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# Electrochemical Studies of the TIN(IV)-Pyrocatechol Violet System

by  
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Research Department

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<p>(U) In an effort to develop simpler methods for the analysis of natural waters for toxic organotin compounds, we have studied the electrochemical properties of pyrocatechol violet (PCV) and the complex formed by this reagent with tin(IV) (Sn(IV)). The reagent and the complex were found to show oxidative response to a glassy carbon electrode. Concentrations of tin as low as 200 parts per billion were detectable by oxidative linear sweep voltammetry. Because of the decrease in the height of a characteristic PCV peak upon addition of Sn(IV), formation of the complex was also detectable by liquid chromatography with electrochemical detection. Neither method proved responsive to organotin, although response was observed upon conversion of organotin to inorganic Sn(IV).</p>					
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## INTRODUCTION

Organotin compounds have found extensive use as antifoulants in coatings for ship hulls. When organotin moieties are leached into harbor waters, their biocidal activity becomes undesirable. Efforts have been made in the development of coatings that release organotin at rates slow enough to minimize hazards to marine life. Organotin is most often added to coatings in the form of tributyltin(IV) compounds, usually chloride, hydroxide, oxide, or acetate. More recently, copolymers of tributyl tin with methyl methacrylate have been used to achieve slower release rates. The species formed in sea water by leaching are believed to be primarily tributyltin(IV) hydroxide ( $\text{Bu}_3\text{SnOH}$ ) or tributyltin(IV) chloride ( $\text{Bu}_3\text{SnCl}$ ), where Bu = butyl (References 1 and 2). These compounds can undergo degradation to dibutyl and monobutyl species and to inorganic tin. Inorganic tin also occurs naturally in sea water in trace amounts as hexahydroxytin(IV) ( $\text{Sn}(\text{OH})_6^{2-}$ ) (Reference 3). In order to monitor rates of leaching, some means of analysis of natural waters for organotin is necessary.

The most accurate method that has been developed involves conversion of the organotin compounds to tin hydrides, followed by chromatographic separation of the hydrides and detection by atomic absorption spectroscopy (References 4 through 6). This method involves expensive apparatus and rather complex work-up procedures. Simpler methods, preferably adaptable to on-site monitoring, are a desirable goal.

The work described in this report resulted from attempts to find a simple electrochemical method for analysis of organotin. Organotin compounds have been determined by polarographic methods involving dropping mercury or hanging mercury drop electrodes (References 7 through 9), but the use of a mercury electrode presents disadvantages for on-site instruments due to the storage, cleaning, and toxicity problems associated with mercury.

There are a variety of methods for determination of inorganic tin(IV) ( $\text{Sn}(\text{IV})$ ). Conversion of organotin(IV) compounds to inorganic  $\text{Sn}(\text{IV})$ , followed by analysis for  $\text{Sn}(\text{IV})$ , would enable determination of both total tin and the fraction present as organotin. Electrochemically, inorganic  $\text{Sn}(\text{IV})$ , like organotin(IV), is usually determined by reduction at mercury electrodes. Spectrophotometrically, the most sensitive method for determination of  $\text{Sn}(\text{IV})$  involves conversion to a complex with pyrocatechol violet (PCV), followed by measurement of the absorbance of the complex. This method has been employed for analyses of environmental samples (References 10 and 11).

The structure of PCV is shown in Figure 1. We may refer to this structure as  $H_4L$ . Studies have shown the optimum pH for spectrophotometric determination to be between 2 and 3; in this region, PCV exists mainly in the form of  $H_3L^-$ , which reacts with  $Sn^{4+}$  to form  $Sn(H_2L)_2$  (Reference 12).



Since the coordinated and uncoordinated ligands contain hydroxyl groups that are electrochemically oxidizable and coordination tends to modify electrochemical behavior of ligands, there is a possibility of determination of the Sn(IV)-PCV complex by oxidative electrochemistry. Because the removal of dissolved oxygen from the solutions being analyzed is not required, oxidative measurements are more convenient than reductive measurements. The use of a solid working electrode, rather than mercury, would be another advantage.

This report summarizes the results of electrochemical investigations of the Sn(IV)-PCV system. During the investigation two techniques were employed: linear sweep voltammetry (LSV) and liquid chromatography with electrochemical detection (LCEC).

#### APPARATUS AND MATERIALS

Voltammetric measurements were made with a polarographic analyzer (Model 174) from Princeton Applied Research, Princeton, N.J., operated in the direct current mode. The working electrode was a glassy carbon electrode (GCE) and the reference electrode was a standard calomel electrode (SCE), both obtained from IBM Instruments, Danbury, Conn. The auxiliary electrode was a platinum wire. All potentials given in this report are relative to SCE. The cell was a glass cell obtained from IBM Instruments that was fitted with a plastic screw-on cover containing inlets for electrodes, and reagent and inert gas addition.

Liquid chromatographic separation with electrochemical detection was carried out with a LCEC Analyzer from Bioanalytical Systems (BAS), West Lafayette, Ind., consisting of a basic high performance liquid chromatograph (HPLC) system, an LC-4B electrochemical detector, LC-22A temperature controller, and a dual pen recorder. All experiments used a 25 cm Biophase ODS C-18 column and a GCE cell with an SCE reference electrode at 25°C.

Tri-n-butyl tin(IV) chloride (95+%) and PCV were obtained from Alfa Products, Danvers, Mass. Standard Sn(IV) was AA Standard solution in 20% hydrogen chloride (HCl) that contained 1000 microgram ( $\mu g$ ) Sn/microliter (mL); this solution was also obtained from Alfa Products.

Solvents for LCEC work were HPLC grade. Salts used in preparing buffer solutions were filtered through 0.20 micrometer ( $\mu\text{M}$ ) filters, obtained from BAS. Nitrogen was bubbled continuously through the mobile phase reservoir. Samples were filtered through 0.5  $\mu\text{M}$  Millipore filters prior to injection.

