a 223 platinum electrode were used as the reference electrode and auxiliary electrode, respectively. All potentials in this paper are given against SCE.

2.3. Preparation of abrasively immobilized MWCNTs graphite electrode

The graphite electrode (GE) was firstly treated according to standard method [15-18]. A small amount of functionalized MWCNTs was put on a smooth sulfate paper. Then, the treated GE was grinded on it for 2 min to prepare the abrasively immobilized MWCNTs electrode, the fabricated electrode was cleaned with distilled water before use.

2.4. Measurement procedure

CPSA with constant current model was applied for the determination of Sn(IV). Bismuth film was formed on AIMWCNTs/GE with in situ plated model [17] in 0.1 mol/L acetate buffer（pH 4.4）and 0.25 μg/L Bi(III). The deposition potential and stripping current was −1.1 V and of 5.0 μA, respectively. The sample was digested by washing method [2]. The content of Sn(IV) in the sample was calculated by standard addition method. The tin determination method of canned food samples was depended on result from interference study which include pH of acetate buffer, concentration of Bi(Ⅲ) and cetyltrimethyl ammonium bromide, deposition potential, accumulation time, stripping current and possible interferences.

3. RESULTS AND DISCUSSION

3.1. Surface morphologies of AIMWCNTs/GE

SEM in was used for examining the morphology of AIMWCNTs/GE. Fig. 1 shows that large quantities of MWCNTs are well distributed on the surface of electrode. Moreover, the profile of individual MWCNTs bundles is clearly seen and these bundles are interconnected together to form netlike nanostructures, suggesting that a thin MWCNTs layer was formed on the surface of GE by abrasively modifying. The morphological structure of abrasively immobilized MWCNT film might improve diffusion of the electro-active species and provide good sensitivity and rapid response [24].

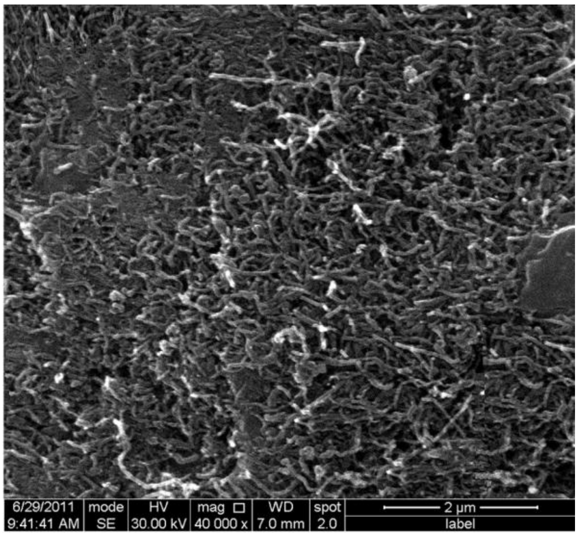

Figure 1. Scanning electron microscopy（SEM）images of abrasively immobilized MWCNTs graphite electrode.

3.2. The optimal solution condition

Some electrolytes, including 0.04 mol/L Britton–Robinson buffers, 0.1 mol/L phosphate buffer saline, 0.1 mol/L acetate-sodium acetate buffer, and 0.1 mol/L citric acid-sodium citrate were investigated, and the best response was obtained using 0.1 mol/L acetate-sodium acetate buffer. Fig. 2 shows that the stripping peak height（*dt/dE*）increases and the relative standard deviation (*RSD*, N=11) of Sn(IV) decreases by increasing of the solution pH from 3.0 to 4.2, then *dt/dE* and *RSD* remain stable when pH changes from 4.2 to 4.6. Finally, *dt/dE* begins to decline and *RSD* begins to incline when pH exceeds 4.6. Therefore, 0.1 mol/L acetate-sodium acetate buffer (pH 4.4) was selected as the supporting electrolyte.

