CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Determination of Tin by Anodic Stripping Voltammetry

Purpose

Unlike the anodic stripping voltammetry (ASV) determinations of lead, cadmium, and zinc, the determination of tin in aqueous media can be a challenging task. Tin can exist in aqueous solution in two oxidation states, Sn(II) (stannite) and Sn(IV) (stannate), the former being more stable at lower pH [1]. F1 shows the differential pulse stripping voltammogram (DPSV) of the two species. The anodic stripping peak current (ip) at approximately -450 mV is due to the oxidation of the tin amalgam to Sn(II). The peak at -130 mV corresponds to the oxidation of the Sn(II) ion to Sn(IV). (The ip of the stannate ion is always smaller than that of the stannite for anodic stripping voltammetry due to the diffusion of Sn(II) ions away from the electrode during the potential scan.)

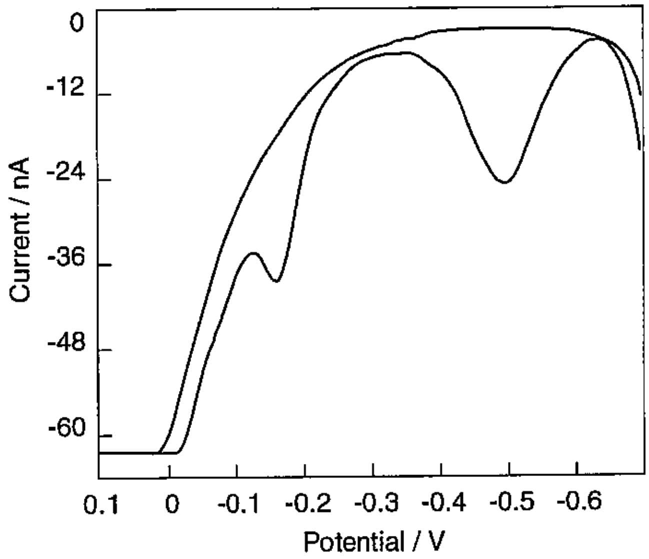

Figure 1. DPSV of solution containing Sn(II) and Sn(IV) species.

Hydrochloric acid is frequently used for tin determinations by ASV for two main reasons. First, the reduction of Sn(II) is irreversible in most non-chloride media. It has been found that the anodic stripping peak height (ip) for Sn(II) is directly proportional to the chloride concentration (up to 4 M) when HCl is used as the supporting electrolyte [2]. Secondly, the chloride ion suppresses the hydrolysis of the Sn(IV) species [3]. This reaction is detrimental because the hydrolysis product is electrochemically inert, and thus can introduce errors in the tin determination. Typically, rather high concentrations of HCl are used for tin determinations because even at lower chloride concentrations, the Sn(IV) species can gradually hydrolyze (a fine white precipitate can be seen after approximately 4 days when using a 0.12 M HCl solution).

However, by choosing HCl as the supporting electrolyte, another potential problem is encountered. The anodic stripping peak for Pb(II), a common contaminant, occurs at the same potential as Sn(II) and even a very small amount of lead can cause positive errors in the determination of Sn(II).

Method

There are a variety of ways to overcome the problem of lead contamination, including prior separation and flow or medium exchange procedures [4]. One of the most common and easiest approaches to tin determination in the presence of lead involves the complexation of the interfering metal before performing ASV. A solution of 1,10-phenanthroline (2.5x10-4 M) as a complexing agent in a supporting electrolyte of 0.4 M oxalic acid has been used to determine tin in canned food samples [5]. F2 shows the DPSV for 100 ppb Sn(II) solution and a subsequent addition of 100 ppb Pb(II) in a 0.12 M HCl solution. F3 shows the DPSV for similar concentrations in a solution of 1,10-phenanthroline/oxalic acid. (Note the separation of the lead and tin peaks due to the complexation of lead with phenanthroline.)