### VOLTAMMETRIC STUDIES

Solutions of PCV, standard Sn(IV) and tributyltin(IV) chloride were examined by LSV. Initially, 0.1 molar (M) sodium chloride (NaCl) was employed as the neutral electrolyte, and the pH was adjusted with hydrochloric acid or ammonium hydroxide. When scanned oxidatively from 0.0 to +1.0 volt (V) at 20 millivolts/second (mV/s), highly acidic solutions of PCV show a single current maximum, at about +0.45 V. This peak shifts to lower potentials with increasing pH and disappears at pH greater than 8.5. At pH greater than 1.0, a wave appears at about +0.75 V. This wave shifts to lower potentials with increasing pH, and has virtually disappeared at pH 10. Representative voltammograms are shown in Figure 2, and principal features are summarized in Table 1. The voltammograms reflect the dependence of oxidation waves on the degree of protonation of the PCV molecule.

Results for a series at constant pH (2.2) with varying PCV concentration are shown in Figure 3. Response is linear over most of the concentration range ( $8.4 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  M) and is best for +0.76 V.

The effect of adding inorganic Sn(IV) to solutions of PCV is shown in Figure 4. Behavior as a function of pH is summarized in Table 2. Studies were confined to acidic pH values in order to minimize hydrolysis of  $\text{Sn}^{4+}$ . The pH region between 2 and 4 appears to be the optimum region for the effect of Sn(IV) on oxidative LSV behavior of PCV. At the current range employed, a concentration of 0.5 parts per million (ppm) tin gave a detectable response.

Subsequent voltammetric studies were run on solutions buffered to pH 2.3 with 0.04 M chloroacetic acid (HClOAc) and 0.01 M sodium acetate (NaOAc). The buffer salts served as the supporting electrolyte. In order to correspond closely to the conditions employed in the LCEC measurements described on page 7 and to permit solubility of tributyltin(IV), most solutions were prepared in a 30/70 volume/volume (v/v) mixture of methanol (MeOH) and water.

Voltammograms for a series with PCV concentration constant at  $5.2 \times 10^{-5}$  M and Sn(IV) concentration ranging from  $1.6 \times 10^{-6}$  M to  $1.3 \times 10^{-5}$  M are shown in Figure 5. Results for a similar series, using a smaller current range and scanning only the region between +0.56 and +0.90 V, are shown in Figure 6. A concentration of  $1.6 \times 10^{-6}$  gram-atoms/L (0.2 ppm) of tin gives a detectable response.

The optimum concentration of PCV was found to be about  $5 \times 10^{-5}$  M. More concentrated solutions showed lower sensitivity to Sn(IV). Results for one such series are shown in Figure 7. Lower current range settings were needed at lower concentrations; this created problems because of the high background current due to uncomplexed PCV--a high offset was needed to bring the voltammograms onscale.

If the current at a given potential is represented by  $i_{obs}$ , the current due to free PCV by  $i_{PCV}$ , the current due to the Sn-PCV complex by  $i_{com}$ , and the base current by  $i_b$ , then

$$i_{obs} = i_{PCV} + i_{com} + i_b \quad (2)$$

If the complexation reaction is given by



where  $q$  is the total charge of the  $n$  complexed PCV ions, then the concentration of free PCV is given by

$$[PCV] = \Sigma PCV - n[Sn(PCV)_n^{4-q}], \quad (4)$$

where  $\Sigma PCV$  = total PCV concentration. Assuming that essentially all of the tin is complexed, we have

$$[PCV] = \Sigma PCV - n\Sigma Sn, \quad (5)$$

where  $\Sigma Sn$  = total tin concentration. If  $i_{PCV}$  is proportional to  $[PCV]$  and  $i_{com}$  is proportional to  $Sn$ , then

$$i_{obs} = k_p[PCV] + k_s\Sigma Sn + i_b = k_p[\Sigma PCV - n\Sigma Sn] + k_s\Sigma Sn + i_b. \quad (6)$$

If we represent  $i_{PCV}$  before addition of any tin by  $i_{PCV}^0$ , then

$$i_{Sn=0} = i_{PCV}^0 + i_b = k_p \Sigma PCV + i_b, \quad (7)$$

and the change in current due to addition of Sn is

$$i_{obs} - i_{Sn=0} = [k_s - nk_p] \Sigma Sn. \quad (8)$$

Hence plots of  $i_{obs} - i_{Sn=0}$  versus  $\Sigma Sn$  should be linear, if  $n$  is constant. Under the conditions of pH and concentration employed here,  $n$  should be close to 2 (Reference 12), and PCV must be kept greater than or equal to 2  $\Sigma Sn$ . Plots for two fixed potentials, using data from Figures 6 and 7, are shown in Figure 8. Such plots were, in general, only approximately linear, with the greatest deviations from linearity occurring at PCV to tin ratios less than 4. In practice, empirical plots of observed current versus tin concentration would be employed as standard curves.

In order to investigate applicability to analysis for organotin, the response of  $Bu_3SnCl$  to PCV was studied. For these experiments, a

solution of  $3.7 \times 10^{-3}$  M  $\text{Bu}_3\text{SnCl}$  in methanol was used as a standard solution. Addition of  $\text{Bu}_3\text{SnCl}$  to the electrolyte solutions employed in the measurements described previously produced no oxidative or reductive waves on the GCE. Addition to solutions of PCV produced no color changes and no changes in oxidative scans. Evidently, the butyl groups in  $\text{Bu}_3\text{SnCl}$  are bound much more strongly to tin than are the coordinated ions in the PCV complex. When a sample of  $\text{Bu}_3\text{SnCl}$  was converted to inorganic tin by fuming with sulfuric acid, and the resultant residue was dissolved in water and added to PCV solution, an oxidative wave was seen. Results from one such experiment are shown in Figure 9. Thus, the detection methods described in this report would not respond to very dilute solutions of organotin, but would require preconcentration and conversion to inorganic tin.

Throughout the investigation, problems with reproducibility of voltammograms were encountered. Such problems are common with solid electrodes, partly because of surface phenomena. Second scans of a given solution usually showed a lower response than the first scans. Polishing the GCE with polishing strips seemed to improve response, but results were not consistent. Aging of solutions also affected response. It would probably be advisable to set up a new standard curve each time the method was employed for analysis.

#### LCEC STUDIES

All mobile phases for LCEC studies were 0.04 M in chloroacetic acid and 0.01 M in sodium acetate. Initial runs were made with mobile phases 30/70 v/v in methanol/water, with the GCE set at +0.700 V and a flow rate of 1.0 mL/minute (min). When solutions of PCV in solvents having the same composition as the mobile phases were injected onto the column, four weak bands with retention times of 3.5, 4.3, 4.8, and 5.3 minutes were observed, plus a much higher, broader band with a retention time of about 21 minutes. Addition of Sn(IV) to the PCV solutions prior to injection produced no consistent effect on the early peaks, but seemed to decrease the height of the late peak.