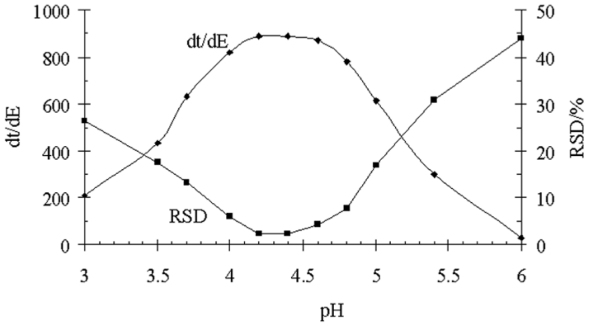

Figure 2. The effect of pH on the stripping peak height (*dt/dE*) and the relative standard deviation (*RSD*, N=11). Supporting electrolyte, 0.1 mol/L acetate buffer; Sn(IV), 10.0 μg/L; Bi(III), 0.4 mg/L; cetyltrimethyl ammonium bromide, 3.0 μmol/L; deposition potential, 1.1 V; accumulation time, 120 s; stripping current, 5.0 μA.

The effect of the concentration of Bi(III) (c_{Bi}) on *dt/dE* and *RSD* was investigated. *dt/dE* increases markedly and *RSD* decreases obviously with c_{Bi} increasing from 0.1 to 0.3 mg/L. While *dt/dE* reaches a plateau and *RSD* increases slightly when cBi increases from 0.3 mg/L to 0.8 mg/L. The decrease of *dt/dE* and obvious increase of *RSD* were observed at c_{Bi} more than 0.8 mg/L, meanwhile, the stripping peak also became wider. A c_{Bi} of 0.4 mg/L was selected as Bi(Ⅲ) plating solution.

The influence of different surfactants, including cetyltrimethyl ammonium bromide (CTAB, a cationic surfactant), sodium dodecylsulfate (SDS, an anionic surfactant) and octylphenyl polyethylene glycol (Triton X-100, a non-ionic surfactant), on *dt/dE* of Sn(IV) at AIMWCNTs/Bi/GE was investigated. Fig. 3a shows that *dt/dE* remains almost unchanged by the addition of 0.1 μmol/L SDS and 0.1 μmol/L Triton X-100, while *dt/dE* increases obviously in the presence of 0.1 mg/L CTAB. The optimal CTAB concentration (c_{CTAB}) range is between 2.0 μmol/L and 4.0 μmol/L as Fig. 3b shown. A c_{CTAB} of 3.0 μmol/L was selected for all further measurements. These results indicate that the AIMWCNTs/Bi/GE has excellent reproducibility and long-term stability, making it attractive for detecting traces tin [25].

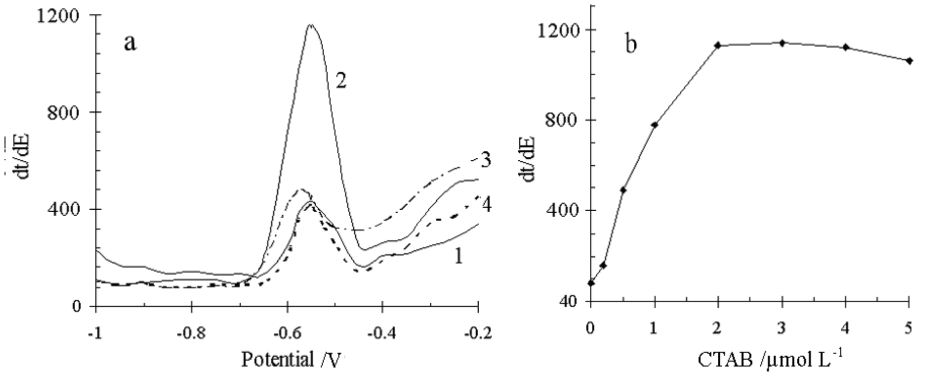

Figure 3. The chronopotentiometric stripping peak of Sn(IV) at AIMWCNTs/Bi/GE (a) in the absence of surfactant (curve 1) , 0.1 μmol/L SDS (curve 2) , Triton X-100 (curve 3) and CTAB (curve 4) and the influence of CTAB concentration (b). Supporting electrolyte, 0.1 mol/L acetate buffer; Sn(IV), 10.0 μg/L; Bi(III), 0.4 mg/L; deposition potential, 1.1 V; accumulation time, 120 s; stripping current, 5.0 μA.

