CHEM-241 **KEY** **EXAM 1**
October 2, 2001 **Name:___________________________**

Score: __________________

Multiple Choice (4 points each) **Questions (1-7)**

Circle the answer (or answers) for each question.

1. The method of least squares for determining the best straight line through a collection of data points is based on what principle?
   a) R2 should be equal to one.
   b) Both sm and sb are negligible.
   c) The slope should be close to 1, and intercept should equal 0.
   d) The sum of the squared y-residuals is minimized.

2. To determine if the result from a chemical analysis is correct, which of the following would be most useful?
   a) Calculate the pooled standard deviation.
   b) Perform many more replicates.
   c) Compare the results to those obtained from another analysis.
   d) Perform a Q-test to reject outliers.

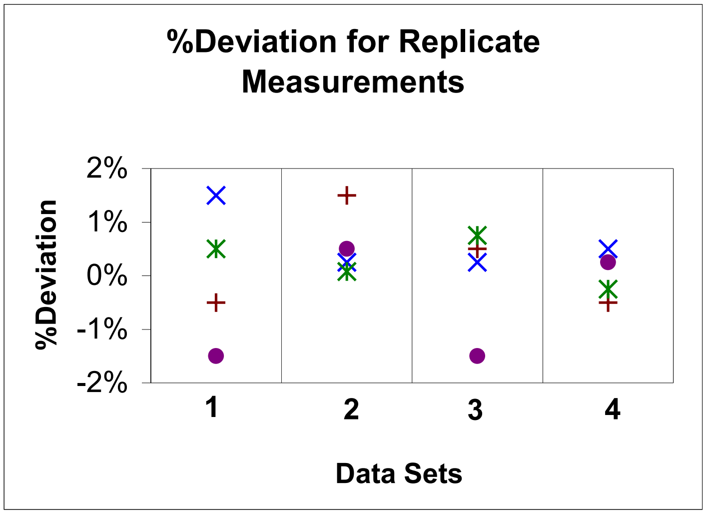
3. What is the best method for determining the concentration of a NaOH solution?
   a) Titrate the solution with HCl until a red/clear endpoint is detected.
   b) Standardize with KHP (potassium hydrogen phthalate).
   c) Check the pH with litmus paper.
   d) Measure the pH of the solution with a calibrated pH electrode.

4. Below several solubility products, K_{sp}, are listed for calcium salts. Which reagent would allow the most complete gravimetric analysis of Ca^{+2}?

salt	K_{sp}		reagent
$CaSO_4$	$2.4x10^{-5}$	a)	0.05M Na_2SO_4
$CaCO_3$	$4.5x10^{-9}$	**b)**	**0.05M Na_2CO_3**
$CaOH_2$	$6.5x10^{-6}$	c)	0.10M NaOH
$CaCl_2$	$1.57x10^{-3}$	d)	0.10M NaCl

5. With which of the following analytical methods is it possible to have the greatest precision?
   a) volumetric titration
   b) linear calibration
   c) gravimetric
   d) spectrophotometric

Figure for question 6 and 7.



6. Which of the data set(s) is the most accurate?
   1 2 3 **4** **(either)**
   Which of the data set(s) is the most precise?
   1 2 3 **4**

7. Which of the data set(s) is the most affected by a systematic error?
   1 **2** 3 4
   Which data set(s) is the most affected by random error?
   1 2 3 4

Calculations and Short Answer. (10 points each) **Questions 8-14**
Work neatly in the space provided. Circle your final answer. To receive partial credit, show all equations and the steps involved for multi-step calculations.