Tests in variations of the GCE potential showed a response for PCV at potentials greater than or equal to +0.50 V. The response increased with increasing potential, with a leveling-off trend noticeable at greater than +0.70 V. A potential of +0.800 V was selected for the remainder of the LCEC studies.

An increase in the fraction of methanol present in the mobile phase produced a dramatic decrease in retention time of the main peak. An increase in peak height for a given concentration of PCV was also noted. Results for solutions containing  $5.2 \times 10^{-4}$  M PCV (200 ppm) are shown in Table 3.

Addition of standard Sn(IV) to PCV solutions prior to injection consistently produced a decrease in height of the principal peak. No additional peaks were seen. The decrease in peak height appeared to be proportional to tin concentration at molar ratios of PCV to tin greater than or equal to 4. This indicates that only uncomplexed PCV is detected by the LCEC under the conditions employed. The decrease in peak height is caused by partial complexation of the PCV by Sn(IV). Representative chromatograms for two experiments are shown in Figures 10 and 11. At PCV concentrations below 50 ppm, interference from peaks near the solvent front became a problem.

Data from a series of solutions containing 100 ppm PCV and 2 to 10 ppm Sn(IV) are shown in Figure 12. Figure 13 is a plot of average decrease in peak height versus Sn(IV) concentration. The decrease is linear up to 8 ppm Sn(IV), which corresponds to molar ratios of PCV to tin greater than or equal to 3.8. The slope of the linear portion corresponds to 5.6 nanoamperes (nA)/ppm or 0.27 nA/nanogram (ng) of tin. The noise level for the 1 nA range of the instrument was about 0.05 nA; this yields a value of 0.54 ng for the minimum detectable quantity of tin injected.

Results of all LCEC runs are summarized in Table 4. The most notable trends are the increase in sensitivity to tin with increasing methanol concentration and with increasing PCV concentration for a given mobile phase.

Attempts were made to form the Sn-PCV complex in situ by injection of standard Sn(IV) solutions into mobile phases containing PCV. Mobile phases containing more than 50 ppm PCV yielded background currents too high to permit onscale current readings, and only the 500 nA range of the instrument (the highest range available) could be employed. No signals ascribable to the Sn-PCV complex were observed.

#### SUMMARY

The investigations described in this report have yielded two novel electrochemical methods for detection and quantitation of inorganic Sn(IV). Although they do not offer enhanced sensitivity, these new methods offer advantages of convenience over known electrochemical methods. The voltammetric method has shown problems of reproducibility that need further study. The optimum concentration range for the voltammetric method appears to be  $1.5 \times 10^{-6}$  to  $5 \times 10^{-5}$  g-atoms/L (200 parts per billion (ppb) to 6 ppm) of tin. The best results for the LCEC method were obtained for tin concentrations of  $2.5 \times 10^{-5}$  to  $1.7 \times 10^{-4}$  gram-atoms/L (3 to 20 ppm). This does not approach the parts per trillion sensitivity needed for on-site monitoring of natural waters. Preconcentration would be necessary, as well as conversion of organotin to inorganic tin.

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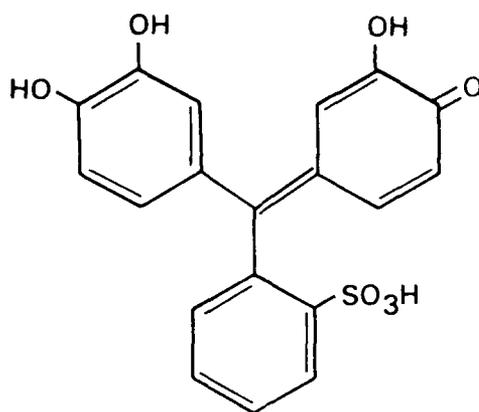


FIGURE 1. Structure of PCV.

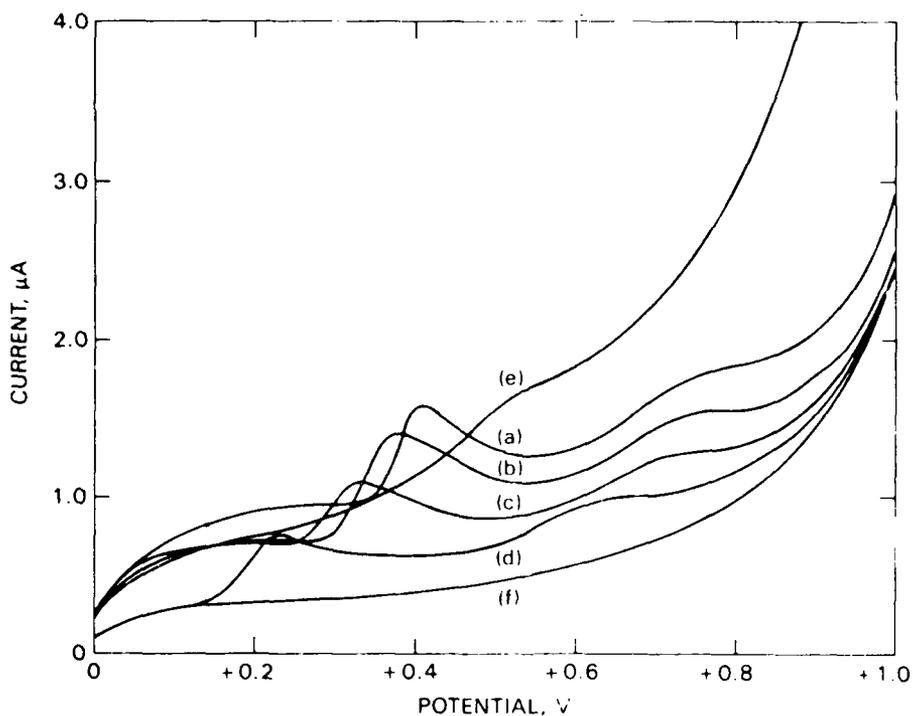


FIGURE 2. Linear Sweep Voltammograms of Solutions of  $2.6 \times 10^{-5}$  M PCV in 0.1 M NaCl, pH Adjusted With HCl, Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ). Scan rate: 20 mV/s. pH: (a) 1.7; (b) 2.2; (c) 3.2; (d) 4.8; (e) 9.1; (f) blank solution (no PCV), pH 1.7.

