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Simultaneous determination of trace Sn(II) and Sn(IV) using differential pulse polarography and application

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A new method was established for the simultaneous determination of Sn(II) and Sn(IV) using differential pulse polarography (DPP). Among several electrolytes, 0.1 M NaOH in the presence of 0.1 M KNO_3 was found to be the most suitable one. In this medium, Sn(II) had 2 peaks, at -0.74 and -1.17 V, which were sharp and very sensitive. Sn(IV), on the other hand, had a very small peak at -0.92 V when its concentration was higher than 4.0×10^{-4} M. Thus, it was decided to determine Sn(IV) after reduction into Sn(II). In the presence of both Sn(II) and Sn(IV), Sn(II) was first determined from the peak at -1.17 V, and then Sn(IV) was determined after its reduction with $NaBH_4$ into Sn(II). The detection limit was 5.5×10^{-7} M and 8.2×10^{-7} M for Sn(II) and Sn(IV), respectively. The interference effect of the most common ions, Fe(III), Cu(II), Pb(II), Cd(II), and Zn(II), was investigated. Only copper and iron had an interfering effect during the speciation procedures, since they oxidized Sn(II), which was formed after reduction of Sn(IV) for its determination. This effect of Cu(II) and Fe(III) ions could be eliminated by the reducing agent $NaBH_4$, which was used for the reduction of Sn(IV). Since Pb(II) and Cd(II) peaks overlap with the first peak of Sn(II) at -0.74V, Sn(II) was determined using the second peak, at -1.17 V. In a synthetic sample containing Sn(II), Sn(IV), and all common ions, the total content of tin (2.0×10^{-5} M) was found to be $(2.07 \pm 0.38) \times 10^{-5}$ M (90% CI, N = 3).

This method was applied for the determination of tin in canned tomato sauce.

Key Words: Speciation, tin, differential pulse polarography, interference elimination, canned tomato sauce

Introduction

Tin is one of the essential trace elements that take place in various metabolic processes in humans, animals, and plants. It may be introduced into the human environment either as inorganic tin or as organotin compounds.

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While its inorganic state is not toxic, its organic compounds are mostly toxic.

Tin compounds are used in food packaging, in some veterinary formulations, in marine antifouling paints on the hulls of ships, in wood preservation, as a stabilizer for polyvinyl chloride, as fungicides for crops, and as electrochemical catalysts. Canned food is known to contain high concentrations of tin. This is particularly true for acidic food stuffs, such as canned tomato sauce and fruit juices. Although tin is not a highly toxic element, high concentrations of it, on the order of 0.1-1.0 g/L, may affect the flavor of the juice and can also cause diarrhea. It is also known that when inorganic tin is introduced to food stuff, there is a possibility of it turning into an organic tin compound. Consequently, there has been growing concern about the significance and toxicity of this element; this has encouraged the development of methods for its trace determination in various sample materials.[1,2] It is reported that Sn(II), as stannous chloride, is readily taken up by human white blood cells (WBC) and can cause damage to DNA.[3] The amount of damage observed was more extensive than that produced by exposure of cells to equimolar amounts of chromium(VI), a known carcinogen and DNA damaging agent. By contrast, Sn(IV) was not taken up by cells, did not cause DNA damage, and did not inhibit stimulation of DNA synthesis in cells.

The most common methods used include electrochemical methods such as voltammetry and polarography, atomic absorption spectrometry (AAS) with hydride generation, and some hyphenated methods such as inductively coupled plasma-mass spectrometry (ICP-MS) and gas chromatography-mass spectrometry (GC-MS). Among these, ICP-MS and GC-MS can only determine organic tin and total tin concentration.[4−6] They are expensive and are not able to determine Sn(II) and Sn(IV) ions selectively.

With the use of flame AAS, Sn(II) ions could be determined in the presence of Sn(IV). This method requires preconcentration and extraction of Sn(II) using a complexing agent.[7] Total tin in sea water was determined using flame AAS.[8] A spectrofluorimetric method was used for total tin in canned food.[9] Sn(II) and Sn(IV) ions could be determined simultaneously using spectrophotometric methods.[10] In some voltammetric methods, various modified electrodes have been used for the determination of Sn(IV).[11,12] For adsorptive cathodic stripping voltammetric determination of Sn(II) on a glassy carbon electrode, some complexing agents, such as catechol[13] and tropolone complex[14], have been used. The complex of Sn(IV)-3,4-dihydroxybenzoic acid (DHBA) was adsorbed on a hanging mercury drop electrode and tin was determined with cathodic stripping voltammetry.[15] Water samples were analyzed using a tin-chloranilic acid complex by adsorption on mercury drop after preconcentration.[16]