Procedure

The tin stock solution was prepared daily by dissolving 800 mg of tin wire (99.999%, Aldrich) in 50 mL 12 M HCl (Ultrex™II, J.T.Baker), diluting to 500 mL with deaerated D.I. water. An argon stream was used to blanket the solution during storage. The stock solution was used for tin additions in both the

HCl and the 1,10-phenanthroline (Baker) /oxalic acid (Mallinkrodt AR) solutions, which were also deaerated before use. Initially, Sn(II) predominated in the deaerated stock solution, as confirmed by a DPSV. Although Sn(II) is very stable in acidic media, dissolved oxygen can oxidize Sn(II) to Sn(IV) [6]. F2 illustrates the decreasing Sn(II) ip over a 60 minute period due to this oxidation.

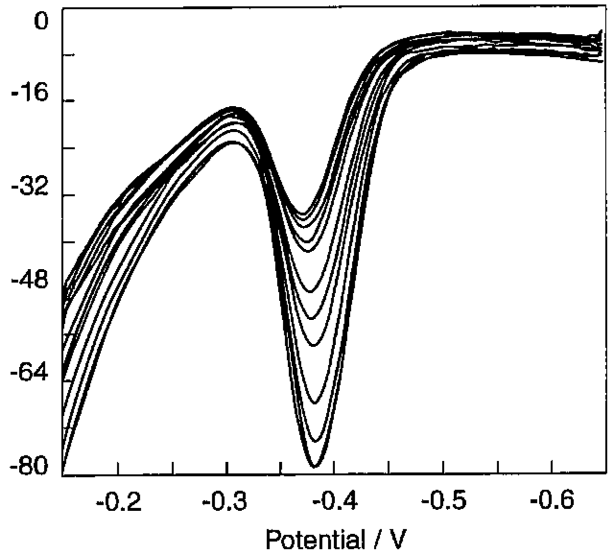

Figure 2. Overlay of voltammograms illustrating the decreasing Sn(II) ip over time due to reaction with O2.

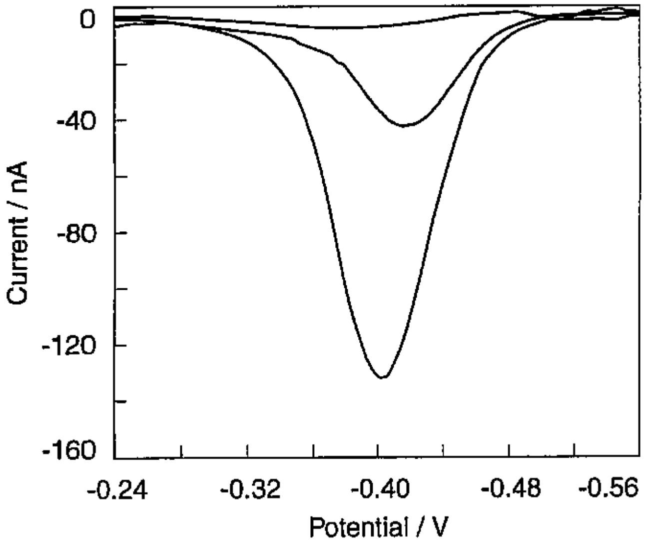

Figure 3. Overlay of Sn(II) voltammograms with and without Pb(II) interference in 0.12 M HCl.

All determinations and data manipulation were carried out using the BAS 100B/W Electrochemical Workstation using the DPSV technique. A Controlled Growth Mercury Electrode (CGME), in the SMDE mode, functioned as the working electrode, with a Ag/AgCl reference and a Pt wire auxiliary electrode. The experimental parameters are found in T1.

Initial E (mV)	-700
Final E (mV)	100
Scan Rate (mV/s)	20
Deposition Time (s)	60
Pulse Amplitude (mV)	50
Pulse Width (ms)	50
Pulse Period (ms)	2

Table 1. DPSV experimental parameters

Results and Discussion

In this investigation, the phenanthroline/oxalic acid medium was used to qualitatively check for lead contamination in aqueous samples while the HCl electrolyte was used for the quantitative determination of tin. Although there are inherent problems associated with the use of HCl for the determination of tin, accuracy and linearity can be greatly improved if a few precautions are taken. Deaeration of the D.I. water used to prepare the tin stock and the use of fresh tin stock for every determination helps to ensure the precision and accuracy of the procedure.

