Anodic Stripping Voltammetry of Lead and Cadmium

Background

Stripping voltammetry is an electro-analytical technique with an extremely low detection limit. The technique of stripping voltammetry involves (a) a step in which analyte is deposited onto an electrode under controlled conditions (pre-concentration) (b) stripping by way of electrolysis of the pre-concentrated material. Electrolysis is done by the application of a potential sweep (linear or pulsed). The magnitude of the peak current of the generated voltammetric stripping wave is a directly proportional to the concentration.

The very low detection limits is attributed to the pre-concentration step. In the determination of Pb^{2+} and Cd^{+2} by anodic stripping voltammetry (ASV), the deposition potential of the (graphite) electrode with a thin film of mercury and analyte ions is carried out by holding the applied potential sufficiently negative to reduce the ions.

$$Pb^{2+} + 2e = Pb \text{ and } Cd^{2+} + 2e = Cd$$

Reduced metal ions accumulate in the mercury layer, since metals are soluble in mercury. Mercury electrode volume is very small relative to the 'test solution' volume. The pre-concentration step ranges from 1 - 30 min.; longer deposition times yields larger signals and lower detection limits. Only a fraction of the total metal ion in solution is deposited on the electrode at a given length of deposition time. The 'test solution' is stirred at a constant rate to enhance the efficiency of deposition.

After the pre-concentration step, the solution is allowed to achieve quiescence.. The potential is then scanned in the reverse direction, when the potential is sufficiently positive; an anodic current is generated due to the oxidation of metals. Each species oxidizes at a particular potential. The oxidation peaks grows and then dies down.

Apparatus	Potentiostat, graphite mini electrode (1mm diameter), auxiliary electrode (platinum),nitrogen tank, deoxygenating system, reference electrode (Ag/AgCl(s)/satd(KCl)), micropipettes 0-100uL (1),0-1000uL (1); pipettes - 1 mL and 15 mL, magnetic stirrer, stir bar.
Chemicals	Metal stock solutions ($Hg(NO_3)_2$ 1000ppm, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ 100ppm each, 1 M potassium nitrate, 6M HNO_3

Method

Pipet a 15.00 mL aliquot of unknown metal ions solution in the cell, add 3.25ml of 1M KNO3 into the cell, 1.00mL 6M HNO3, add 750µL of 1000ppm Hg(II). Place the stir bar in the cell. Position the electrodes and pass oxygen-free nitrogen for 5 min with the magnetic stirrer turned on.

Set the deposition parameters and select Square Wave Stripping Voltammetry parameters from the Experiment menu as shown below.

Parameters (Deposition):

Deposition E (mV)	-1000	Deposition Time (sec)	10
Use Initial E as Deposition E	√	Quiet Time (sec)	10
Stir during Deposition	√	Purge during Deposition	-

SWV (Stripping)

Initial E, mV	-1000	Step E, mV	4
Final E, mV	-200	SW Amplitude, mV	25
Full Scale	10 mA	SW Frequency, Hz	15
		Sample Period	1 mSecond
Sample Period	1 mSecond		

Run the experiment. Save the experiment data file (and every data file generated during the experiment as well.)

Add 25uL of standard (100ppm each) metal ions solution to the above solution. Repeat the procedure, and obtain the stripping voltammogram. Add four more 25uL aliquots and obtain the ASVs after each addition. Save all voltammograms.

(Alternately, mix equal volumes of the 100ppm lead and cadmium solutions and introduce 25uL of this solution as the standard addition.)

B. Using the *last* solution investigated, obtain a series of voltammograms for

a. Different deposition times varying from 10, 20, 30, 40, 60, 120 sec (other parameters held constant)
b. Different scan rates, varying from 10, 20, 50, 100, and 200 (300) mV/s for deposition time of 10 seconds (but other parameters held constant).

Treatment of Data:

1. Prepare the standard addition plots (i_p vs concentration *and* charge vs. concentration) for each ion for part A.
2. Generate the best fit lines (correcting for the dilution). Determine the concentration of the unknown.
3. Plot i_p vs. scan rate v; i_p vs. scan rate $v^{1/2}$ for one of the two ions. Comment on their linearity?
4. Plot i_p vs. deposition time for one of the two ions. Comment on their linearity?