Experiment 7: Anodic Stripping Voltammetry: Formation of Metallic Lead

SYNOPSIS Lead is reduced to metallic lead and concentrated into the small volume of the mercury drop. After a set concentration period the lead in the drop is monitored by it's enhanced oxidation peak. The limit of detection can be adjusted by the concentrating time. Contaminate metals do not interfere because of the potential dependence of the method. Organics in the matrix may affect the mercury drop stability, since the surface tension of the mercury drop is affected by adsorbates and by the salt concentration in the solution. A standard addition method will be used. (1, 2, 3). The solution conditions can be manipulated to chemically resolve the Pb from the Sn peak.

READINGS *pages 285-291 in Critical Reviews.* Three articles are attached. The first illustrates chemical methods of resolving Pb from Cd using Br complexation. The second article discusses the effect of Br on inducing Pb adsorption to Hg surfaces. The third article gives a method for lead analysis in blood by use of a mercury plated microelectrode.

Modulating Potentials to Achieve Resolution

To resolve Pb^{2+} and Sn^{2+} in the anodic stripping lab the potential associated with stripping the lead in the presence of a chelate must be calculated as compared to stripping tin. The basic idea is a LeChatlier's principle:

$Pb \times Pb^{2+} + 2e + xL \times PbL + PbL_2 + PbL_3 + ...$

By adding the ligand to the solution the reaction is shifted to the right (oxidation).

In electrochemistry reactions are always written as reduction reactions:

$Pb^{2+} + 2e \times Pb$ $\qquad\qquad$ E^o_{pb}

$$E_{equil} = E_{Pb} - \frac{RT}{nF}\ln\frac{[Pb]}{[Pb^{2+}]} = E_{Pb} - \frac{0.059V}{n}\log\frac{1}{[Pb^{2+}]}$$

To solve this equation we must make use of our strategy used during the alpha fraction plots:

$$Pb_{total} = [Pb^{2+}] + [PbL] + [PbL_2] + ...$$

which can be written as:

$$Pb_{total} = [Pb^{2+}] + K_{f1}[Pb^{2+}][L] + K_{f1}K_{f2}[Pb^{2+}][L]^2 + K_{f1}K_{f2}K_{f3}[Pb^{2+}][L]^3$$

This is equation can be reduced to:

$$\frac{1}{[Pb^{2+}]} = \frac{1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3}{Pb_{total}}$$

Finally our equation for the reduction of lead becomes:

$Pb^{2+}_{total} + 2e \times Pb$

and the Nernst equation becomes:

$$E = E^o - \frac{0.0591}{n}\log\left[1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3\right] - \frac{0.0591}{n}\log\frac{1}{[Pb_{total}]}$$

The first two right hand side terms represent the new formal potential, $E^{o'}$, or apparent formal potential observed.

From the above you can easily set up an excel sheet to see what would be the potential of lead vs tin reduction as a function of the concentration of some ligand.

The citrate solution system will be more complicated because it will depend upon pH and the deprotonation of the acid.

For chloride in the spread sheet set up column one as pL (-log[L]). The second column is then [L] (=10^(-a#)). The third column then can be the apparent formal potential for lead and the fourth column the apparent formal potential for tin.

One only needs to set up a few rows at the top of the spread sheet for the appropriate constants for the formation of the ligand/metal species.

INSTRUMENTATION

PAR 364 polarographic analyzer, HP 2000 Chart recorder, Fisher Scientific 120 magnetic stirrer, Carbon electrode.

GLASSWARE 2 4 neck flasks

1 L volumetric flask
50 mL volumetric
500 mL volumetric

SOLUTIONS

1 L of 0.12 HCl + 10 mM NaCl
conc. HCl = 12.1 M, so 10 mL conc. HCl/1L = 0.12 M.
For this a graduated cylinder is sufficient.
NaCl
(x g)(1 mole/58.44 g)/1L = 0.01 M
x = 0.5844 g

500 mL of 0.01 mM $HgCl_2$ in 0.12 M HCl
(x g)(1 mole $HgCl_2$)/271.50g)/0.5L = 0.01 mM
x = 1.3575 g

1000 ppm Pb stock solution
1000 ppm Cd stock solution = 1 g Cd/10^3g soln = 1 g Cd/L

