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Differential Pulse Polarographic Behavior of Selenite and Its Application to Determination of Tin in Canned Food

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The polarographic reduction of tin gives rise to an additional peak at more positive potentials than tin in the presence of selenite. It is found that when the selenite concentration exceeded the tin concentration, only one peak for tin was observed, enabling the determination of both these ions. A procedure for the direct determination of trace amounts of tin by the addition of selenite is described. It was possible to determine trace amounts of tin and selenium using this peak. Tin and selenium in a synthetic sample at 5×10^{-6} M Sn(II) and 2.5×10^{-6} M Se(IV) concentrations could be determined with –6.0% and –8.0% relative errors, respectively. This procedure was applied to canned corn, and 5.95 ± 0.54 μg/g tin could be determined with a 9.1% relative standard deviation.

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Tin is known as an essential trace element in various metabolic processes in humans, animals and plants. It may be introduced into the human environment either as inorganic tin or as organo-tin compounds, through they are used as fungicides in crops, in food packaging, in some veterinary formulations, in marine anti-fouling paints on the hulls of ships, in wood preservation, as a stabilizer for poly(vinyl chloride) and as electrochemical catalysts.[1] Canned food is known to contain high concentrations of tin. This is particularly true for acid food stuffs, such as canned tomato sauce and fruit juices. Although tin is not a highly toxic element, high concentrations of tin, on the order of 0.1 and 1.0 g l^{-1}, affects the flavor of the juice and can also cause diarrhoea. Consequently, there has been growing concern about the significance and toxicity of this element; this fact encouraged the development of methods for its determination in various sample materials. The most commonly used methods include atomic absorption spectrometry (AAS) with hydride generation[2] and electrochemical analysis[1,3,4] based on polarography or stripping voltammetry. Of these, the electrochemical methods are capable of better sensitivity and selectivity.

It is known that selenium is also present next to many trace elements; according to some former electroanalytical studies,[5-7] selenium interferes with the determination of these elements. During our DPP studies, we observed that selenite and some ions, such as copper, lead and cadmium, diminished the peak of each other. Because of this interference, care must be taken in the polarographic determination of the mentioned ions. A method was suggested for the correct determination of these ions when they are in the same medium. Selenium and lead in blood samples were determined by the applying this method.[8]

During our polarographic studies for the determination of tin, strong interference was observed when selenium was present in the same solution, which made their correct determination impossible. This fact is very important, since both of these ions may be present with great probability in the same sample. However, our further studies have shown that this interference can be used for the trace determination of tin using the new peak formed in the presence of both of these ions. No work has been found concerning this interference. The aim of our present work is to improve the method for determining tin and selenium, and to apply it to canned foods.

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Experimental

Apparatus

A PAR (Model 174 A) polarographic analyzer system, equipped with a PAR mercury drop timer, was used. The drop time of a mercury electrode was in the range 2 – 3 s (2.37 mg s^{-1}). A Kalusek electrolytic cell with reference saturated calomel electrode (SCE), separated by a liquid junction, was used in the three-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^{-1} and a pulse amplitude of 50 mV.

Reagents

All of the reagents used were of analytical-reagent grade (pro-analysi). Triply distilled water was used in the preparation of all solutions. The mercury used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter-paper. Before use, a polarogram of this mercury was recorded in order to confirm the absence of impurities.

A 0.1 M stock standard selenite solution was prepared by dissolving 1.1977 g of SeO_2 in 100 ml of hot water. A 0.1 M stock standard tin solution was prepared by dissolving 2.2663 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of a 6.0 M HCl solution, and 1.0×10^{-3} M and 1.0×10^{-4} M working solutions were prepared by daily dilution.

