Brooklyn College
Department of Chemistry

Chem 79001

Instrumental Analysis — Anodic Stripping Voltammetry

Analysis of a Pb(II) Unknown via Standard Addition

Experiment:

In this experiment you use Anodic Stripping Voltammetry (ASV) to determine the concentration of Pb(II) by the method of standard addition. ASV is commonly used for the determination of metal ions at trace levels because of its excellent detection limit (typically 10^{-9} to 10^{-12} M).

During the first step of the determination, the analyte together with Hg(II) is deposited via reduction to its elemental form at the working electrode by controlled potential electrolysis in a stirred solution. In the second step, the stirring is turned off and the potential of the electrode is scanned so that the deposited lead and then mercury are oxidized back to their ionic forms, *i.e.* anodically stripped from the electrode back into solution.

A computer controlled CH Instruments Electrochemical Analyzer 620A is utilized in a three-electrode setup with a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum counter electrode.

Standard Solution: 25 ppb Pb(II) is provided
Unknown: A solution of Pb(II) of unknown concentration in 0.1 mM Hg(II) and 0.2 M KNO_3, and 0.3 M HNO_3 is provided.

Instrument Setup

Turn on the computer, printer, and analyzer. Click on the 'Chi620a' icon on the computer desktop to start the software that controls the analyzer.

Choose: Setup→Technique→LinearSweepVoltammetry→OK
Choose: Setup→Parameters and set accordingly:

Init E	-1.00 V	starting potential
Final E	+1.00 V	upper limit of potential window
Scan Rate	0.040 V/s	
Sample interval	0.001 V	frequency of data collection
Quiet time	30 s	time delay between deposition/stripping
Sensitivity	1e-004 A/V	
Check boxes	Unmark all	
OK		

Choose: Setup→Control→StrippingMode
Enable stripping mode, disable purging and stirring
Mark deposition E, Quiet E
Set Deposition E and Quiet E to -1.00 V and deposition time to 120 s.

Cell Setup

Place 8 mL of the unknown Pb(II) solution and the stirring bar into the glass cell. Be careful not to lose the stirring bar, it is quite small.

Wet a small section of the polishing pad with deionized water. Polish the glassy carbon electrode on the pad using small circular movements.

Place the Ag/AgCl reference electrode, the polished glassy carbon working electrode, the platinum wire counter electrode, and the gas tube through the cell top and into the solution.

Connect the electrodes, as follows:

Green	glassy carbon working electrode
White	Ag/AgCl reference electrode
Red	platinum wire counter electrode

Initial Measurement

Degas the solution by opening the gas tank valve and bubbling nitrogen through the solution for 10 min. Adjust the regulator to provide a slow, steady stream of bubbles to the cell. After 10 min, raise the degassing tube out of solution, leaving it in the cell.

Turn on the magnetic stirrer.

Start the experiment using the computer. Observe the timer on the screen. After exactly 120 s, turn the stirrer off.

The experiment starts by applying the deposition potential (-1.00 V) for 120 s followed by a 30 s delay (Quiet time, no stirring). The potential is then increased towards positive values and the first peak to be observed should be the Pb oxidation peak at approximately -0.45 V *vs*. Ag/AgCl. The Hg oxidation peak should follow at +0.2 V.

Saving Data

After stripping is finished, save the recorded curve in a file. File→Save will save it as a binary (.bin) file which the Chi620a program can read. After it is saved, you can convert it to a comma separated value text file that MS Excel can read by File→Convert to Text.

Replicating the Measurement

In order to replicate the experiment, it is critical to repeat the same experimental conditions in each deposition/stripping, so do not change the stirrer speed, position, stirring time, etc. However, you will have to remove, polish, and replace the working electrode before every measurement. Take care not to displace the glass cell, or magnetic stirrer in this process. After the working electrode is polished and replaced, lower the gas tube into the solution and degas for 5 min. Raise the gas tube above the solution surface prior to repeating the measurement. Repeat this step to ensure you have three replicates.

Deposition Time Response

Repeat the experiment with deposition times of 60 s, 120 s, and 240 s. Only a single replicate at each deposition time needs to be recorded, but remember to polish the electrode between experiments. Plot the Pb oxidation current (i_p) *vs*. deposition time to evaluate if and where saturation begins.

Standard Additions

Set the deposition time back to 120 s and, without displacing the glass cell, or magnetic stirrer, add 60 μL of the 25 ppm Pb(II) standard stock solution to the unknown solution in the cell. After polishing the glassy carbon working electrode, measure the voltammagram the sample.

Add an additional 60 μL of the 25 ppm Pb(II) standard stock solution to the unknown sample (120 μL in total). Make sure to polish the electrode between each measurement.

Again, repeat the experiment after the addition of another 60 μL of the 25 ppm Pb(II) standard stock solution (180 μL added in total).

Perform the experiment once again, but this time disable stripping mode, and change the Quiet Time from 30 s to 0 s.

Data Processing and Analysis

Open the recorded files and find the oxidation peak current. Use Manual Results (or MS Excel) if automatic mode shows incorrect analysis. Note the shape of the peak – define it appropriately in Peak Definition (Graphics Menu).

To determine the Pb(II) concentration in the unknown, plot the Pb oxidation current (i_p) *vs*. concentration of standard **added** (note the concentration of Pb in the original sample in these coordinates !). Perform a non-linear least squares fitting of your data and determine the best-fit straight line. From the resulting equation, calculate or extrapolate the Pb concentration in your original unknown at $i_p = 0$. Include this value along with the standard deviation in concentration (see Eqn 1-8 in the text) in your

Abstract in both ppm and in molarity. Calculate the preconcentration factor based on a comparison of the voltammagrams recorded with and without deposition.

Report

Follow the outline of a regular laboratory report as provided on the course web site. Make sure to provide the concentration of the unknown, and its error, in the Abstract. Provide all data in the Results and Discussion along with a brief explanation of how the data were collected and the error analysis. Use the Nernst equation as the basis from which to discuss your results. Using a graph you create, discuss the method of standard addition and how you used it to determine the concentration of the unknown. Discuss the roles of the Hg(II) and KNO_3 in the solution, the purpose of deoxygenation, and stirring in the experiment. If you do this experiment after the Cyclic Voltammetry experiment, discuss the advantages/disadvantages of the Standard-Addition and External-Standard Calibration Methods.