The effects of tropolone,[17] hyamine-2389,[18] catechol, gallic acid, tiron,[19] and various other compounds[20,21] on the voltammetric behavior of tin have been investigated, and it was found that in the presence of tropolone, 8×10^{-9} M tin could be determined with anodic stripping voltammetry.[17] Sn(II) and Sn(IV) could be determined using anodic stripping voltammetry in water and methanol solvents.[22] In the presence of lead with a rotating ring disk electrode using stripping voltammetry, the detection limit for tin was found to be 20 nM.[23] Using DPP, 3×10^{-4} M Sn(II) could be determined in 1 M HCl.[24] It was possible to determine tin with linear sweep polarography in fruit juice.[25] Tin content in the Pacific Ocean has been found to be 0.58 μg/L using anodic stripping voltammetry.[26] With the use of the intermetallic compound formation between tin and selenite, the tin content in canned corn could be determined using DPP, and the content was found to be 5.95 ± 0.54 μg/g.[1] The total tin content in canned tomato sauce was determined using DPP in acetate buffer, in the presence of EDTA, and 26 μg/g was found.[27] Some environmental samples were analyzed after preconcentration using DPP. The detection limit found was 1 × 10^{-6} M.[28]

Most of the above mentioned methods relate to the total tin determination or to either Sn(II) or Sn(IV) ion determinations. These methods essentially require many time consuming pretreatment and preconcentration procedures, such as complexation, decomposition, extraction, or derivatization with danger of contamination.

Electrochemical methods are preferred for speciation purposes, since each oxidation state of each element will appear at a different potential. In the event of overlapping peaks, by changing either the electrolyte or pH, this effect may be overcome. These methods offer useful alternatives, since they allow faster, cheaper, and safer analysis. The results obtained with the DPP method are very reproducible, since, with the use of a dropping mercury electrode (DME), the behavior of the electrode is independent of its past history.

The aim of this work was to develop a new and simple method for the trace determination and, at the same time, for the speciation of Sn(II) and Sn(IV) compounds without any pretreatment or preconcentration procedures.

Experimental

Apparatus

A PAR (Model 174A) polarographic analyzer system equipped with a PAR mercury drop timer was used. The natural drop time of the mercury electrode was in the range of 2-3 s (2.37 mg/s). A Kalousek electrolytic cell with a reference saturated calomel electrode (SCE), separated by a liquid junction, was used in the 3-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X-Y recorder. DP polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV/s, and a pulse amplitude of 50 mV.

Reagents

All chemicals used were of analytical reagent grade (Merck, Darmstadt, Germany), and triply distilled water was used in the preparation of their solutions and at all stages of analysis. Solutions of 10^{-3} M and more dilute solutions were prepared before every use in order to avoid the aging process of the solution.

The mercury used in the dropping mercury electrode was obtained from Merck. Contaminated mercury was cleaned by passing it successively through dilute HNO_3 (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. The collected mercury was dried between sheets of filter paper. Before use, a DPP polarogram of this mercury was recorded in order to confirm the absence of impurities.

Nitrogen gas (99.999%) was used in order to expel the oxygen present in the solution. Cr(II) solution (containing mercury-covered zinc granules) was used in gas washing bottles to reduce any trace oxygen in nitrogen gas.

A 1.0 M HAc/Ac^- buffer was prepared by adding 6.0 g of NaOH, washed with distilled water in order to remove the carbonate formed, into 57 mL of 1.0 M HAc and diluting it into 1.0 L.

Preparation of Sn(II) and Sn(IV) solutions

Since speciation studies were made in both acidic and basic solutions, stock Sn(II) and Sn(IV) solutions were prepared accordingly.

Preparation of 0.1 M Sn(II) solutions (for acidic work): 0.56g of $SnCl_2.2H_2O$ was dissolved in 25 mL of 3.0 M HCl while heating. To protect from air oxidation, it was prepared daily.

Since 10^{-2} and 10^{-3} M solutions of Sn(II) were easily oxidized, these solutions were prepared from the 0.1 M solution by dilution with 1 M HCl prior to each experiment.

Preparation of 0.1 M Sn(IV) solution (for acidic work): It was prepared by oxidation of Sn(II) using Na_2O_2. For this purpose, 1.0 g of Na_2O_2 was added to 25 mL of 0.1 M Sn(II) solution (in 3.0 M HCl) and boiled for 15 min. The final solution volume was increased to 25 mL by adding water.

Preparation of 0.1 M Sn(II) solution (for basic work): 0.56 g of $SnCl_2.2H_2O$ was dissolved in 25 mL of 2.0 M NaOH.

To protect from air oxidation, 10^{-2} and 10^{-3} M Sn(II) solutions were prepared prior to each measurement. A Jones reductor was used in gas-washing bottles throughout the experiments in order to protect Sn(II) from oxidation with the oxygen that might have been present in nitrogen.