A Britton–Robinson (B-R) buffer solution was prepared in such a way that 2.3 ml of glacial acetic acid, 2.7 ml of

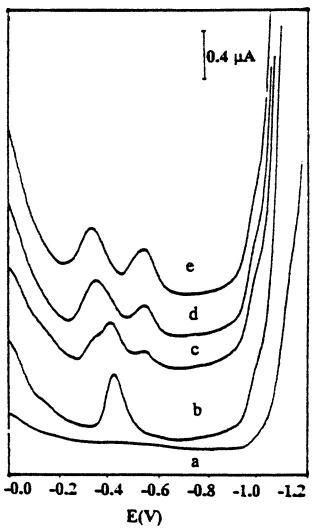


Fig. 1 Effect of selenite additions on tin(II) peak (pH = 2.2). (a) 10.0 ml B-R buffer solution (pH = 2.2), (b) 5×10^{-6} M Sn(II), (c) b+ 25 μl 1×10^{-3} M Se(IV), (d) c + 25 μl 1×10^{-3} M Se(IV), (e) d + 25 μl 1×10^{-3} M Se(IV).

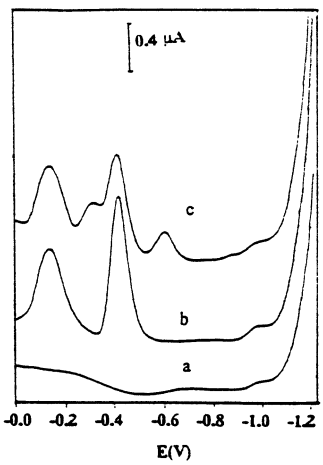


Fig. 2 Effect of selenite additions on tin(II) peak (pH = 2.9)(tin has two peaks). (a) 10.0 ml B-R buffer solution (pH = 2.9), (b) 1.5×10^{-5} M Sn(II), (c) b + 50 μl 1.0×10^{-3} M Se(IV).

phosphoric acid (85%) and 2.4720 g of boric acid dissolved by dilution with water to 1.0 L; 50.0 ml portions of this solution were taken, and the pH was adjusted to between 2 and 3 by the addition of an appropriate amount of 2.0 M NaOH.

Digestion of the canned corn

Some of the canned corn was dried for 48 h in an oven at 120˚C to remove the water content and to obtain a constant weight of 2.0 g of dried sample; 10.0 ml of HNO_3:$HClO_4$ (1:1) was transferred into a 100 ml long-necked glass flask. This mixture was left standing for about 30.0 min, then heated for 2 h at 150˚C using a heating-mantle. After evaporating half of the mixture and cooling the flask for about 5 min, 3.0 ml of HNO_3:$HClO_4$ (1:1) was added and re-evaporated until white fumes were nearly finished. For complete digestion, 2.0 ml of H_2SO_4 was added and evaporated to nearly 1.0 ml of the final volume; then, 2.0 ml of 35% H_2O_2 was added and boiled. In this way, all of the tin was converted to tin(II). The digested sample was transferred into a 10.0 ml calibrated flask, and made up to the mark with triply distilled water. This was kept in a Teflon bottle.

Voltammetric determination

A 10.0 ml volume of acid solutions (0.1 M HCl, 0.1 M HNO_3) or buffer solutions (B-R and acetic acid-acetate) in a polarographic cell was de-aerated by a stream of nitrogen gas (99.999%) for 3.0 min; then, according to the need, 50 – 100 μl 1.0×10^{-3} M Se(IV) and Sn(II) solutions were added. Polarograms were taken by scanning the potential in the negative potential direction from 0.0 V to –1.5 V at a scan rate of 5 mV s^{-1} and a pulse amplitude of 50 mV.

For application to real samples, 5.0 ml of a digested sample was put into a polarographic cell and diluted up to 10.0 ml with 0.1 M HCl; the above voltammetric procedure was then applied.

Results and Discussion

During the polarographic determination of tin, in the presence of selenium, it has been observed that when selenite or tin solution was added for the standard addition procedure, the peak of one of these ions was diminished. This behavior, in fact, would cause wrong results in the determination of both of these ions. To investigate this situation, solutions of various compositions were prepared and their DPP peaks were observed under different conditions. New determination methods for tin and selenium ions have been recommended to obtain accurate results in spite of the interference between these ions.