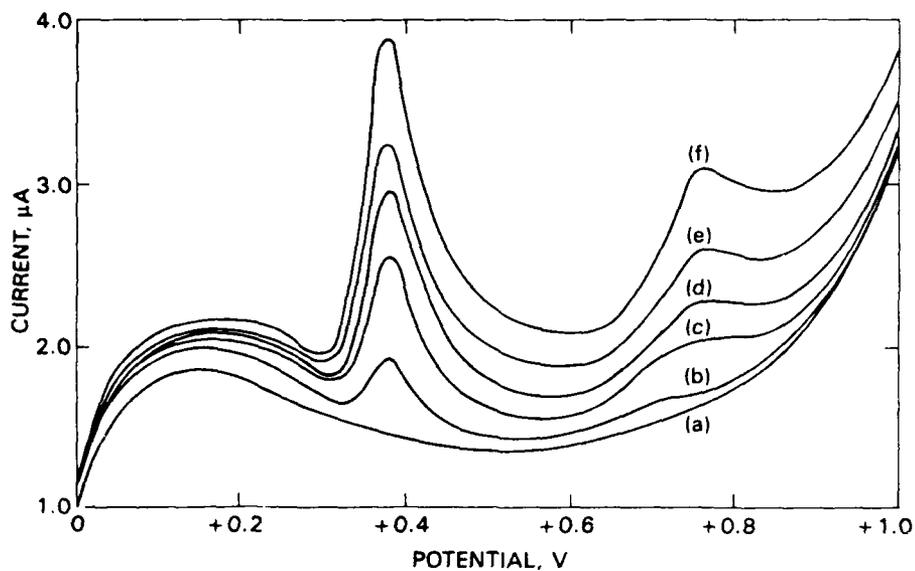


FIGURE 3. Linear Sweep Voltammograms of PCV in 0.1 M NaCl, pH = 2.2 (HCl). Scan rate: 20 mV/s. Concentration of PCV, M: (a) 0.0; (b)  $8.4 \times 10^{-6}$ ; (c)  $3.4 \times 10^{-5}$ ; (d)  $5.0 \times 10^{-5}$ ; (e)  $5.9 \times 10^{-5}$ ; (f)  $1.0 \times 10^{-4}$ .

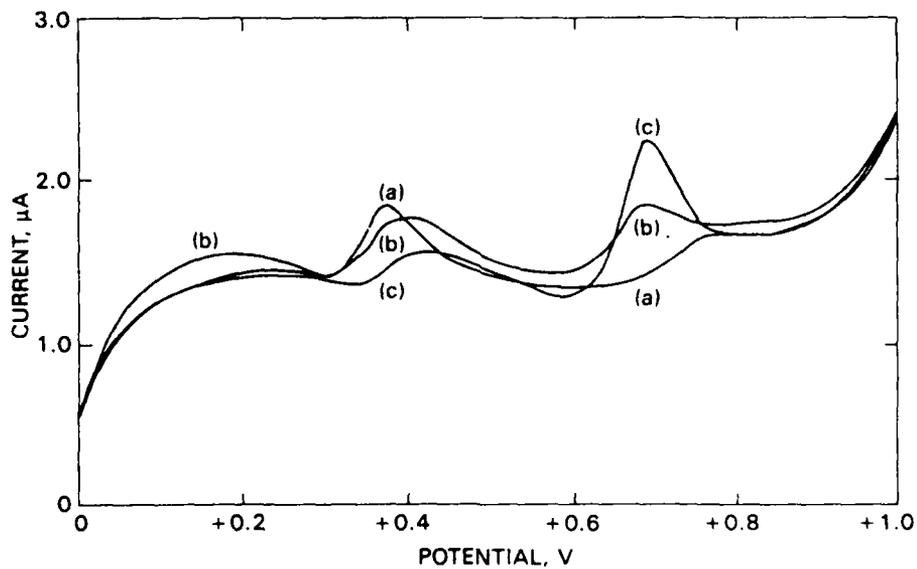


FIGURE 4. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 0.1 M NaCl, pH = 2.0 (HCl). Scan rate: 20 mV/s. Concentration of PCV:  $2.5 \times 10^{-5}$  M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b)  $8.6 \times 10^{-6}$ ; (c)  $1.7 \times 10^{-5}$ .

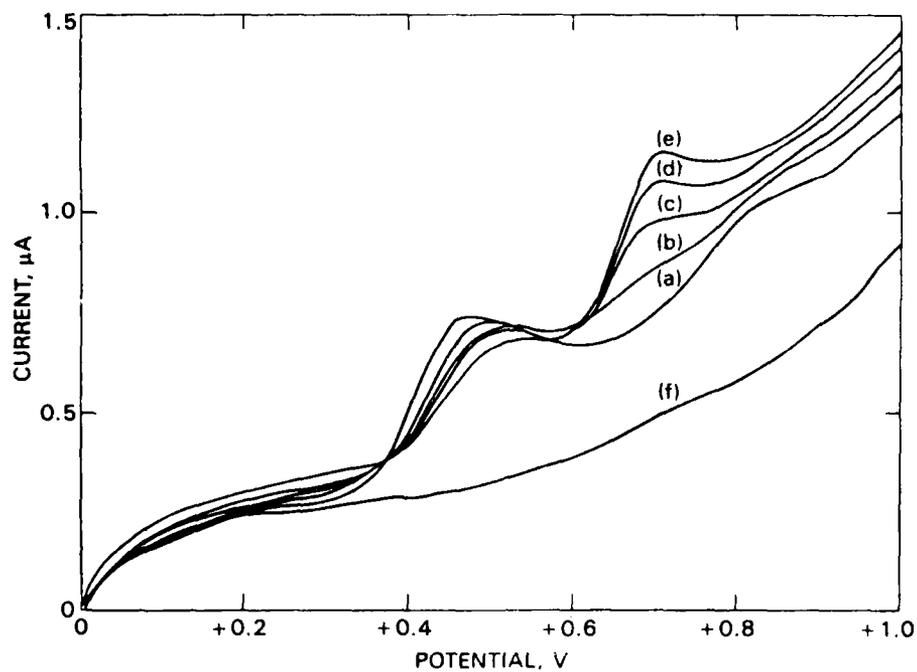


FIGURE 5. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV:  $5.2 \times 10^{-5}$  M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b)  $3.2 \times 10^{-6}$  (0.38 ppm); (c)  $6.5 \times 10^{-6}$  (0.77 ppm); (d)  $9.6 \times 10^{-6}$  (1.1 ppm); (e)  $1.3 \times 10^{-5}$  (1.5 ppm); (f) blank solution (no PCV).