Preparation of 0.1 M Sn(IV) solution (for basic work): 0.25 g of Na_2O_2 was added to 25 mL of 0.1 M Sn(II), prepared in a 2.0 M NaOH solution, and boiled for about 30 min. The stannite (SnO_2^{2-}) form was turned into the stannate (SnO_3^{2-}) form after this procedure. The excess Na_2O_2 was expelled by boiling. The final solution was increased to 25 mL by adding water.

Preparation of canned tomato sauce sample

To a 2.0 g of canned tomato sauce, 20 mL of 1.0 M NaOH was added and boiled for about 30 min. It was sieved through filter paper after it cooled. Residues on filter paper were washed down several times. The filtrate obtained was 10 mL.

Results and discussion

The chemical forms of tin solutions

Solutions of Sn(II) and Sn(IV) may be present in various forms with different pH values. Thus, their chemical forms at various pH values have to be known.

Sn(II) chloride can dissolve in less than its own mass of water without apparent decomposition, but as the solution is diluted, hydrolysis occurs to form an insoluble basic salt. Equation 1.[29]

$SnCl_2(aq) + H_2O(l) \leftrightarrow Sn(OH)Cl(s) + HCl(aq)$ (Eq. 1)

According to Eq. 1 above, HCl has to be added in order to shift the reaction to the left.

Sn(II) is in the hydroxide form at pH 2-11, as given below in Eq. 2.

$SnCl_2 + 2\,OH^- \rightarrow Sn(OH)_2 + 2\,Cl^-$ (Eq. 2)

At a pH higher than 11, it will be in the stannite form, SnO_2^{2-}, Eq. 3.

$SnCl_2 + 4\,OH^- \leftrightarrow SnO_2^{2-} + 2\,Cl^- + 2H_2O$ (Eq. 3)

Since Sn(II) will be in the precipitate form between pH values of 2-11, Sn(II) solutions have to be prepared at pH values higher than 11. Thus, for basic solutions, Sn(II) is prepared in 2.0 M NaOH.

Sn(IV) will be in the hydroxide form in the pH range of 1-10, Eq. 4.

$SnCl_4 + 4\ OH^- \rightarrow Sn(OH)_4 + 4\ Cl^-$ (Eq. 4)

At a pH higher than 10, it will be in the stannate (SnO_3^{2-}) form, Eq. 5.[29]

$SnCl_4 + 6\ OH^- \leftrightarrow SnO_3^{=} + 4\ Cl^- + 3\ H_2O$ (Eq. 5)

Selection of the most suitable medium for the speciation of tin

In order to find a suitable electrolyte medium, polarograms of Sn(II) and Sn(IV) solutions were taken in 0.1, 0.2, and 0.5 M HCl; in 1 M acetate buffer (pH 4.3, pH 4.8), in 0.5 M NaOH, and in 0.1 M NaOH containing 0.1 M KNO_3.

In the 0.1, 0.2, and 0.5 M HCl media, while 1.0×10^{-5} M Sn(II) had a large (50 mm) and sharp peak at about -0.45 V, 1.0×10^{-5} M Sn(IV) had a small peak (6-7 mm) at -0.44 V in 0.2 M HCl. Because of overlapping peaks, this medium (HCl) is not suitable for the speciation of tin compounds. However, this medium can be used for the determination of Sn(II) in the absence of Sn(IV), because of the sharp and large peak (Table 1).

In 1.0 M HAc/Ac^- buffer (pH 4.3, pH 4.8), while 1.0×10^{-5} M Sn(II) had small and broad peaks at -0.14, -0.49, and -1.03 V, Sn(IV) had no peak, not even at a 6.0×10^{-4} M concentration. This medium seems to not be suitable for the determination of lower concentrations.

In a 0.5 M NaOH medium, 1.0×10^{-5} M Sn(II) had sharp peaks at -0.80 and -1.18 V, which were about 15 mm. On the other hand, 1.0×10^{-4} M Sn(IV) had peaks at -0.92 and -1.5 V that were small and broad (Table 1).

In 0.1 M NaOH containing 0.1 M KNO_3, the peaks of 1.0×10^{-5} M Sn(II) at -0.74 and -1.17 V were sharp and 25 mm. In this medium, even at 1.0×10^{-4} M concentrations, Sn(IV) had no peak. Only when the concentration of Sn(IV) was 4.0×10^{-4} M did a small and broad peak appear at -0.92 V (Table 1).

Both NaOH solutions, with and without KNO_3, can be used for the speciation of Sn(II) and Sn(IV) compounds. However, since Sn(II) peaks in NaOH containing KNO_3 were larger than those in the solution without KNO_3, this medium can be used for the determination of Sn(II) in the presence of Sn(IV). In this medium, Sn(IV) can be observed only when its concentration is higher than 4.0×10^{-4} M. Thus, for speciation purposes, in the case of lower concentrations of Sn(IV), it has to be reduced into Sn(II) and then determined.