Effect of selenite additions on the tin peak

Tin(II) has either one or two peaks, depending on the pH of the solution. In 0.1 M HCl and 0.1 M HNO_3, tin(II) shows one peak at about –0.4 V which corresponds to its reduction. At pH values higher than 2, it has two peaks, one for the oxidation of tin(II) to tin(IV) at about –0.15 V and the second at about –0.5 V for its reduction. Because of the poor reversibility of the first one, the second peak is being used mostly for its determination. The selenite ion has a peak changing from –0.54 V to –0.65 V between pH values of 1 to 4.

When a small amount of selenite was added to a solution containing tin(II), in pH = 2.2 buffer, a new peak at –0.32 V appeared, and the peak for tin(II) at –0.44 V decreased, a small peak for selenite became observable, as can be seen in Fig. 1. The height of the new peak at –0.32 V increased with the continuous addition of selenite and the peak for tin decreased. When the peak for tin(II) disappeared, the height of the new peak became constant. The same behavior was observed in 0.1 M HNO_3, 0.1 M HCl, and pH 2 to 4 acetate and B-R buffer solutions. Since Sn(II) has two peaks at pH = 2.9, the effect of Se(IV) at this pH also has to be controlled. As can be seen in Fig. 2 , a solution of 1.5×10^{-5} M Sn(II) showed two peaks at –0.14 and at –0.44 V in a pH = 2.9 B-R buffer. When 5×10^{-6} M Se(IV) was added to this solution, a new peak at –0.35 V appeared, the peak for tin decreased and a peak for selenium was observable.

Effect of tin(II) additions on the selenite peak

When a tin(II) solution was added to a selenite solution in 0.1 M HNO_3, the peak for selenite at about –0.57 V decreased, and again a new peak at –0.3 V appeared (this peak became constant by the continuous addition of tin(II) solution). The addition of selenite did not increase the new peak, since all tin was used by selenite (Fig. 3). That means there was no tin to react with

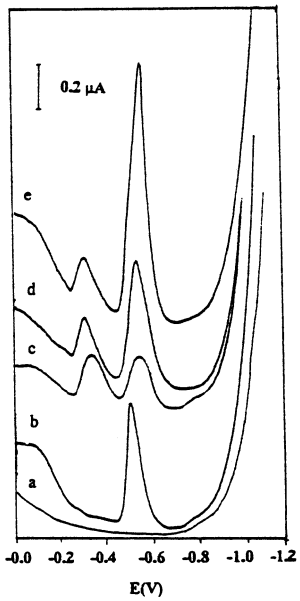


Fig. 3 Effect of tin(II) additions on selenite peak. (a) 10.0 ml 0.1 M HNO_3, (b) 5×10^{-6} M Se(IV), (c) b + 50 μl 1×10^{-3} M Sn(II), (d) c + 50 μl 1×10^{-3} M Se(IV), (e) d + 50 μl 1×10^{-3} M Se(IV).

selenite to form the new peak. Thus, the same results were obtained, although the initial solutions were different. This behavior was also observed for different electrolytes, such as HNO_3, HCl, B-R and acetate buffers, at different pH values of between 1 and 4.

Effect of pH on the peak potentials

The effects of pH on the tin and selenium peak potentials together with the new peak potentials are summarized in Table 1. The new peak, which was formed in the presence of tin and selenium, is represented as Sn-Se. The peak potential for selenium shifted to more negative potentials with increasing pH, as expected, (Table 1). The peak which was formed only when selenium(IV) and tin(II) were present together, always appeared at more positive potentials than that of tin(II) reduction. The peak potential of this new peak shifted to more negative potentials with increasing pH. As can be seen from Table 1, addition of EDTA shifted the reduction potential of tin(II) to more negative values.