3.3. The influence of the accumulation potentials and time the stripping current

The influence of deposition potential (E_d) on *dt/dE* and *RSD*（ N=11) was investigated. As shown in Fig. 4, the negative shift of E_d from −0.6 to 1.1 V can increases *dt/dE* of Sn(IV) obviously. While, *dt/dE* decreases and *RSD* increases remarkably as E_d becomes more negative than −1.3 V due to the hydrogen evolution of electrode at very negative E_d. Therefore, −1.1 V was adopted for the following experiments. The result showed that *dt/dE* increased and *RSD* remained almost unchanged along with the accumulation time (t_a) prolonged from 60 to 300 s. As t_a longer than 300 s, the curves of *dt/dE* versus t_a began to leave off with the increase of *RSD*, this can be attributed to slow electron transfer in a thick bismuth film as ta is too long. For this reason, t_a should be in the range of 60 to 300 s and considers the satisfactory compromise between sensitivity and analysis time. The difference in the composition can explained by the long-lasting depletion effect that takes place in the electrolyte during the achievement of the steady-state deposition conditions [26].

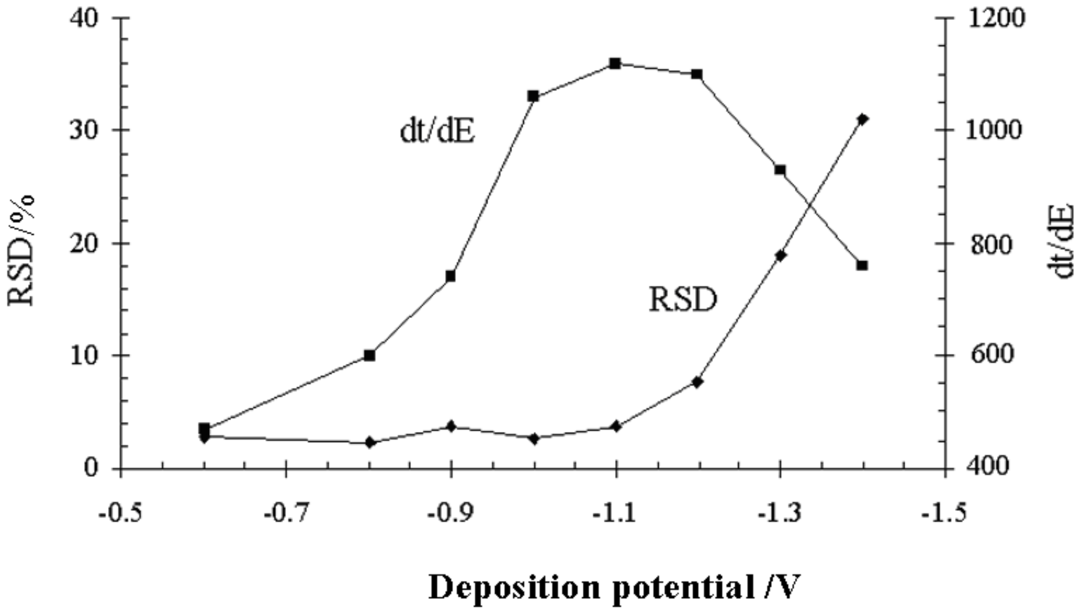

Figure 4. The influence of deposition potential on *dt/dE* and *RSD*. Supporting electrolyte, 0.1 mol/L acetate buffer; Sn(IV), 10.0 µg/L; Bi(III), 0.4 mg/L; cetyltrimethyl ammonium bromide, 3.0 µmol/L; accumulation time, 120 s; stripping current, 5.0 µA

The effect of stripping current (i_s) upon *dt/dE* and *RSD* was also investigated. *dt/dE* decreased significantly as i_s increased from 0.2 to 10.0 µA, indicating that lower i_s is beneficial to enhance analytical sensitivity, but the reproducibility may become poor along with a obviously prolonged period and a stronger background baseline when much lower i_s was applied [27]. Thus, a i_s of 5.0 µA was considered.

3.4.The chronopotentiometric stripping behavior of Sn(IV)

Fig. 5 displays a comparison among the stripping peak of 10.0 µg/L of Sn(IV) at bare GE (a), Bi/GE (b) and AIMWCNTs/Bi/GE(c). No stripping peak was observed at the bare GE with a strong background contribution. While, a stripping peak near 0.60 V can be observed at Bi/GE and AIMWCNTs/Bi/GE. In contrast, the stripping response of Sn(IV) at AIMWCNTs/Bi/GE is almost two times higher than that at Bi/GE along with a well-defined stripping peak, implying that the sensitivity of the bismuth film electrode towards Sn(IV) has been significantly enhanced by MWNTs. It was also found in other research that the evolution of hydrogen gas from the CNT electrode surface started to occur at −1.2V and could damage the bismuth film when more negative potential was applied. This explains the significant stripping signal decreases below−1.4 V [27]. Overall, the data of Fig. 5 indicates that coating bismuth layer on AIMWCNTs/GE electrode dramatically improves the ability of electrode to detect trace Sn(IV) as compared with coating bismuth layer on bare GE.