Determination of Sn(II)

In a 0.1 M NaOH + 0.1 M KNO_3 medium, the oxidation peak of Sn(II) at -0.74 V and the reduction peak at -1.17 V[30] responded well to standard additions (Figure 1). In all further measurements, the peak at -1.17 V was used, since, as will be shown, the peaks of cadmium and lead appeared at about -0.74 V. Thus, in the presence of these ions, overlap will occur and the determination will not be correct. In this medium, 1.0×10^{-5} M Sn(II) could be determined as $(1.03 \pm 0.09) \times 10^{-5}$ M with a 90% CI (N = 3). The quantification limit was 1.1×10^{-6} M and the detection limit was 5.5×10^{-7} M.

Table 1. Polarographic behavior of Sn(II) and Sn(IV) in various electrolytes.

Medium	Ion	Peak potential E_{peak} (V)	Peak height* (mm)	Peak shape
0.1 M HCl	1×10^{-5} M Sn (II)	-0.43	54	Sharp
0.2 M HCl	1×10^{-5} M Sn(II)	-0.45	54	Sharp
	1×10^{-4} M Sn(IV)	-0.44	69	Sharp
0.5 M HCl	1×10^{-5} M Sn(II)	-0.47	43	Sharp
1 M HAc/Ac$^-$ (pH = 4.3)	1×10^{-5} M Sn(II)	-0.14/-0.49/-1.03	-/10/-	Broad/sharp/broad
	1×10^{-4} M Sn(IV)	No peak	No peak	No peak
	6×10^{-4} M Sn(IV)	No peak	No peak	No peak
1 M HAc/Ac$^-$ (pH = 4.8)	1×10^{-5} M Sn(II)	-0.15/-0.54/-1.03	-/4/-	Broad/broad/broad
	1×10^{-4} M Sn(IV)	No peak	No peak	No peak
	6×10^{-4} M Sn(IV)	No peak	No peak	No peak
0.5 M NaOH	1×10^{-5} M Sn(II)	-0.80/-1.18	16/13	Sharp/sharp
	1×10^{-4} M Sn(IV)	-0.92/-1.5	1/4	Broad/broad
0.1 M NaOH + 0.1 M KNO_3	1×10^{-5} M Sn(II)	-0.74/-1.17	25/25	Sharp/sharp
	1×10^{-4} M Sn(IV)	No peak	No peak	No peak
	4×10^{-4} M Sn(IV)	-0.92	5	Broad

* All peak heights are given under the same conditions.

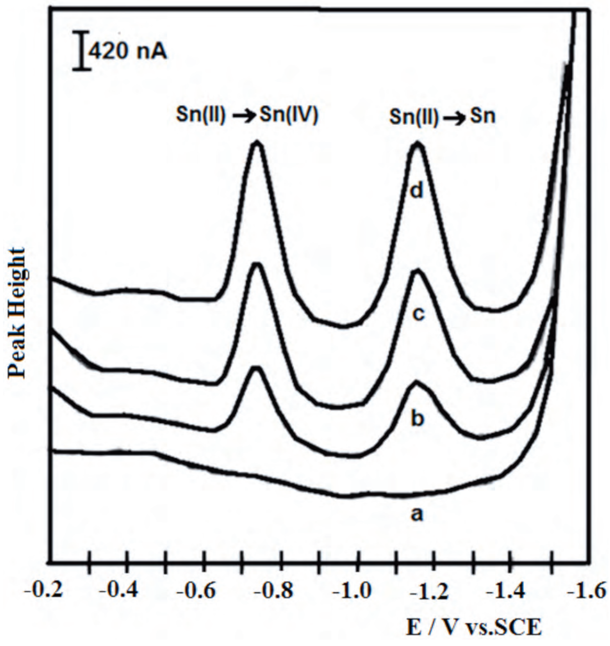

Figure 1. Determination of 1.0×10^{-5} M Sn(II) in 0.1 M NaOH + 0.1 M KNO_3 medium. (a) 10 mL of 0.1 M NaOH + 0.1 M KNO_3. (b) a + 0.1 mL of 1.0×10^{-3} M Sn(II). (c) b + 0.1 mL of 1.0×10^{-3} M Sn(II). (d) c + 0.1 mL of 1.0×10^{-3} M Sn(II).

Determination of Sn(IV)

As was shown, the most suitable electrolytes for speciation were 0.5 M NaOH and 0.1M NaOH + 0.1 M KNO_3. Although in these media there was no overlap for Sn(II) and Sn(IV), the peak for Sn(IV) was small, which could not be used for lower concentrations. Thus, it was decided to determine it after it was reduced to Sn(II). In this work, we used $NaBH_4$ (borohydride) for the reduction. For its determination, 0.1 M NaOH + 0.1 M KNO_3 was taken as the electrolyte, since the Sn(II) peak was largest in this medium.