The mechanism

Under polarographic conditions selenite is reduced on the mercury surface to elemental selenium at between 0.0 and –0.2 V. In the presence of tin, there is clearly a reaction between the reduced selenium and the tin ion, which decreases their peaks. This reaction should take place during the scanning. To check a chemical reaction between these two ions, a solution containing these ions was prepared and their polarograms were taken between certain time intervals. No reaction was observed in a 2 – 3 h period. Thus, the decrease in their peaks is not caused by a chemical reaction, it must be an electrochemical reaction.

As can be observed from Table 1, the new peak always appeared at more positive potentials than tin ion and its potential shifted with pH to more negative potentials, as was the case for tin(II) ion. Most probably, therefore, the reduction process in the new peak should contain the reduction of tin. There must be a process which makes the reduction of tin easier.

Table 1 Effect of the pH on peak potentials (V) of Sn(II), Se(IV) and Sn-Se

pH	Sn(II)	Se(IV)	Sn-Se
1.0 (0.1 M HCl)	–0.43	–0.54	–0.30
1.0 (0.1 M HNO_3)	–0.40	–0.54	–0.29
2.2 (B-R)	–0.44	–0.56	–0.32
2.9 (B-R)	–0.14/–0.44	–0.58	–0.35
2.9 (B-R, 2.5×10^{-4} M EDTA)	–0.14/–0.50	–0.57	–0.42
4.0 (0.5 M HAc/0.1 M Ac^-)	–0.15/–0.51	–0.65/–1.20	–0.40

Combining these results leads to the following mechanism:

$$6H^+ + SeO_3^{2-} + 4e^- \rightleftharpoons Se_{(ads)} + 3H_2O \quad (1)$$

$$Se_{(ads)} + Sn^{2+} + 2e^- \rightleftharpoons SnSe_{(ads)} \quad (2)$$

The peak at about –0.3 V was attributed to the formation of an intermetallic compound, which was formed from elemental selenium adsorbed on the electrode surface with the tin ion was reduced at the electrode. This peak was formed because of the reduction of tin ion. This reduction took place at more positive potentials than tin reduction. The formation of the intermetallic compound makes the reduction of tin(II) easier. The same kind of behavior was observed for copper, lead and cadmium in the presence of selenite in DPP studies[7] and also during ASV[5] and CSV[6,9] determinations of selenium in the presence of copper. This was explained by the formation of an intermetallic compound[7] in DPP, in ASV studies,[5] however, the new peak was found to be formed by reduction of the intermetallic compound.

Determination of tin in the presence of selenium

According to the above observed results, a correct determination of either tin or selenium will not be possible in the presence of the second ion. The presence of the second ion either decreased, or even annihilated, the next peak. Thus, none of them will have its own true peak height. Depending to the ratio of these two ions, the peaks and peak heights will change. Either selenium or tin may be in excess in the solution under investigation. For these two situations, two different determination methods have been proposed.

Samples containing excess selenite

As can be seen from Fig. 1, when the selenite concentration was larger than the tin concentration only one peak was observed for tin (Fig. 1-e), all tin was in the Sn-Se peak. On the other hand, when selenium was less than tin, two peaks were observed for tin (Fig. 1-c), one for tin (–0.4 V) and the second for Sn-Se (–0.3 V). A DP polarogram of 10.0 ml of 0.1 M HNO_3 containing 2×10^{-5} M Se(IV) and 5×10^{-6} M Sn(II) was taken as an example. As can be seen from Fig. 4b, two peaks were observed: the first at –0.3 V for Sn-Se and the second at –0.54 V for selenium. For the determination of the tin content in this sample, known amounts of tin solution were added. As can be seen in Fig. 4c – d, while the selenite peak decreased, the peak for Sn-Se at –0.3 V increased continuously by standard additions. From this increase the tin content can be calculated. The selenium content, on the other hand can be found from two peaks; that at –0.3 V is equal to the Sn present in this peak. On the other hand, the selenium present in the –0.54 V peak can be found by standard selenium additions. The total selenite content is the sum of the selenium present in both of these peaks. The above mentioned method was applied to two solutions in