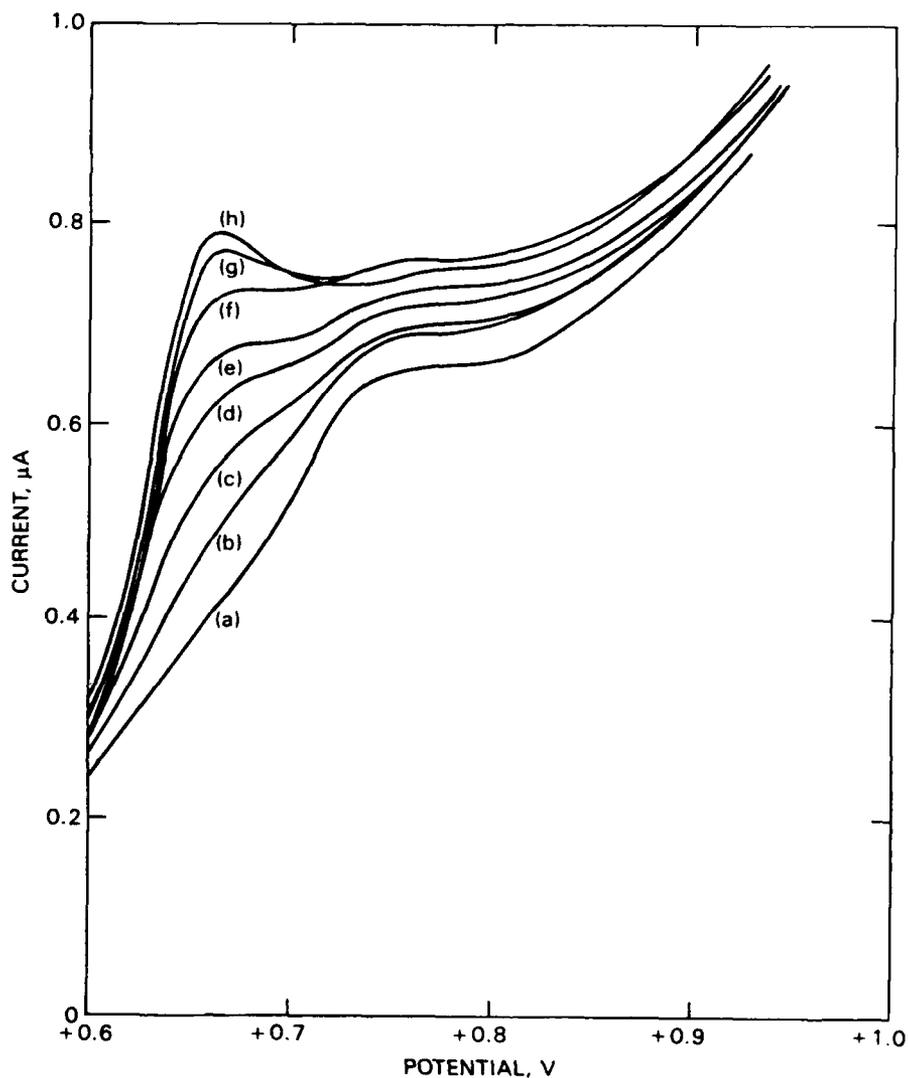


FIGURE 6. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV:  $5.2 \times 10^{-5}$  M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b)  $1.6 \times 10^{-6}$  (0.19 ppm); (c)  $3.2 \times 10^{-6}$  (0.38 ppm); (d)  $4.8 \times 10^{-6}$  (0.58 ppm); (e)  $6.5 \times 10^{-6}$  (0.77 ppm); (f)  $8.1 \times 10^{-6}$  (0.96 ppm); (g)  $9.6 \times 10^{-6}$  (1.1 ppm); (h)  $1.3 \times 10^{-5}$  (1.5 ppm).

