Chemistry 4440 First Test
Thursday, September 22, 2011

1. (***20 points***) Your TA made a series of dilutions to a liquid, Mn-containing sample that you analyzed by AAS. Her dilutions involved taking 1.00 ml of that sample containing some manganese and boiling it with concentrated nitric and hydrofluoric acid for 15 minutes. The liquid left was diluted to 100.0 mL with Mn-free water with mixing. A 25 μL aliquot of that solution was diluted to 25.00 mL volume with more Mn-free water and mixed well. Finally 5 mL of this well-mixed solution was transferred to a 50-mL volumetric, 5 mL of concentrated HNO_3 was added to the flash which was diluted to the line with Mn-free water and mixed. This solution was determined to have 23.45 ppb Mn. What was the percentage by mass of Mn in the original solution assuming that solution has a density of 1? You can use the back of this page if necessary.

2. (***20 points***) A well characterized AAS Mn calibration procedure, run many times and shown to be reproducible produced the following data (Mn ppm, **$Abs_{279.61nm}$**): 0.0, **0.0290**; 2.0, **0.173**; 6.0 **0.453**; 10.0, **0.702**; 14.0, **0.956**; 18.0, **1.244**. The LLS fit for these data is y = 0.0665x + 0.0381. The same data were corrected for the absorbance of the 0.0, **0.0290** sample and the new data set yielded a new LLS fit of y = 0.0665x +0.009.

A week after this calibration was carried out, a sample from the field and blank containing no added Mn were analyzed with the same method. The sample's absorbance at 279.61 nm was 0.261 and the blank reading was 0.042. A) Calculate the concentration of manganese in that field sample. B) **How exactly were the data corrected** for the second LLS fit?

3. (***15 points***) Determine the volume of a 6.345 x 10^{-2} M $Ba(NO_3)_2$ stock solution (in units of μL) necessary to dilute to a final volume of 25.00 mL to make a solution whose final concentration is 25.00 mg barium per L. What is the concentration of nitrate in that diluted sample in ppm? Show your calculations for full points. Use the back of this sheet for work if necessary.

4. (***10 points***) Subtract the binary number 101010_2 from the base ten number 1235_{10} and report the result in hexadecimal.

5. (10 points) I have a proposed new colorimetric reagent for the determination of cocaine metabolite in saliva. When I dissolve 0.00125 moles of the new reagent in 50.00 mL of ethanol, mix well, and transfer 2.00 mL to a 1.5-cm, fused silica cuvette, put pure ethanol in the reference beam and measure the absorbance at 285 nm it is found to have an absorbance if 0.55. What is the molar absorptivity (cm^{-1} M^{-1}) of this new reagent? Is it a good candidate for cocaine metabolite detection?

6. (10 points) Although it's invisible to the naked eye, 190 nm is on the edge of the vacuum UV what is the energy of an Einstein of these photons?

1. (***15 points***) Match the **best answer** given the following:

1. internal standards _____

2. external standards _____

3. molar absorptivity _____

4. corrected absorbance _____

5. A_{254} = 25.0% T _____

6. assumption that sample density is 1 _____

7. assumption that you need sample density to determine ppm analyte _____

8. LLS intercept close to 0 _____

9. double beam spectrophotometer_____

10. stopping voltage _____

A. absorbance reading of sample subtracted from that of blank

B. cigarettes cause lung cancer

C. good if sample is very dilute

D. A_{254} = -1.39

E. prepared separately from a sample

F. for standard data corrected for blank reading

G. for standard data not corrected for blank reading

H. 0.32 mm i.d.

I. A_{254} = 0.602

J. A_{254} = 1.39

K. amount of absorbance

L. useful for S- and P-containing analytes

M. corrects for poor nebulizer uptake

N. THC

O. depends on chemical composition of the photocathode

P. large when light intensity is low

Q. uses noble gas lamps like Kr and Ar

R. blank absorbance subtracted from sample absorbance

S. added to samples, blanks, and calibration standards

T. a unit of chromatographic resolution

U. good if sample is concentrated with analyte

V. corrects for light emission by AAS flame

X. corrects for drift of HCL

Y. corrects for drift of HCl

Z. proportionality constant

Formulae that <u>may</u> be useful:

$$\Delta f = \frac{1}{3t_r}$$

$$c_x = \frac{(S_1 c_s V_s)}{[(S_2 - S_1) V_x]}$$

Beer's Law: A = εbc

$$\nu = \sqrt{4kTR\Delta f}$$

$$\text{Frequency} = \frac{1}{\text{Conversion rate}}$$

Equation for a line: y = mx + b

E= hν

mass electron 9.11 x 10^{-28} grams

$$C_x = \frac{S_1 c_s V_s}{(S2 - S1)V_x}$$

h = 6.626 x 10^{-34} Js

$$i_{rms} = \sqrt{2Ie\Delta f}$$

$$s = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2 / N}{N-1}}$$

speed of light = 3.00 x 10^8 m/s

$$\gamma = \frac{m}{S_S}$$

c =λν

$$A = \log \frac{P_0}{P}$$

A =-log T

$$E = \frac{1}{2} mv^2$$

1J = kg·m^2 sec^{-2}

photons rest mass = 0