According to the literature,[31] when Sn(IV) solution was boiled with $NaBH_4$ in 1.0 M NaOH, it was reduced quantitatively into Sn(II). The reduction was not quantitative in 5.0 M NaOH. On the other hand, when 0.2 M or lower concentrations of NaOH were used, Sn(IV) was reduced into metallic tin.[31]

Then 10 mL of 0.1 M $NaBH_4$ (in 1.0 M NaOH) was taken and nitrogen gas was passed for 10 min. After that 0.1 mL of 0.1 M Sn(IV) was added and boiled for about 20 min. According to our previous studies, 15 min of boiling was not sufficient for the reduction. Here the $NaBH_4$ present was 100 times larger in concentration than Sn(IV). From this solution, 0.3 mL was taken and added into 10 mL of 0.1 M NaOH + 0.1 M KNO_3 in the polarographic cell. The polarogram of the reduced Sn(IV) sample is given together with the polarograms of standard additions in Figure 2. It was possible to determine 1.0×10^{-5} M Sn(IV) after reduction as $(9.8 \pm 0.8) \times 10^{-6}$ M, 90% CI (N = 4). As a result, one can say that Sn(IV) can be reduced with high efficiency under the given conditions. The quantification limit was 2.5×10^{-6} M and the detection limit was 8.2×10^{-7} M.

Determination of Sn(II) and Sn(IV) in a synthetic sample

First, the Sn(II) present was determined by adding 0.1 mL of sample solution, containing 10^{-3} M Sn(II) + 10^{-3} M Sn(IV), into a polarographic cell containing 10 mL of 0.1 M NaOH + 0.1 M KNO_3. Two peaks, at -0.74 and -1.17 V, were observed, both of which responded well to standard additions (Figure 3). In this medium, 1.0×10^{-5} M Sn(II) could be determined as 0.94×10^{-5} M using both of the peaks.

For the determination of Sn(IV), 1 mL of 0.1 M $NaBH_4$ was added to 1 mL of synthetic sample, and by boiling for about 20 min, its volume was decreased to 1 mL. From this solution, 0.1 mL was taken, and by standard addition, the total quantity of 2.0×10^{-5} M Sn(II) present (this value includes Sn(IV) after reduction) was determined as 1.9×10^{-5} M. For the determination of Sn(IV), the quantity of Sn(II) was subtracted from the total tin, and 1.0×10^{-5} M Sn(IV) was found as 0.96×10^{-5} M.

Interference studies

The interference effect of the most common ions, Fe(III), Cu(II), Pb(II), Cd(II), and Zn(II), were investigated from 2 points of view:

1. There may be a peak overlap with Sn(II).
2. These ions may oxidize Sn(II).

a) The peak potentials of these ions were determined in 0.1 M NaOH + 0.1 M KNO_3 medium, and it was found that the peak of Sn(II) at -0.74 V may overlap with the peaks of Pb and Cd. However, the peak at -1.17 V had no overlap with the peaks of the mentioned ions. Thus, this peak at -1.17 V was chosen for the determination of Sn(II).

b) Standard electrode potentials of ions.

The standard reduction potential of Sn(IV) is 0.16 V. According to standard electrode potentials, only Cu(II) (0.34 V) and Fe(III) (0.77 V) may oxidize Sn(II) to Sn(IV).When iron and copper ions were added into a solution containing Sn(II), it was observed that the Sn(II) peak decreased (oxidized). In a sample solution containing only Sn(II) and these ions, there would be no problem, since the Sn(II) present after the reaction would be determined.

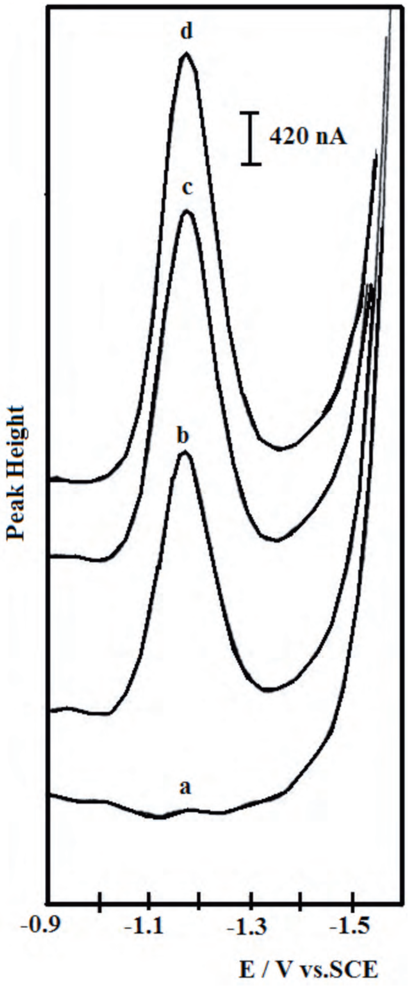

Figure 2. Determination of Sn(IV) after reduction into Sn(II). (a) 10 mL of 0.1 M NaOH + 0.1 M KNO$_3$. (b) a + 0.3 mL of reduced Sn(IV) sample. (c) b + 0.1 mL of 1.0 × 10^{-3} M Sn(II). (d) c + 0.1 mL of 1.0 × 10^{-3} M Sn(II). Sample: 0.1 M BH$_4^-$ + 10^{-3} M Sn(IV).