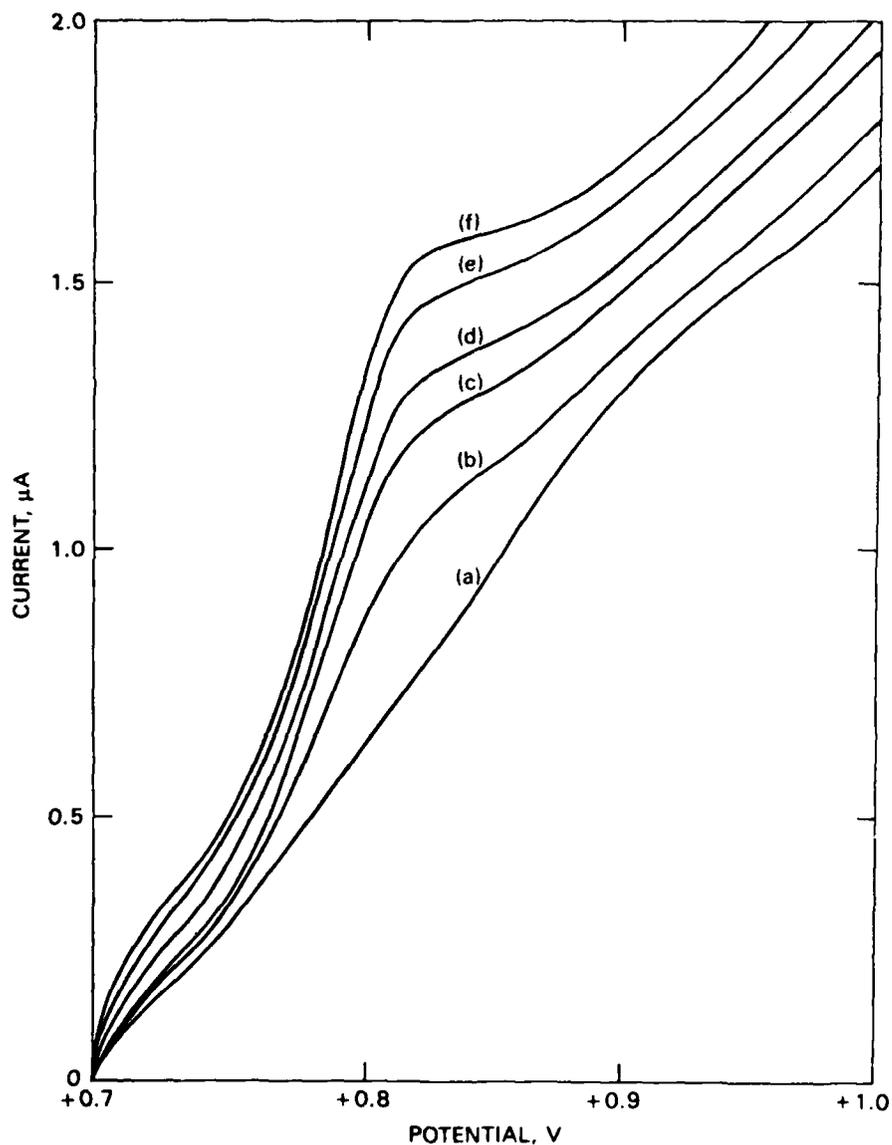


FIGURE 7. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV:  $2.6 \times 10^{-4}$  M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b)  $4.2 \times 10^{-6}$  (0.50 ppm); (c)  $8.4 \times 10^{-6}$  (1.0 ppm); (d)  $1.3 \times 10^{-5}$  (1.5 ppm); (e)  $1.7 \times 10^{-5}$  (2.0 ppm); (f)  $2.1 \times 10^{-5}$  (2.5 ppm).

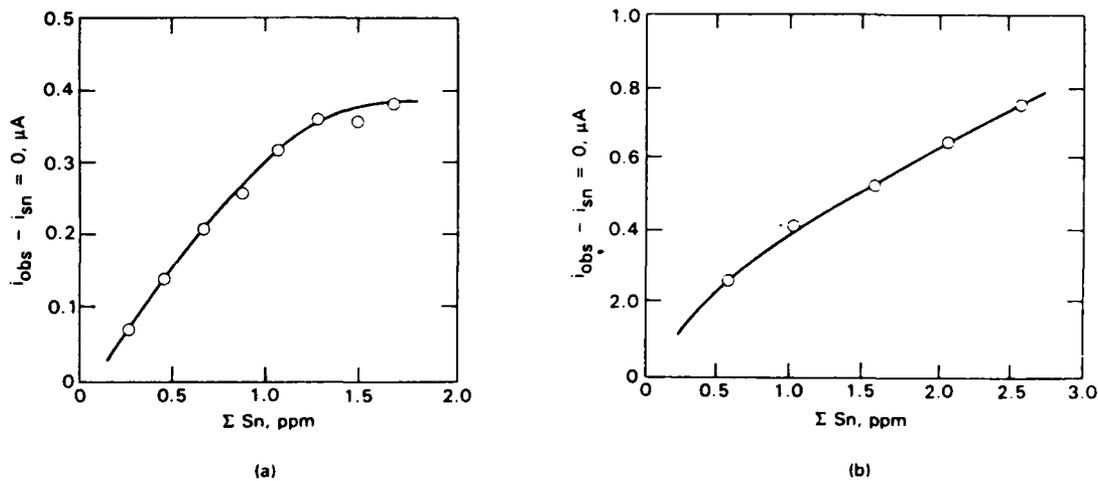


FIGURE 8. Plots of  $i_{\text{obs}} - i_{\text{Sn}=0}$  versus  $\Sigma \text{Sn}$  for (a) data from Figure 6 for  $E = +0.650 \text{ V}$  and (b) data from Figure 7 for  $E = +0.820 \text{ V}$ .

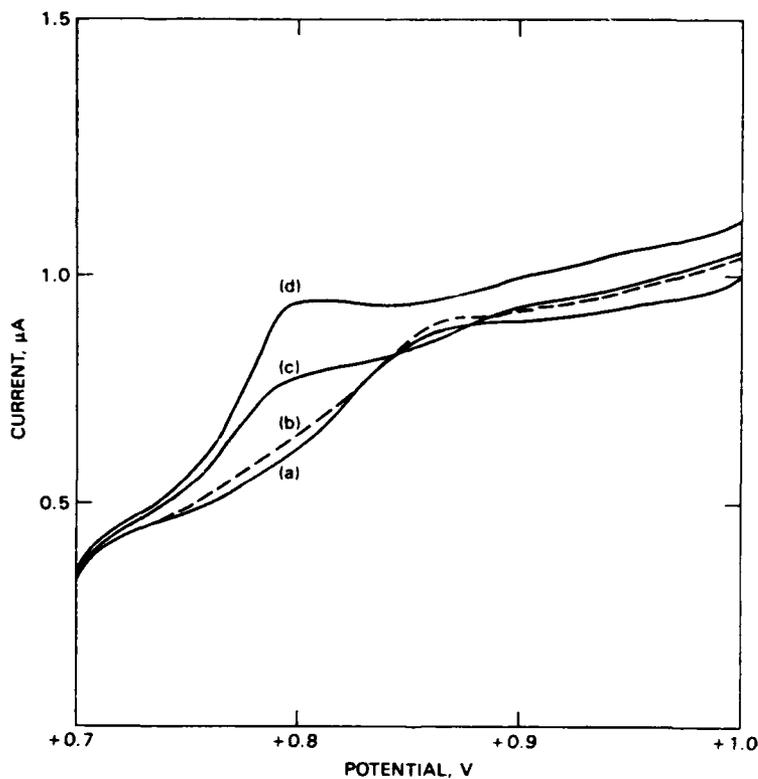


FIGURE 9. Linear Sweep Voltammograms With Conditions as in Figure 5. (a) PCV,  $5.2 \times 10^{-5} \text{ M}$ ; (b) Same PCV solution plus  $\text{Bu}_3\text{SnCl}$  (2.4 ppm); (c)  $\text{Bu}_3\text{SnCl}$ , after fuming with  $\text{H}_2\text{SO}_4$ , dilution and addition to  $5.2 \times 10^{-5} \text{ M}$  PCV (equivalent to 0.88 ppm tin); (d) same, with  $\text{Bu}_3\text{SnCl}$  equivalent to 1.76 ppm tin.

