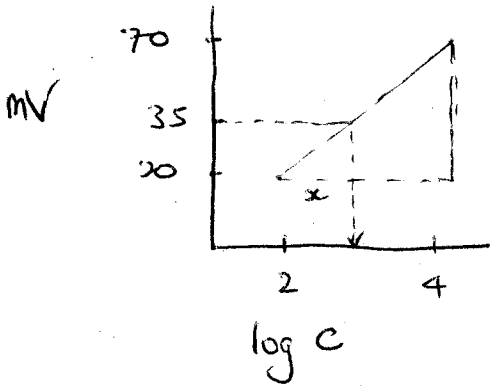
Chem. 312, Spring 2007. Exam # 2. **Name:** Solutions

Read everything before doing anything. Answer all the questions. Not all the questions are weighted equally; plan your time accordingly. Merit is attached to clarity of presentation (up to 5 points will be ~~deducted~~ awarded). There are six questions in total. Use the back of the sheets if you need more space.

1. You are the manager of an analytical laboratory that has been awarded a contract to determine chromium and mercury in the environment in Western Massachusetts. Your lab already has molecular spectrometry instrumentation, but you are thinking about maybe adding electrochemical and atomic spectroscopy instruments to help with the variety of analytical problems that are likely to arrive. The first task is the determination of chromium and mercury in the Quabbin reservoir, for which you need a procedure with a detection limit of a few ppb and a few ppt, respectively. Which of the following do you buy: an ion-sensitive electrode and high impedance voltmeter, apparatus for anodic stripping voltammetry, an atomic absorption spectrometer with an electrothermal atomizer, an atomic fluorescence spectrometer? (5 points) Explain your decision (10 points).

Best choice ETAAS and AFS (for the mercury).
The issue is detection limit(s). ISE will not reach ppb/ppt concentrations. ASV is not a good choice for Cr but might work for Hg^{2+} (easy to reduce and collect). Hg not so good by ETAAS (difficult to prevent losses during drying and ashing).

2. The sales representative for the company that sells a mercury ion-sensitive electrode has brought a system to demonstrate. She has two standard solutions: one containing 100 ppb and the other 10.0 ppm. She records the voltmeter responses for these solutions as 20.0 mV and 70.0 mV. You give her an "unknown" solution for which she measures the response to be 35.0 mV. What concentration does she calculate for your test solution in ng mL^{-1}? (10 points)



$\frac{x}{2} = \frac{15}{50}$ ∴ $x = 0.6$

∴ $\log C_x = 2.6$

∴ $C = 398$ ppb (same as $ng\,mL^{-1}$)

Three digits is OK.

The equation of the line is $mV = 25 \log C - 30$

↑ in ppb

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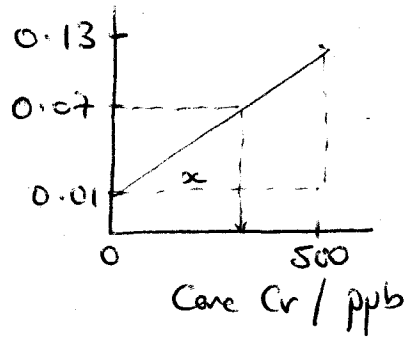
3. You ask your chief analyst to check out a flame atomic absorption procedure with the following description: A 100.0 mL of a standard solution containing 500 ppb chromium was passed through a column containing a filter material that is selective for chromium and all the chromium was retained. Then 10.0 mL of nitric acid was passed through the column to dissolve all the chromium. One hundred mL of the water used to make the standards and solutions was taken through the same procedure, as was 100.0 mL of soil extract solution. If the absorbances of the standard, blank and sample solutions were 0.130, 0.010 and 0.070, respectively, what is the concentration of chromium in the soil extract solution in ppb? (15 points). If the mass of soil taken was 250 mg, calculate the concentration of the extractable chromium in ppm (on a mass/mass basis). (10 points)

All solutions are treated the same. So plot calibration against concentration of standard before preconcentration.



$$\frac{x}{500} = \frac{0.06}{0.12} \quad \therefore \quad x = 250 \text{ ppb.}$$

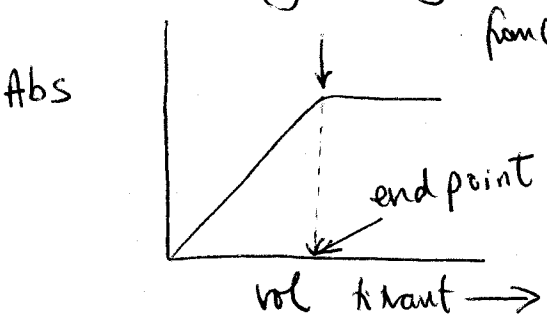
Total mass of Cr in 100 mL extract = 250 × 100 ng