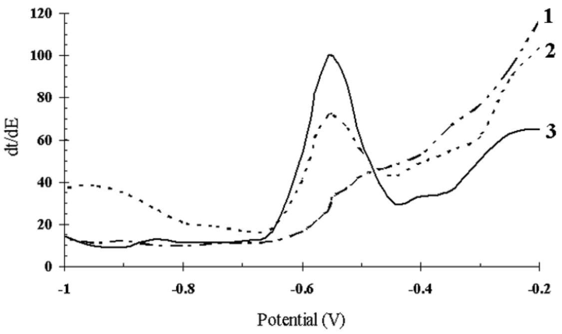

Figure 5. The stripping peak of Sn(IV) at bare GE (curve 1), Bi/GE (curve 2) and AIMWCNTs/Bi/GE (curve 3). Supporting electrolyte, 0.1 mol/L acetate buffer (pH 4.4); Sn(IV), 10.0 µg/L; Bi(III), 0.4 mg/L; cetyltrimethyl ammonium bromide, 3.0 µmol/L; deposition potential, 1.1 V; accumulation time, 120 s; stripping current, 5.0 µA.

3.5 Interference study

The determination of tin in the presence of lead by polarography or ASV is much difficult owing to the very close oxidation potentials of tin and lead [13-14, 16-17]. Oxalic acid has been shown to enhance resolution between neighbouring Sn(IV) and Pb(II) signals at mercury film electrode [13] and bismuth film electrode [16], however, the effect of oxalic acid at CNTs/BiE was unknown. Fig. 6 shows the response of 10.0 µg/L Sn(IV) and Pb(II) in the absence or presence of oxalic acid at AIMWCNTs/Bi/GE. Curve 1 shows that very weak stripping signal of Sn(IV) and Pb(II) with poor resolution is observed in the absence of oxalic acid.

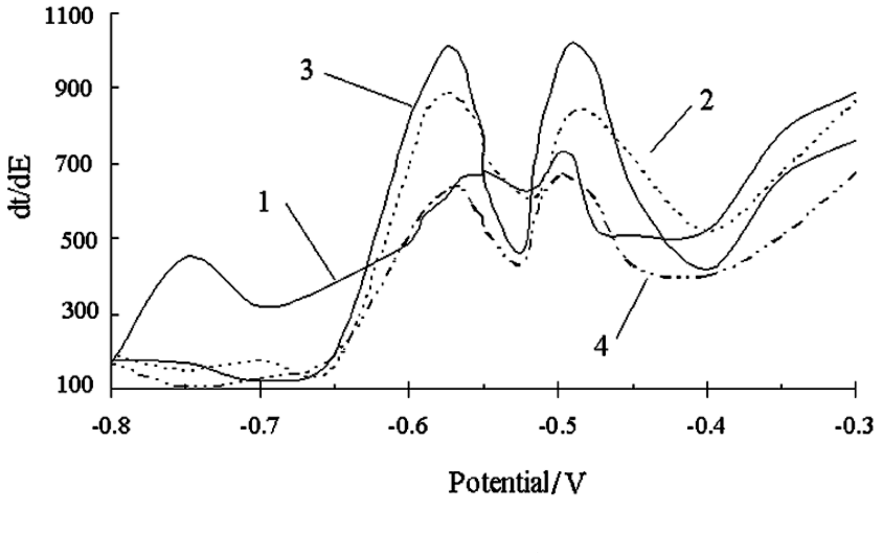

Figure 6. The chronopotentiometric stripping behaviors of Sn(IV) and Pb(II) at AIMWCNTs/Bi/GE in the absence (curve 1) , presence of 0.02 mol/L oxalic acid (curve 2), 0.15 mol/L oxalic acid (curve 3) and at BiFE in the presence of 0.15 mol/L oxalic acid (curve 4) .