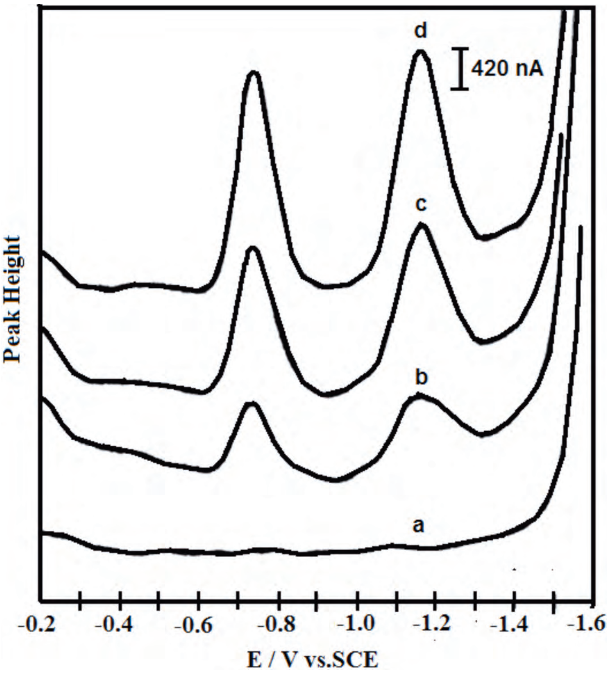

Figure 3. Determination of 1 × 10^{-5} M Sn(II) in a synthetic sample containing Sn(IV). (a) 10 mL of 0.1 M NaOH + 0.1 M KNO$_3$. (b) a + 0.1 mL of synthetic sample. (c) b + 0.1 mL of 1.0 × 10^{-3} M Sn(II). (d) c + 0.1 mL of 1.0 × 10^{-3} M Sn(II). Synthetic sample: 10^{-3} M Sn(II) + 10^{-3} M Sn(IV).

On the other hand, in case of Sn(IV) determination, it must be reduced to Sn(II) first and then determined from the Sn(II) peak. However, in the presence of Fe(III) and Cu(II), the Sn(II) formed will be oxidized by these ions and the Sn(IV) cannot be determined correctly. This interference effect can be solved by the addition of $NaBH_4$, which will reduce both of these ions so that they cannot oxidize Sn(II).

In order to find out the quantity of $NaBH_4$ needed for the reduction of these ions, a synthetic sample containing Fe(III), Cu(II), Pb(II), Cd(II), and Zn(II), each at 1.0×10^{-3} M, and Sn(II) in a 2.0×10^{-3} M concentration (1.0 M NaOH) was prepared (final volume, 10 mL). After mixing, it was left to wait for about 1 h. To 1 mL of this sample, 2 mL of 0.1 M $NaBH_4$ (100 times larger than Sn(II) in the sample) was added and boiled for 30 min. The final volume became 1.0 mL. From this solution, 0.1 mL was taken and added to a polarographic cell. In the polarogram, a peak of Pb(II) and Cd(II) appeared at about -0.70 V, and a peak for Fe(III) appeared at about -0.90 V. No peak of Sn(II) at -1.17 V could be observed, which is an indication that the Cu(II) and Fe(III) present in the sample oxidized the Sn(II). That is, the quantity of $NaBH_4$ was not enough to reduce Fe and Cu. In other studies, samples containing all ions in 10^{-3} M concentrations were investigated with various quantities of $NaBH_4$. After working with 0.015, 0.15, 0.30, and 0.45 g of $NaBH_4$, it was found that 0.45 g (6000 times larger than the concentration of total tin) was suitable for the speciation purposes in the presence of Fe(III) and Cu(II). That much addition also protects from the air oxidation of Sn(II) during the procedure. In the case of a natural compound, the quantity of borohydride can be found by trial. It was found that, using this procedure, tin content could be determined with high accuracy.

Total tin quantity in a synthetic sample in the presence of interfering ions

A synthetic sample containing 1.0×10^{-3} M Fe(III), Cu(II), Pb(II), Sn(II), and Sn(IV) ions was prepared in 1.0 M NaOH. It was left to sit for about 20 min for the reaction to take place. To 2 mL of this solution, 0.45g of $NaBH_4$ was added, and it was boiled for about 30 min, and then the volume was adjusted to 1 mL.