Table 2 Determination of Sn(II) and Se(IV) in synthetic samples under different conditions

pH	Sn and Se in synthetic sample/M		Sn and Se found/M		Relative error, %	
	Sn(II)	Se(IV)	Sn(II)	Se(IV)	Sn(II)	Se(IV)
2.9 (B-R)[Ia]	5.0×10^{-6}	1.0×10^{-5}	5.2×10^{-6}	1.1×10^{-5}	+ 4.0	+ 10
2.2 (B-R)[IIa]	5.0×10^{-6}	2.5×10^{-6}	4.7×10^{-6}	2.3×10^{-6}	– 6.0	– 8.0
1.0 (HCl)[IIb]	2.0×10^{-5}	1.0×10^{-5}	1.9×10^{-5}	0.9×10^{-5}	– 5.0	– 10

Ia: Se(IV) in excess. IIa, IIb: Sn(II) in excess.

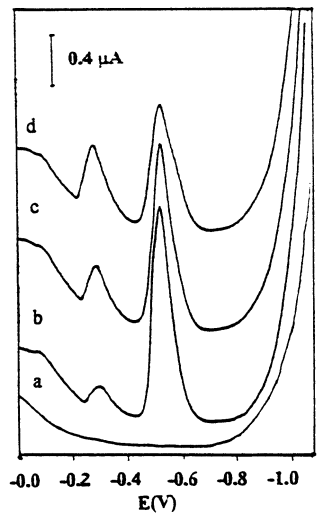


Fig. 4 DP polarogram of Se(IV) and Sn(II) with selenium in excess. (a) 10.0 ml 0.1 M HNO_3, (b) 2×10^{-5} M Se(IV) and 5.0×10^{-6} M Sn(II), (c) b+50 μl 1×10^{-3} M Sn(II), (d) c+50 μl 1×10^{-3} M Sn(II).

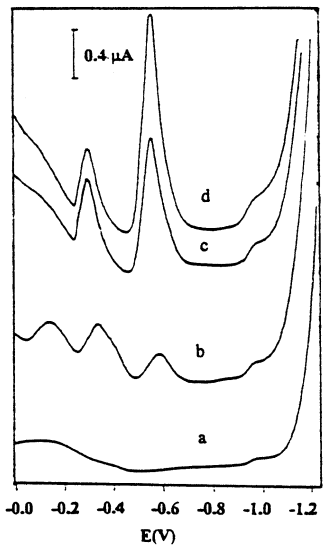


Fig. 5 DP polarogram of Sn(II) and Se(IV) with tin in excess. (a) 10.0 ml B-R buffer solution (pH = 2.9), (b) 1.5×10^{-5} M Sn(II) and 5.0×10^{-6} M Se(IV), (c) b+150 μl 1×10^{-3} M Se(IV), (d) c+50 μl 1×10^{-3} M Se(IV).

different pH and different media. For a solution containing 5×10^{-6} M Sn(II) and 1.0×10^{-5} M Se(IV), values of 5.2×10^{-6} M for Sn(II) and 1.1×10^{-5} M for Se(IV) were obtained with relative errors of +4% and +10% respectively. The results are given in Table 2 as Ia.