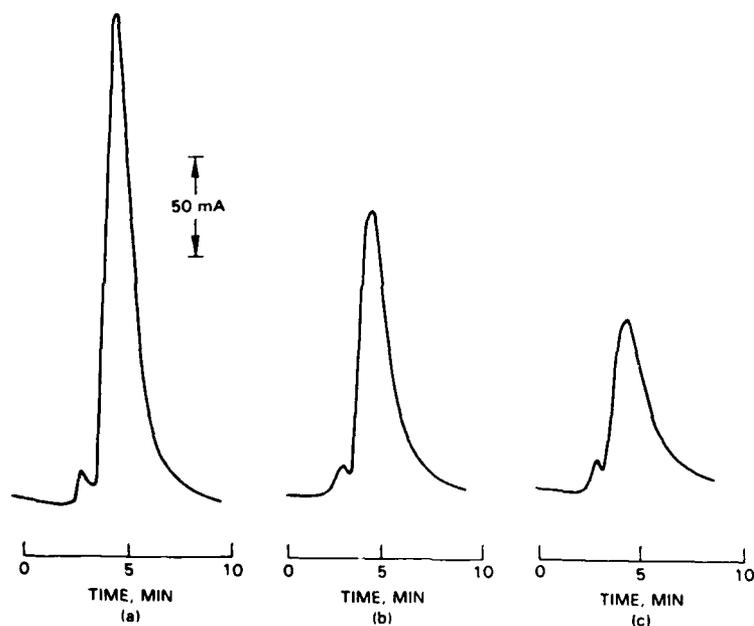


FIGURE 10. LCEC Chromatograms of Solutions Containing 200 ppm PCV, With Sn(IV) Concentrations of (a) 0 ppm; (b) 10 ppm; (c) 20 ppm. Mobile phase: 0.04 M HClOAc/0.01 M NaOAc in 50/50 v/v methanol/water. Flow rate: 1.0 mL/min. Injection volume: 20 L. Potential of GCE: +0.800 V (SCE).

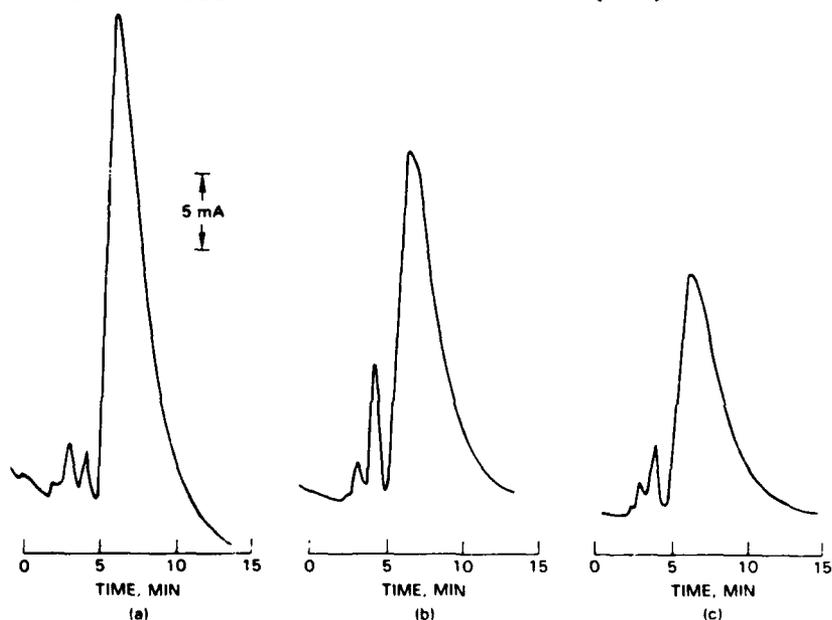


FIGURE 11. LCEC Chromatograms of Solutions Containing 50 ppm PCV, With Sn(IV) Concentrations of (a) 0 ppm; (b) 2 ppm; (c) 4 ppm. Mobile phase: 45/55 v/v methanol/water. Other conditions as in Figure 10.

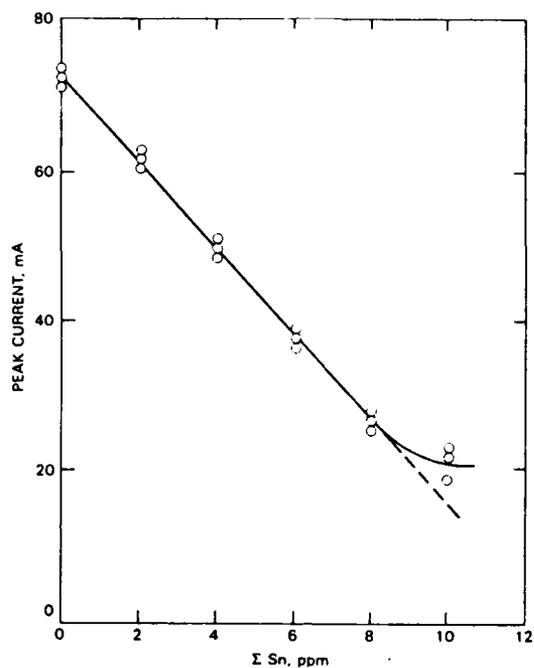


FIGURE 12. Peak Current vs Sn(IV) Concentration for Solutions Containing 100 ppm PCV. Results for 3 runs at each concentration are shown. Conditions as in Figure 11.

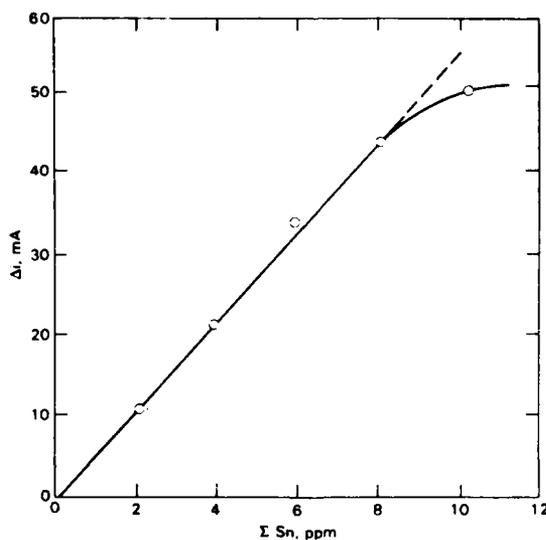


FIGURE 13. Decrease in Peak Current  $i$  versus Sn(IV) Concentration Using Average Values for Series Shown in Figure 12.