After the reduction process, a 0.1 mL sample was taken and added to a polarographic cell containing 10 mL of 0.1 M KNO_3 and 0.1 M NaOH. A peak for Sn(II) was observed at -1.17 V, and the quantity of Sn(II) was determined with the standard addition method (Figure 4). The result for 2.0×10^{-5} M Sn(II) in a synthetic sample in the presence of Fe(III), Cu(II), and Pb(II) (N = 6) was found to be $(2.05 \pm 0.16) \times 10^{-5}$ (Table 2).

Thus, it can be concluded that in natural compounds, Sn(II) and Sn(IV) can be determined with high accuracy in the presence of most common ions, such as Fe(III), Cu(II), Pb(II), and Cd(II).

Application to canned tomato sauce, determination of Sn(II) and Sn(IV)

For the determination of Sn(II), the sample was prepared as described in section reagents. From 10 mL of sample solution, 0.4 mL was taken and added to a polarographic cell containing 10 mL of 0.1 M KNO_3 and 0.1 M NaOH. No peak at -1.17 V was observed, indicating the absence of Sn(II). When standard Sn(II) was added to this tomato sauce medium, 2.0×10^{-5} M Sn(II) could be determined as 1.9×10^{-5} M. This shows that in this medium, Sn(II) can be determined with high accuracy (Figure 5).

For the determination of Sn(IV) in canned tomato sauce, 0.45 g of $NaBH_4$ was added to 10 mL of sample solution, prepared as described in reagents section, and boiled for about 30 min. The volume was adjusted to 10 mL, and 0.4 mL was taken and added to a cell containing 0.1 M KNO_3 and 0.1 M NaOH. A sharp peak at about -1.21 V was observed, which increased with the standard addition of Sn(II) solution (Figure 6). The quantity of tin found in this canned tomato sauce was 306 ± 35 μg/g for 3 independent determinations of the same canned tomato sauce (Table 3). In our former study, total tin content was found to be 26 μg/g.[27] As can be seen, there was more than 10 times the difference between the 2 canned tomato sauces. There might be several reasons for this. They were from different companies, one sample was taken about 15 years ago, and the last sample was taken especially from the walls of the can.

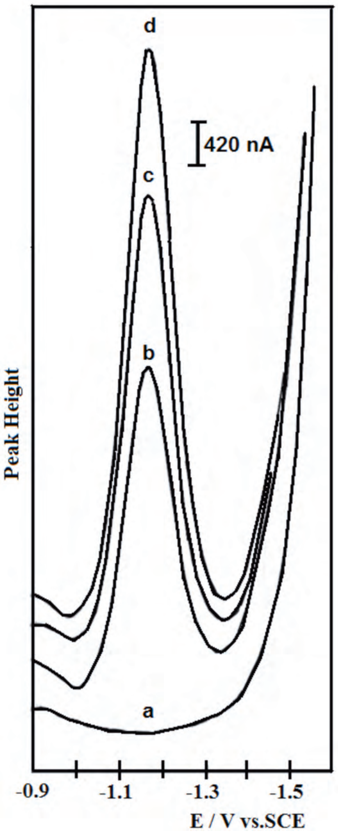

Figure 4. Determination of total tin in a synthetic sample containing Fe(III), Cu(II), Pb(II), Sn(II), and Sn(IV) in a 1.0×10^{-3} M concentration. (a) 10 mL of 0.1 M NaOH + 0.1 M KNO_3. (b) a + 0.1 mL of reduced synthetic sample. (c) b + 0.1 mL of 1.0×10^{-3} M Sn(II). (d) c + 0.1 mL of 1.0×10^{-3} M Sn(II). Synthetic sample: 1mL of Fe(III), Cu(II), Pb(II), Sn(II), and Sn(IV), each 1.0×10^{-3} M, + 0.45 g of $NaBH_4$.

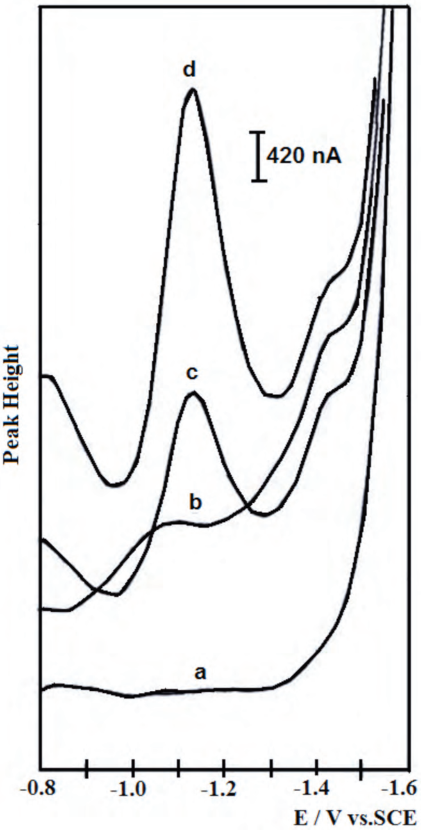

Figure 5. Determination of Sn(II) in canned tomato sauce. (a) 10 mL of 0.1 M NaOH + 0.1 M KNO_3. (b) a + 0.4 mL of tomato sauce sample. (c) b + 0.2 mL of 1.0×10^{-3} M Sn(II). (d) c + 0.2 mL of 1.0×10^{-3} M Sn(II). Sample: 2.0 g of tomato sauce + 20 mL of 1.0 M NaOH. After boiling and filtering, the final volume was 10 mL.

