Chem 454 – Voltammetry

Study points:

- Mass Transport in Voltammetry
- Signal to Background Concepts in Voltammetry
- The Axes System in Voltammograms
- Why does voltammetric require 3-electrodes?
- Why is there a need to make sure the sample solution has adequate electrolyte?
- Stripping Voltammetry
- Cyclic Voltammetry

1] A cyclic voltammetric analysis was conducted on a sample containing an aqueous analyte. A 1.00 g sample was dissolved in 100.0 mL of nitric acid. A 50.0 mL aliquot gave an CV ip signal of 5.00 μA. On the other 50.0 mL aliquot was added a spike of 10.0 μL of 1.00e-2 M analyte and gave a signal of 6.00 μA. What is concentration of that analyte in the sample? [1]

2] An anodic stripping voltammetric (ASV) analysis was conducted on a soil sample for leachable Cd^{2+} (AW 112.411 g/mol). A 100-gm sample of soil was extracted with 100-mL of 10% CH_3COOH(aq). ASV analysis of that 100-mL extract yielded a Cd(0) oxidation current of 4.31 μA. A 10-μL spike of 1.51e-3 M solution of Cd^{2+} was added to the sample solution and the ASV current was measured as 6.77 μA. What is the concentration of Cd^{2+} in ppb the original sample? [2]

3] Sketch a cyclic voltammogram of a hypothetical reversible redox couple $A + e^- = A^-$. Label the major features and the approximate E^0. [3]

4] Sketch a cyclic voltammogram in which the electrochemical product is completely consumed in a chemical reaction:

$A + e^- = P$

$P \rightarrow D$

Assume that D is not observed to participate in any further electrochemical or chemical reactions. [4]

5. A voltammetric signal gave a peak current of 10.1 uA for $Cd^{2+} + 2e^- = Cd(s)$ in a 20.00 mL water sample. A spike of 0.00100 mL of 0.025 M Cd^{2+} to this sample gives a current of 23.1 μA. What is the concentration of Cd^{2+} in the sample? [5]

6] A cyclic voltammetric analysis was conducted on a solution with a quinone that gave a peak current at -0.114 V vs. SCE. A calibration curve was conducted with the following results:

Concentration (mM)	Current (μA)
0.095	6.64
0.198	13.29
0.403	26.44
0.594	45.49
0.989	60.11

An unknown solution of that quinone gave a CV peak current of 36.2 uA. What is the concentration of that solution? What is the slope, and intercept of that best fit line? What are the R^2, S_r, S_m, and S_b of that fitted line? [6]

Answers

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[1] Conc. of analyte in spiked sample = (10.0e-6 L)*(1.00e-2 mol/L)*(1/0.0500 L) = 2.00e-6 M

calculate slope of 2-point curve: Slope = (6.00-5.00μA)/2.00e-6 M = 5.00e5

so we have: y = 5.00e5(x) + 5.00 find x-int = -1.00e-5 M

[2] Plot current vs. $[Cd^{2+}]_{spike}$. Conc of spike = (10e-6 L * 1.51e-3M)/0.100-L = 1.51e-7 M

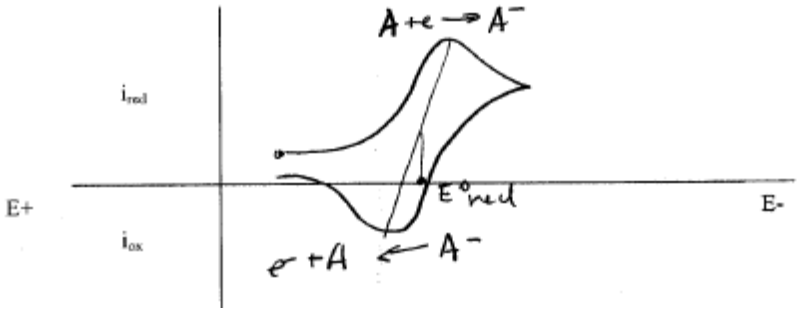
Slope = (6.77 – 4.31 μA) / (1.51e-7 M - 0) = 1.63e7 uA / M y-int = 4.31 uA

line: y = (1.63e7 uA / M) x + 4.31 uA

x-int: 0 = (1.63e7 uA / M) x + 4.31 uA x = - 2.65e-7 M

conc in 100-gm sample

2.65e-7 M * 0.100-L * 112.411 g/mol * 10e9/100-gm = 29.8 ppb (5 points)