$\therefore$ Conc^n in soil = $\frac{250 \times 100}{250}$ ng mg^{-1} (= μg g^{-1} = ppm)

= 100 ppm

4. Some samples may contain minor (as opposed to trace) amounts of chromium, so you make sure that your lab can determine chromium by spectrophotometric titration. A 25.00 mL sample of pulp mill waste solution is titrated with 0.0100 M diphenylcarbazide solution at pH 1.5. This reagent solution is colorless, but the reagent forms a bright red product with chromium. Suggest a wavelength at which the titration could be followed by measuring the absorbance as a function of the volume of titrant added. (5 points). Sketch the titration curve and indicate the end point. (5 points) If it requires 12.34 mL of the diphenylcarbazide solution to reach the end point, calculate the concentration of chromium in the pulp mill waste solution in % (m/V). The molar mass of Cr is 51.9961 g mol^{-1}. (10 points)

If solution is red, it must absorb at the blue end of spectrum so any wavelength between 400 and 500 nm would be OK.



from Qb $\quad Cr + 2R \longrightarrow CrR_2$ (red product)

mol DPC used = $12.34 \times 0.01 \times 10^{-3}$

$\therefore$ # mol Cr = $0.5 \times 12.34 \times 0.01 \times 10^{-3}$

$\therefore$ conc Cr = $\frac{0.5 \times 12.34 \times 0.01 \times 10^{-3}}{25} \times 10^{3}$ M

= 2.468×10^{-3} M.

$\therefore$ Conc^n in g L^{-1} = $2.468 \times 51.9961 \times 10^{-3}$
= 0.12832

$\therefore$ Conc^n in g per 100 mL = 0.0128 (three digits)
(% in g per 100 mL)

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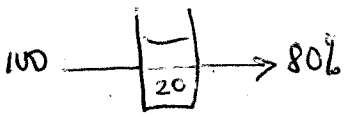
5. What about visible absorption spectrometry? Mercury reacts with dithizone to form a colored complex with molar absorptivity 2,000 L mol^{-1} cm^{-1} at 600 nm. If a test solution absorbs 20.0% of the radiation in a 1.00-cm cell, what is the concentration of Hg in the solution, in ppm, if the mercury dithizone complex contains only one Hg atom? (10 points) Estimate the limit of detection (in ppb) for the spectrophotometric determination of Hg with this reagent. (5 points). The molar mass of Hg is 200.59 g mol^{-1}.



$A = 2 - \log(\%T) = 2 - \log 80 = 0.09691$

$\therefore 0.09691 = 2000 \times 1 \times C$ where C is conc of Hg in $mol\,L^{-1}$

$\therefore C = 4.8456 \times 10^{-5}$ M

$\therefore$ conc in gL^{-1} $= 4.846 \times 10^{-5} \times 200.59$
$= 9.72 \times 10^{-3}$ gL^{-1}

$\therefore$ conc in mgL^{-1} (ppm) $= \underline{\underline{9.72}}$ (3 digits).

If the lowest concentration that can be measured gives 0.002 abs then $0.002 = 2000 \times 1 \times C_{LOD}$

$\therefore C_{LOD} = 1.0 \times 10^{-6}$ (M)

$C_{LOD} = 2 \times 10^{-9}$ gL^{-1}

$= \underline{\underline{200}}$ ppb (μgL^{-1}).

If abs 0.09691 corresponds to 9.72 ppm then 0.002 abs corresponds to 0.2 ppm ie $\underline{\underline{200\ ppb}}$ (1 digit for detection limit)

6. Write instructions for the preparation of the 0.0100 M diphenylcarbazide titrant. (10 points) Diphenylcarbazide forms a 2:1 complex with chromium (i.e. two molecules of diphenylcarbazide react with one chromium ion), its formula is $C_{13}H_{14}N_4O$, the molar mass is 483 g mol^{-1}, and it is not very soluble in water.

If the compound is not very soluble it will not be a good plan to try to make a concentrated solution and then dilute it. So go straight for the 0.0100 M solution. Choose a convenient volume, say 1 L. Mass needed would be 4.83 g.

So Weigh by difference approximately 4.83 g of diphenylcarbazide and transfer to a 500 mL beaker. Add about 250 mL of water and warm with stirring. When no more material dissolves, transfer to a 1 L calibrated flask and repeat with a further 250 mL of water. When all the material has dissolved, dilute to the mark with distilled water.

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