Table 2. Determination of total tin in a reduced sample containing Fe, Cu, Pb, Sn(II), and Sn(IV) in a 0.1 M NaOH + 0.1 M KNO_3 medium (90% CI, N = 6).

Medium in polarographic cell	Total tin content in cell (M)	Total tin content determined (M)	$\overline{X}$	s	$\overline{X} \pm ts/\sqrt{N}$
1×10^{-5} M (Fe(III), Cu(II), Pb(II), Sn(II), Sn(IV))	2.0×10^{-5}	1.80×10^{-5} 1.80×10^{-5} 2.10×10^{-5} 2.19×10^{-5} 2.19×10^{-5} 2.20×10^{-5}	2.05×10^{-5}	0.19×10^{-5}	$(2.05 \pm 0.16) \times 10^{-5}$

$\overline{X}$:arithmetic mean, s: standard deviation, t: Student's t-test.

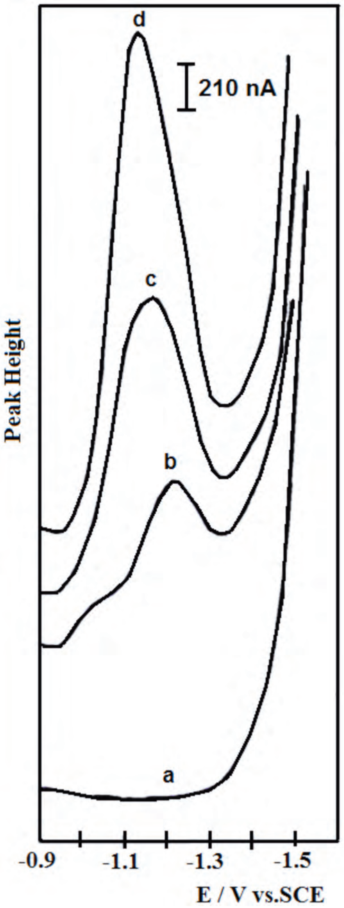

Figure 6. Determination of total tin in reduced tomato sauce. (a) 10 mL of 0.1 M NaOH + 0.1 M KNO_3. (b) a + 0.4 mL of reduced tomato sauce sample. (c) b + 0.2 mL of 1.0 × 10^{-3} M Sn(II). (d) c + 0.2 mL of 1.0 × 10^{-3} M Sn(II). Sample: 2.0 g of tomato sauce + 20 mL of 1.0 M NaOH. After boiling and filtering, the final volume was 10 mL; to this, 0.45 g of $NaBH_4$ was added and boiled, and the final volume was 10 mL.

Table 3. Total tin content in canned tomato sauce (90% CI, N = 3).

Medium in polarographic cell	Tomato sauce (g)	Total tin determined (μg/g	$\overline{X}$	s	$\overline{X}\pm$ ts/$\sqrt{N}$
0.1M NaOH + 0.1 M KNO_3	2.0	300 290 330	306	21	306 ± 35

$\overline{X}$: arithmetic mean, s: standard deviation, t: Student's t.

Conclusions

In most of the previous studies, methods have been proposed for total tin determination. In this work, a new DP polarographic method was established for the determination of Sn(II) and Sn(IV) in the same sample. It was found that 0.1 M NaOH containing 0.1 M KNO_3 was the most convenient electrolyte for speciation of Sn(II) and Sn(IV).

Sn(II) was determined from the peak at -1.17 V; Sn(IV), on the other hand, was determined after reduction into Sn(II) with $NaBH_4$. It was shown that this reduction was quantitative in 1M NaOH. The quantification limits found were 1.1×10^{-6} M and 2.5×10^{-6} M, and the detection limits were 5.5×10^{-7} M and 8.2×10^{-7} M, for Sn(II) and Sn(IV), respectively.

The interference effect of most common ions, such as Fe(III), Cu(II), Pb(II), Cd(II), and Zn(II), were investigated. It was found that while there was no peak overlap with these ions, only Fe(III) and Cu(II) could oxidize Sn(II). In this case, when Sn(IV) is reduced with $NaBH_4$, the Sn(II) formed will be oxidized by Fe(III) and Cu(II), and this will create an error in the determination of Sn(IV). However, the addition of $NaBH_4$ will reduce both of these ions so that they can no longer oxidize Sn(II). It was shown that Sn(II) and Sn(IV) could be determined with high accuracy in the presence of these ions with the use of $NaBH_4$.

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