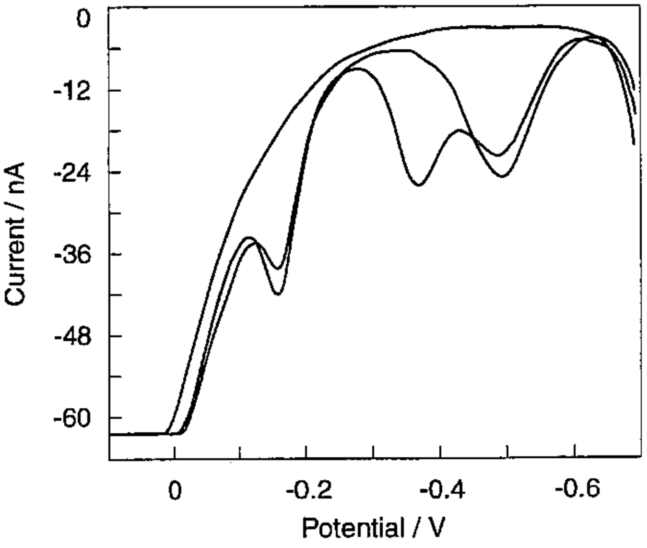

Figure 4. Overlay of Sn(II) voltammograms with and without Pb(II) interference in 2.5e-4 M 1,10-phenanthroline/ 0.4 M oxalic acid electrolyte.

The precision was estimated by recording a voltammogram of a 100 ppb Sn(II)/0.12 M HCl solution ten times sequentially throughout a given day. The RSD value for the Sn(II) ip was less than 5% throughout this investigation.

A calibration curve (F5) was constructed using the 0.12 M HCl solution and a fresh Sn(II) stock solution. Linearity was exceptional from 0 to 6 ppm. Peak to peak noise was estimated to be 4 nA for a background scan of the 0.12 M HCl solution. Using a signal to noise ratio of 3, and the sensitivity obtained from the calibration curve, the estimated detection limit for Sn(II) was 85 ppb.

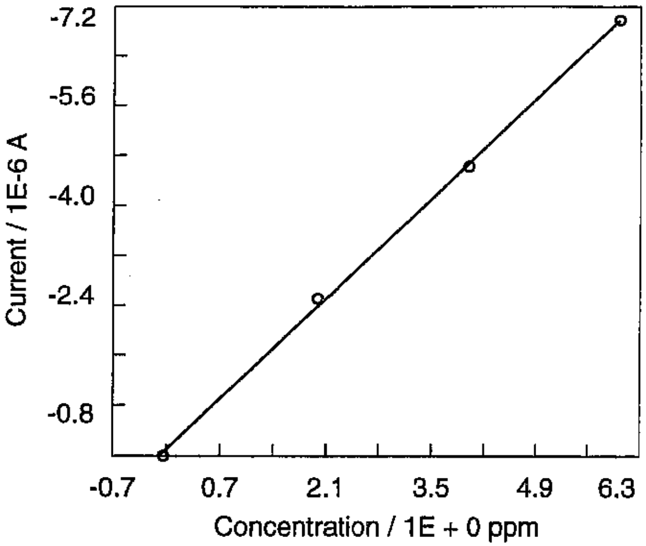

Figure 5. Calibration curve for Sn(II) in 0.12 M HCl supporting electrolyte.

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2. *T.M. Florence and Y.J. Farrar, Electroanal. Chem. and Interfac. Electrochem 51 (1974):191.*
3. *I. M. Kolthoff and J. J. Lingane,"Polarography," Interscience Publishers, NY (1952).*
4. *J. Wang and J. Zadeii, Talanta 34 (1987): 909.*
5. *W. Lin, Y. Wang, D. Zhang, and C. Chen, Shipin Kexue (Beijing) 59 (1984): 50.*
6. *A. Bard, R. Parsons, and J. Jordan, "Standard Potentials and Aqueous Solutions," Marcel Dekker, Inc., NY(1985).*