While higher stripping signal of Sn(IV) and better resolution between neighbouring Sn(IV) and Pb(II) signals are obtained with the increase of oxalic acid (c_o) from 0.02 mol/L (curve 2) to 0.15 mol/L (curve 3) at AIMWCNTs/Bi/GE. A c_o of 0.15 mol/L was selected for the measurement of tin in the presence of lead. The stripping signals obtained from AIMWCNTs/Bi/GE (curve 3) and BiFE (curve 4) under c_o of 0.15 mol/L reveal that the resolution between Sn(IV) and Pb(II) stripping signals is much better at AIMWCNTs/Bi/GE than that at BiFE, indicating that MWCNTs modified on the electrode can improve the resolution of Sn(IV) signals from Pb(II) effectively.

The possible interferences of some inorganic species were investigated by addition of different inorganic ions to a solution containing 10.0µg/L of Sn(IV) and 0.15 mol/L of oxalic acid. 200-fold concentration of K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, NH_4^+, Cl^-, SO_4^{2-}, NO_3^- and 10-fold concentration of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} did not cause significant interference. In addition, Hg^{2+} could increase the stripping peak current of Sn(IV) due to the formation of amalgam on the electrode surface.

3.6. Analytical performance characteristics of the method

The linear range of AIMWCNTs/Bi/GE for detection of Sn(IV) was determined under the optimal conditions mentioned above. A good linear relationship was obtained between dt/dE and the concentration of Sn(IV) within the range of 2.0 µg/L to 100.0 µg/L with the linear regression equation $dt/dE = 1.12\ c - 3.23$ ($r^2 = 0.998$) at a t_a of 120 s, where, *dt/dE* is the peak height, *c* is the concentration of Sn(IV) (µg/L). According to the method recommended by IUPAC, detection limit (CL)=$3S_b/S_x$, where, 3 is confidence factor, S_b is background noise standard deviation, S_x is the measurement sensitivity (The slope of the standard curve). S_b and the average *dt/dE* for 21 repetitive determinations were calculated, as the result, the detection limit for 120 s and 300 s t_a were 0.1 µg/L and 0.06 µg/L, respectively. The repeatability of the method was evaluated by analyzing seven replicates of 10.0 µg/L Sn(IV), *RSD* was found to be 2.61% at t_a of 120 s. Thus, the results herein indicate that the modified electrode has an excellent repeatability in both preparation and determination steps [24].

3.7. Analysis of samples

Table 1. Rate constant (k) for $2HI(g) \rightarrow H_2(g) + I_2(g)$ at absolute temperature (T) ^{a}

Sample	By this method		Added /mg/kg	Found /mg/kg	Recovery /%	By ICP-MS /mg/kg
	Average / mg/kg	RSD/(%.n= 5)				
Pork luncheon meat	57.6	5.7	50.0	106.3	97.4	54.7
Canned stewed beef	51.1	3.5	50.0	98.4	94.6	52.1
Canned tuna	60.9	4.1	50.0	113.7	105.6	63.7
Canned stewed pork chops	40.3	3.3	50.0	88.3	96.0	37.3
Canned corn	63.2	2.9	50.0	112.4	98.4	59.8
Canned yellow peach	101.9	1.8	100.0	207.3	105.4	97.3
Canned arbutu in syrup	87.6	4.1	100.0	192.3	104.7	91.1
Canned strawberry	111.2	2.3	100.0	207.5	96.3	116.3
Canned pickle	97.8	3.1	100.0	195.5	97.7	101.4

The proposed method was applied to the determination of tin in different canned products. The results of tin in the samples obtained by the proposed method were compared with those obtained by ICP-MS. As Table 1 shows, good accuracy and recovery for the samples were obtained and the results obtained by the proposed method were consistent well with the results obtained by ICP-MS. From these results, we can conclude that AIMWCNTs/Bi/GE could provide a satisfactory method for the determination of tin in canned food [2-3,7-8].

4. CONCLUSIONS

A simple yet stable method for the fabrication CNTs modified bismuth film electrode by abrasive immobilized MWCNTs and in-situ plated bismuth film on graphite electrode is presented. The so fabricated electrode has several advantages over traditional CNTs electrode, including environment-friendly, stability, much easy to prepare. The electrode was applied in the chronopotentiometric stripping analysis of trace tin, the sensitivity of bismuth film electrode towards Sn(IV) has been significantly enhanced by abrasive immobilized MWCNTs, and better resolution between neighbouring Sn(IV) and Pb(II) signals was obtained at abrasively immobilized MWCNTs/GE in the presence of oxalic acid. The proposed method can be used as a promising alternative for the determination of tin at trace levels.

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