8. Calculate the average and standard deviation of the following replicate values:
   5.1, 5.3, 4.8, 5.4, 5.2, 5.6

   average: **5.2_3** **standard deviation:** **0.2_7**

   Which of the following values, if any, would be considered abnormal, at the 90% confidence level?

   t=(90%,(6-1))=2.015 conf interval: x ± t*s/(n)^.5 =2.015*0.27/2.45=**$5.2_3 \pm 0.2_2$**
   Values in the range: 5.01 to 5.45 are within the 90% confidence interval.
   The following {BOLD} numbers are not.
   4.2 **4.4** **4.6** **4.8** **5.0** 5.2 5.4 **5.6** **5.8** **6.0** **6.2**

9. The following calcium levels were measured for a patient on two different days.

<u>Day 1:</u> 55.8; 57.4, 60.6, 64.2   <u>Day 2:</u> 61.2, 64.6, 67.9, 67.5, 69.3

x=59.5_0 s=3.7_1 x=66.1_0 s=3.2_3

Calculate the pooled standard deviation for the patient's calcium level.

S_p=((3*(3.7_1)^2+4*(3.2_3)^2)/(4+5-2))^.5

s_p=3.4_5

At what percent confidence are the patient's calcium levels on these two days statistically different?
(Remember to show equations and calculations for partial credit.)

t_{calc}=((59.5-66.1)/3.45*(4*5/9)^.5)=2.8_6

df=(5+4-2)=7   t(95%,7)=2.365

t(98%,7)=2.998   *by iteration: t_{calc} ~ 97.3%*

t_{calc}>t(95%) but t_{calc}<t(98%)

The two mean calcium levels are different at a greater than **95% confidence level**.

10. To prepare a 100-ml, 0.005 M NaOH solution from a 0.098 ±0.002 M stock solution, how many milliliters of the stock solution need to be diluted?

$M_1V_1=M_2V_2$ V_1=.005*.100/.098*1000   **V_1=5.1_0 ml**

What is the absolute uncertainty of the concentration of the dilute solution that was prepared? Assume the 100-ml flask is accurate to ±0.2 ml and the pipette used is accurate to ±1%.

$M_2=M_1V_1/V_2$ re(M_2)=((reM_1)^2+(reV_1)^2+(reV_2)^2)^.5

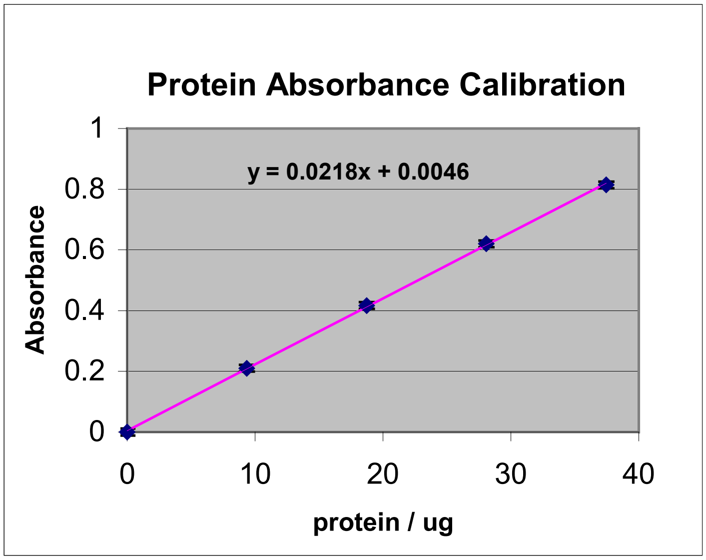
=((.0204)^2+(.01)^2+(.002)^2)^.5

re(M_2)=0.02_{28}

e(M_2)=re(M_2)*M_2=0.0228*0.005

e(M_2)=±0.0001_1 M

Figure for problem 11.