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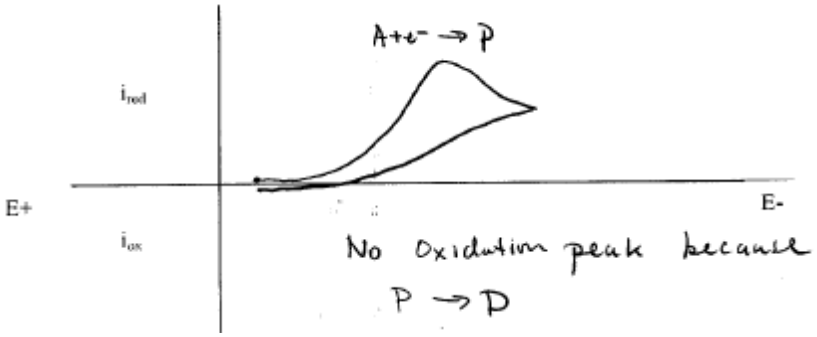

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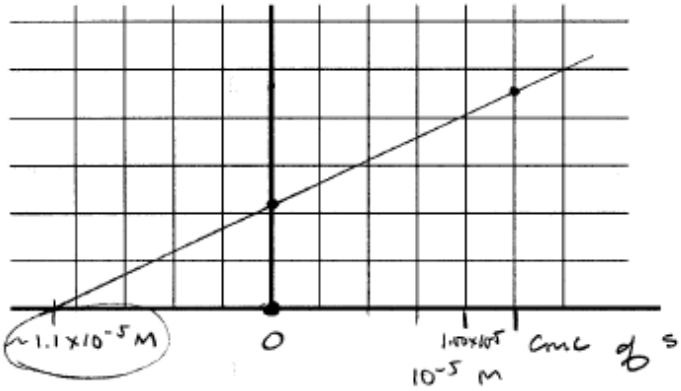


$\frac{0.0100}{20.01}\ 0.025\,M = 1.25\times10^{-5}\,M$

Compare

$y = \frac{23.1 - 10.1\,\mu A}{1.25\times10^{-5}\,M}\,x + 10.1\,\mu A$

$0 = 1.04\times10^{6}\,x + 10.1\,\mu A$

$x = 0.971\,M$

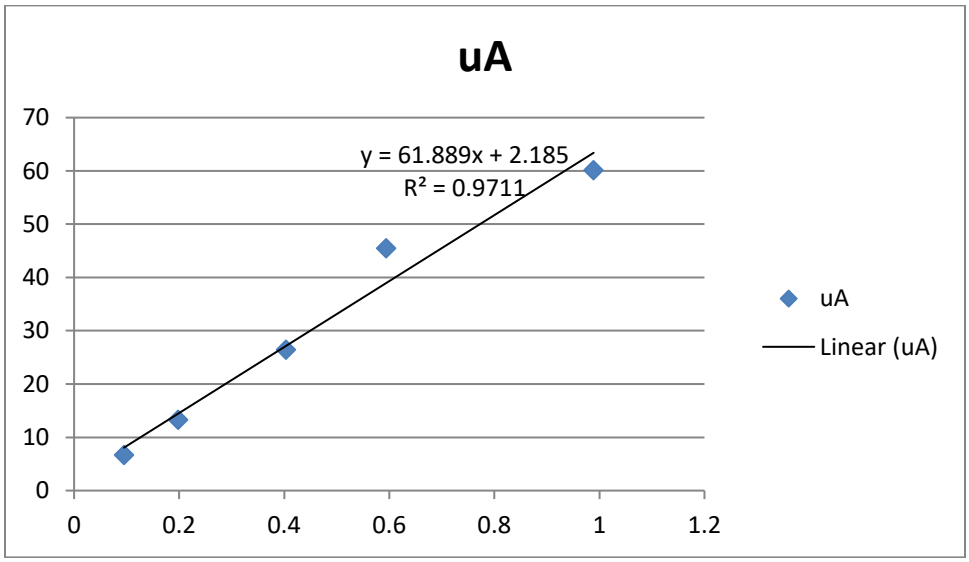
6

n	x [unk]	y uA	x^2	y^2	xy
5	0.095	6.64	0.009025	44.0896	0.6308
	0.198	13.29	0.039204	176.6241	2.63142
	0.403	26.44	0.162409	699.0736	10.65532
	0.594	45.49	0.352836	2069.34	27.02106
	0.989	60.11	0.978121	3613.212	59.44879

sum	2.279	151.97	1.541595	6602.34	100.3874
avg	0.4558	30.394			

Sxx	0.502827
Syy	1983.363
Sxy	31.11946

m =	61.88903
b =	2.184979
Sr =	4.37454
Sm =	6.16912
Sb =	3.425495



enter Unk # determ.	y-unk =	36.2
	M =	4
	x - unk =	0.549613
	Sc =	0.047522
	%Sc =	8.646425 %