TABLE 1. Effect of pH on Voltammetric Properties of PCV.<sup>a</sup>

pH	Color	E <sub>p</sub> , <sup>b</sup> V	E <sub>wave</sub> , <sup>c</sup> V
-0.5	Cherry red	+0.455	...
0.22	Orange-red	0.43	...
1.0	Orange	0.42	...
1.5	Yellow	0.395	+0.80
2.0	Yellow	0.37	0.80
3.0	Yellow	0.34	0.80
4.1	Yellow	0.295	0.75
4.8	Yellow	0.23	0.65
6.5	Dull yellow	0.18	0.60
7.8	Greenish purple	0.08	0.55
8.3	Purple-blue	0.1 <sup>d</sup>	0.55
8.7	Purple	...	0.55
9.1	Violet	...	0.55 <sup>e</sup>
10.0	Violet	...	0.52 <sup>f</sup>

<sup>a</sup> Data from linear sweep voltammograms of solutions in 0.1 M NaCl, pH adjusted with HCl, NH<sub>4</sub>OH. PCV concentration:  $2.6 \times 10^{-5}$  M. Scan rate: 20 mV/s.

<sup>b</sup> E<sub>p</sub> = potential at peak.

<sup>c</sup> E<sub>wave</sub> = potential of wave.

<sup>d</sup> Plateau.

<sup>e</sup> Shallow.

<sup>f</sup> Very shallow.

TABLE 2. Effect of Addition of Sn(IV) on Linear Sweep Voltammograms of PCV.<sup>a</sup>

pH	Effect of Sn(IV) addition	Potentials and values of maximum $\Delta i$ [V: $\mu A$ ] <sup>b</sup>
0.22	Small maximum at +0.30, wave about +0.7	[+0.30:0.14], [+0.70:0.17]
1.0	Small maximum at +0.29, shift of maximum at +0.37 to +0.45, wave about +0.72	[+0.30:0.12], [+0.46:0.20], [+0.72:0.24]
1.5	Small maximum at +0.26, shift of maximum at +0.39 to +0.44, wave at +0.72. Color change from yellow to orange.	[+0.27:0.15], [+0.39:0.27], [+0.70:0.23]
2.0	Shift of maximum at +0.37 to +0.42, appearance of peak at +0.69. Color change from yellow to orange-red.	[+0.37:0.50], [+0.69:1.07]
3.0	Shift of maximum at +0.34 to +0.39, appearance of peak at +0.69. Color change from yellow to orange-red to purple.	[+0.34:0.51], [+0.69:1.05]
4.1	Small wave at +0.17, shrinkage of peak at +0.29, appearance of peak at +0.69. Color change from yellow to deep rose to purple.	[+0.29:0.46], [+0.69:1.12]

<sup>a</sup> Concentration of PCV =  $2.6 \times 10^{-5}$  M; Concentration of Sn(IV):  $8.6 \times 10^{-6}$  M. Other conditions as in Table 1.

<sup>b</sup>  $\Delta i$  = Change in current, V = potential, volts vs. SCE;  $\mu A = \Delta i$ , microamperes.

TABLE 3. Effect of Mobile Phase Solvent Composition on Retention Time and Height of Main Peak for Solutions Containing 200 ppm ( $5.2 \times 10^{-4}$  M) PCV.

% MeOH	$t_R$ , min	Average peak height, nA <sup>a</sup>
30	21.0	85
45	4.9	135
48	4.3	159
50	3.9	241

TABLE 4. Summary of Results of LCEC Runs for Solutions of PCV Plus Sn(IV).<sup>a</sup>

% MeOH	ΣPCV, ppm	ΣSn, ppm	t <sub>R</sub> , min	Peak height, nA <sup>b</sup>	ΔnA/ng Sn <sup>c</sup>
30	200.0	30.0	23.0	24.4	0.10
30	200.0	20.0	22.0	32.4	0.13
30	200.0	10.0	21.0	52.0	0.16
30	200.0	0.0	21.0	84.8	...
40	25.0	2.0	9.6	5.4	0.11
40	25.0	1.0	9.4	7.7	0.11
40	25.0	0.0	9.4	9.8	...
40	10.0	0.8	10.5	1.96	0.067
40	10.0	0.4	10.7	2.55	0.060
40	10.0	0.0	10.2	3.03	...
45	100.0	10.0	4.2	22.1	0.25
45	100.0	8.0	4.2	27.3	0.28
45	100.0	6.0	4.1	37.1	0.29
45	100.0	4.0	4.0	50.0	0.27
45	100.0	2.0	4.0	61.1	0.27
45	100.0	0.0	4.0	71.9	...
45	50.0	4.0	4.4	18.4	0.22
45	50.0	3.0	4.3	19.2	0.28
45	50.0	2.0	4.3	23.9	0.30
45	50.0	1.5	4.3	27.1	0.29
45	50.0	1.0	4.2	29.7	0.31
45	50.0	0.0	4.1	35.8	...
45	25.0	2.0	4.4	11.8	0.16
45	25.0	1.0	4.5	14.0	0.22
45	25.0	0.0	4.2	18.3	...
50	200.0	20.0	4.2	87.0	0.40
50	200.0	10.0	4.1	148.0	0.48
50	200.0	0.0	3.9	245.0	...
50	100.0	10.0	5.0	31.2	0.29
50	100.0	7.0	5.3	39.6	0.36
50	100.0	5.0	5.1	55.5	0.34
50	100.0	3.0	4.9	73.1	0.27
50	100.0	0.0	4.5	89.3	...

<sup>a</sup> Mobile phases were methanol/water, buffered to pH 2.3 with HClOAc/NaOAc. Flow rate = 1.0 mL/min. Potential of GCE = +0.800 V versus SCE.

<sup>b</sup> Average values for 2 to 5 runs.

<sup>c</sup> ΔnA = decrease in peak height from run with no tin; average values for 2 to 5 runs.

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