Output of LINEST Function

m=	0.021774	0.0046	=b
s_m=	0.000192	0.004391	=s_b
R^2=	0.999768	0.005669	=s_y

11. UV absorbance values for four protein samples were measured and corrected by subtracting the absorbance from a blank solution. An unknown sample gave an absorbance of 0.507 after correcting for the blank absorbance. Calculate the concentration of protein in the sample.

y=m*x+b   x=(y-b)/m   =(0.507-.0046)/.02177

x=23.1 ug of protein (or 23.0_7)

Propagate the error from the least-squares statistical analysis (LINEST) and report the absolute uncertainty of the protein concentration.

x=(y-b)/m   re(y-b) =(e(y)^2+e(b)^2)^.5/(y-b)

=((.00567)^2+(.00439)^2)^.5/(.507-.0046)

=0.014_3

re(x) =(re(y-b)^2+re(m)^2)^.5

=((0.0143)^2+(.000192/.02177)^2)^.5

=0.016_8

e(x) =re(x)*x

=0.016_8*23.0_7

e(x) =±0.3_9 ug protein

12. What is noise in a spectroscopic measurement, and how can we reduce it?

a) Noise in spectroscopy can come from random fluctuations in the current (e^-) in the phototransducer of the detector. This comes in two parts, thermal noise and/or shot noise. Noise can also come from random fluctuates in stray light that reaches the detector.
b) The noise can be reduced relative to the signal by collecting and averaging many measurements; this is called ensemble averaging. Digitally smoothing the data, e.g. boxcar average, which averages n adjacent points and plotting the new average values, can reduce the appearance of the noise. It is best to find a way to eliminate the noise, by lower the temperature of the detector or by using a shutter or filter to prevent stray light from reaching the detector.

13. Six iron tablets containing $FeSO_4$-$7H_2O$ were dissolved in 100-ml of 0.1M HNO_3 with gentle heating. All of the Fe^{2+} is converted to Fe^{3+} by the strong oxidizing conditions. After the solution had cooled to room temperature 2.5-ml of 35wt% NH_4OH was added. The precipitate Fe_2O_3-xH_2O that was filtered weighed 0.345g. Thermogravimetric analysis of the crude product showed a 10.5% weight loss below 150 C.

    How many waters of hydration were in the precipitate? (i.e. Solve for x in Fe_2O_3-xH_2O.)

    moles of H_2O=Mass*(wt%/100)/FW-H_2O =0.345*.105/18.01
    =0.00201 molH_2O
    moles of Fe_2O_3=mass*((1-wt%)/100)/FW-Fe_2O_3 =.345*.895/159.69
    =0.00193_3 mol Fe_2O_3

    mol Fe_2O_3/ molH_2O=0.962 **x=1** **Fe_2O_3*$1H_2O$**

    How much iron was in each of the tablets? Report the average mg-Fe per tablet.

    from above: analysis gave 0.00193_3 mol Fe_2O_3
    Mass of Fe =$.00193_3$ mol Fe_2O_3*2mol-Fe/mol-Fe_2O_3*55.845g/mol-Fe
    =0.215_9 g Fe

    mg Fe/ Tablet =0.215_9 g-Fe/6-tablets*1000mg/g
    =35.9_8 or 36.0 mg-Fe/tablet

14. Approximately 44% of the light at 250-nm was transmitted through a 0.0025 M solution containing caffeine. 91% of the light at 300-nm was transmitted through the same solution. Assuming a 1-cm path length calculate the molar absorptivity coefficient at each wavelength.

    T_{250}=0.44 A_{250}=-log(T) =-log(.44)=0.35_7
    A=e*l*[C] ε=A/l/[C] ε_{250}=0.357/1/0.0025 **ε_{250}=140 $(cm*M)^{-1}$**

    A_{300}=-log(T) =-log(.91)=0.041_0
    A=e*l*[C] ε=A/l/[C] ε_{300}=0.0410/1/0.0025 **ε_{300}=16 $(cm*M)^{-1}$**

    Which wavelength would be the most useful for constructing a calibration curve? Why?

    A calibration at 250-nm would be better because more light was absorbed by the caffeine solution at 250 nm than at 300 nm. According to Beer's Law the slope of a linear calibration plot should equal the molar absorptivity coefficient (m~ε) (as calculated above). Since the molar absorptivity at 250 nm is almost 10 times larger than at 300 nm, a calibration plot at 250 nm would be approximately 10 times more sensitive to changes in caffeine concentration.