Samples containing excess tin

A DP polarogram of 10 ml of pH = 2.9 BR buffer solution containing 1.5×10^{-5} M Sn(II) and 5×10^{-6} M Se(IV) was taken. Since the tin concentration was larger than that of selenium, a peak for Sn-Se at –0.35 V, a shoulder for tin at the –0.44 V and a small peak for selenium were observed (Fig. 5b). Because of the overlap of the tin peaks, a known excess of selenite was added in order to bring all tin into Sn-Se phase. The selenite concentration can be taken as two times the tin concentration, the more dilute is the tin, the more concentrated selenium that can be used. Selenite addition can be made until all tin is shown with the new peak, no free tin peak; should be observable. By standard additions, both tin and selenium present could be determined. While selenium could be calculated from the increments of the peak at –0.56 V by standard selenium additions and from the peak at –0.32 V by standard tin additions, tin could only be determined from the peak at –0.32 V by the standard addition of tin. The selenium in the sample solution is equal to the difference between total selenite calculated and the added selenite. For a solution at pH = 2.2 (B-R buffer), containing 2.5×10^{-6} M Se(IV) and 5.0×10^{-6} M Sn(II), values of 2.3×10^{-6} M Se(IV) and 4.7×10^{-6} M Sn(II) were obtained with relative errors of –8% and –6% respectively. The results are given in Table 2 as IIa. The results obtained at pH = 1.0 (HCl) are given as IIb.

According to the above results, it is clear that if tin and selenium are present together, their determination is not possible by the direct standard addition procedure. The above mentioned corrections have to be applied depending to the composition of the solution.

Application to real samples

This method can be applied to real samples by using the Sn-Se peak which appeared at about –0.3 V, depending on pH. According to our former studies,[7] lead ion has also a Pb-Se peak in the presence of selenium at about –0.3 V, which would interfere with the Sn-Se peak. However, we have shown that in acetate buffer at about pH 4, because of complex formation, the Pb-Se peak disappears. Thus, in a sample containing lead, the determination of tin can be done safely at about pH 4, since the Sn-Se peak is still present at this pH.

Tin in canned corn

A 5.0 ml sample of digested canned corn is added into 5.0 ml of a 0.1 M HCl solution in a polarographic cell. After de-aeration of the solution, the DP polarogram is taken, starting from –0.2 V to –1.0 V. The polarogram had two overlapping peaks at –0.43 and at –0.58 V, as can be seen in Fig. 6. The tin peak appeared as expected at –0.43 V at this pH. By the addition of selenite ion, a peak at –0.32 V became observable, which must belong to Sn-Se peak, since it was shown to occur

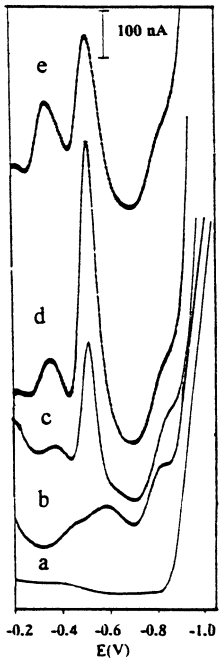


Fig. 6 DP polarogram of canned corn sample. (a) 5.0 ml 0.1 M HCl, (b) a+5.0 ml digested canned corn sample, (c) b+50 μl 1×10^{-3} M Se(IV), (d) c+50 μl 1×10^{-3} M Se(IV), (e) d+50 μl 1×10^{-3} M Sn(II).

at this potential (Table 1). Thus, a peak which was hidden as a shoulder first, could be observed as a peak by the addition of selenite. According to the preliminary experiments, when the selenite ion concentration was larger than the tin concentration, tin was quantitatively converted to Sn-Se. To reach this condition, once more, selenite was added (Fig. 6d). The tin content of the solution was determined by standard additions (Fig. 6e). The results obtained for four separately digested corn samples, taken from the same can, were 5.95 ± 0.54 μg/g Sn with a 9.1% relative standard deviation. In a former study using adsorptive stripping differential pulse voltammetric procedure,[10] the tin content of corn was found to be 1.4 ppm.

In polarographic determination, the peak of tin is not very sensitive to tin additions. However, by the addition of Se(IV) the new peak became more sensitive, and thus smaller concentrations of tin were possible to determine.

In summary, the described method provides a simple and direct procedure for the determination of trace amounts of tin and selenium, in spite of the interference between these ions. Since the new peak is pH dependent, the interference of different ions can be eliminated by simply changing the pH if there are overlapping peaks. The proposed method can be safely applied to many biological samples.

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