(x g $CdCl_2$)(1 mole $CdCl_2$/183.30 g $CdCl_2$)(1moleCd/mole$CdCl_2$)(112.4gCd/mole Cd) = 1
x g $CdCl_2$ = 2.03 g in 1 L or 0.2 g/100 mL

Also add Sn solution (separate w/ oxalate)**. Sn will work better than Cd.**

PROCEDURES

Deposit Mercury Film

1. Purge 30 mL of your mercury solution for 3 minutes with N_2 to remove O_2.
2. While the solution is purging polish your carbon electrode (gently!) with alumina and rinse with large amounts of D.I. water. Look at the surface under a microscope.
3. Pull the nitrogen out and cap tightly. Begin purging 30 L of blank solution.
4. Connect up leads. The carbon electrode is the working (WE) electrode, the SCE is the reference (RE) electrode and the small stub of Pt is the counter (CE) electrode. You may have to connect the ground wire also.
5. Connect up the N_2 purge and begin purging.
6. Turn on stir bar. The bottom of the flask is curved so turn past "2" until freely moving and then back down to "2".
7. Deposit mercury by sitting at -900 mV for 3.5 minutes. You should observe a gray mercury film on the surface.

Potentiostat for ASV

1 Turn on AT computer at c prompt type Run250.
2. Use cursor to point, move to set up, new technique, and select cyclic voltammetry (CV).
3. Set the Dept. time to 3.75 minutes and equil. time to 15s, initial potential to -900 mV, vertex potential to -200 mV, and final potential to -200 mV, scan rate to 100 mV/x. change scan increment to 0.001.
4. Move cursor to run, hit enter twice.
5. Turn on cell switch (one place).
6. Stop the run during the 15 second equilibration time by hitting "s". You should observe a mercury film on the surface.

Anodic Stripping Voltammetry: Optimization

1. Place mercury film carbon electrode in 30 mL (measured) deaerated blank solution of HCl and NaCl.
2. Start the stirrer
3. Using a pipette inject 15 µL of 1000 ppm Pb solution. Deposit lead at -900 mV for 15 to60 s. Turn off stirrer for at least 15 s (rest time). Take a scan and plot, determine currents.
5. Repeat scan three times.
6. Change deposition time from 30 s, 90s, and 120 s.
7. Create a standard curve by adding successive amounts of 15 µL Pb. You should have at least 5 points.
8. When you are done with the standard addition, add enough Pb to have a total addition of 1 mL. Add 1 mL of stock Cd to solution and repeat scan at 60 s deposition time.

Samples

1. Take 25 mL of your sample and add 15 mL of the matrix modifier.
2. Deaerate, and obtain ASV under same conditions as for the standard curve.

REPORT In addition to material, methods and results, include:

1. Use the std. add. method data to calculate the LOD, LOQ, linear range, and r value of your standard curve for this method.
2. How does the LOD of this method compare with the value necessary to measure the soil samples?
3. What is the relative standard deviation for your measurement of 3 ppm Pb. How does it

compare with previous measurements?

4. What constitutes a blank in this procedure? What are the sources of error embodied in the standard deviation of the blank? How would you determine the source of error attributed solely to the ASV?
5. How does sample matrix affect your results?
6. What was the estimated time for turn around in samples?
7. Are there any problems with disposal of hazardous materials?
8. How easy would it be to instruct a technician on this method?
9. How easy would it be to construct a paper trail for this method?
10. How does preconcentration time (deposition) scale with the signal?
11. Which metals will interfere the most with Pb? How well resolved was the Cd peak from the Pb peak?
12. How was the baseline handled in this experiment?
13. What is the advantage of the standard addition method?
14. What is the point of the N_2 purge?
15. Why does the ASV experiment show a peak? Why does the peak current decay to background?
16. What is the point of the added HCl and NaCl?
17. Calculate the resolution of the Pb and Cd peaks.

References Cited

1. Goncalves, M. de L. S., L. Sigg, L. Stumm, Env. Sci. Tech. 1985, 19, 141-146.

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3. Aldstadt, J. H. and H. D. Dewald, Anal. Chem. 1992, 64, 3176-3179.