CHEM 241 **EXAM #1**
February 4, 2003

Name: Answer Key

1. True/False----Indicate whether the following statements are **True** or **False** in the space next to the statement. Make sure you carefully read each statement ! (2 points each)

False a) In comparing two analytical methods, the method with better precision will always be the most accurate method to measure the concentration of a given analyte.

False b) The Q-Test is often used to determine whether the mean values measured by two different analytical methods are statistically different than one another.

True c) The Volhard method involves a back titration of excess reagent silver ions with thiocyanate, as a means to determine the concentration of halides that form insoluble precipitates with the silver ion reagent.

False d) The method of least squares for determining the best straight line through a collection of data points is based on maximizing the sum of the squared y-residuals.

False e) In modern combustion analysis methodology used for C,H,N, and S analysis of organic compounds, the nitrogen content is measured by the separation of nitrogen dioxide gas (NO_2), the oxidation product of elemental nitrogen, by gas chromatography.

False f) In gravimetric methods of analysis based on formation of insoluble salts, it is essential that the solubility product (K_{sp}) of the precipitate be as high as possible so that a very large percentage of the analyte ion (>99.9%) will precipitate without having to add too great an excess of reagent. .

False g) Salicylate is the conjugate acid of salicylic acid.

False h) The number 0.00300043 has 3 significant figures.

False i) When propagating errors in adding or subtracting two numbers with a certain degree of uncertainty, the final uncertainty will be the square root of the sum of the two relative uncertainties squared for the respective numbers.

True j) Masking involves adding a reagent to reduce the effect of another species in the sample that would otherwise interfere with the measurement of the analyte.

2. Multiple Choice Questions:--Please circle the best answer for each question or the best choice to finish the phrase (4 points each).

-A solution of 1.00 x 10^{-6} M solution of $CaCl_2$ would have how many ppb (parts per billion) of Ca^{++} (assume atomic mass of Ca =40.0)?

a) 111 ppb
b) 40 ppb
c) 10 ppb
d) 400 ppb

- In UV-Vis spectrophotometric methods of analysis, if the solution has an absorbance value of 0.025 (determined with appropriate blank), then the % transmittance is:

a) 9.44%
b) 97.5 %
c) 94.4 %
d) 2.50%

- The true concentration for an analyte in a given sample can only be determined by:

a) performing at least 10 measurements with the most precise method available and averaging the 10 results.

b) performing thousands of measurements on the same sample using methods that are known to suffer only random sources of errors, and averaging the results.

c) making thousands of measurements on the sample using a method that is known to suffer from a determinate source of error, and then averaging the results.

d) making hundreds of measurements on the sample using a method that is known to yield a gaussian distribution of results, and then averaging the results.

The solubility product (Ksp) for $AgBr_{(s)}$ is 5.0 x 10^{-13}. What would be the concentration of soluble silver ion in a 0.05 M NaBr solution that was saturated with $AgBr_{(s)}$?

a) 7.1 x 10^{-7} M
b) 2.5 x 10^{-11} M
c) 1.0 x 10^{-11} M
d) 5.0 x 10^{-2} M

- An aspiring young analytical chemist used 9.25 (±0.02) mL of NaOH base with a molarity of 1.05 (± 0.02) M to reach the end-point for the titration of an unknown acid solution. The number of <u>moles</u> of acid present and the uncertainty of this number is best reported by which of the following:

a) 9.71 (±0.03) moles
b) 9.71 (±0.02) moles
c) 0.00971 (±0.02) moles
d) 0.00971 (±0.0002) moles

Problems

3. Two methods were used to measure the specific activity of an enzyme. One unit of an enzyme is defined as the amount of enzyme that catalyzes the formation of one μmole of product per minute under specified conditions. The results for six replicate measurements by each method were as follows:

Method 1: 135, 147, 159, 158, 150, 160 $\bar{X}_1 = 151.5$; $s = 9.7$
Method 2: 159, 165, 168, 170, 166, 169 $\bar{X}_2 = 166.2$ $s = 4.0$

a) Decide whether any data obtained by a given method can be rejected with 90% confidence; b) Then, for method #2, determine the range of values in which the true value likely falls with 95% confidence; c) Finally, determine whether the mean values obtained by the two methods are statistically different at the 95% confidence level. (15). (Show work for partial credit)!!

a) Q-Test : Method 1 ; $Q = \frac{|gap|}{|range|} = \frac{12}{25} = 0.48$

$0.48 < 0.56$ (Q for n=6)

∴ Can not reject 135 value

Method 2 ; $Q = \frac{6}{11} = 0.55 < 0.56$

∴ Can not reject 159 value

b) $\mu = \bar{X}_2 \pm \frac{st}{\sqrt{n}} = 166.2 \pm \frac{(4.0)(2.57)}{\sqrt{6}} = 166.2 \pm 4.2$

$t = 2.57$ (df = 5)

range = 162.0 − 170.4

162.0 − 170.4

c) $t = \frac{|\bar{X}_1 - \bar{X}_2|}{S_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$

$S_{pooled} = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n-1)}{n_1 + n_2 - 2}} = \sqrt{\frac{9.7^2(5) + 4.0^2(5)}{10}}$

$= 7.42$

$t = \frac{|151.5 - 166.2|}{7.42} \sqrt{\frac{6 \times 6}{12}} = \frac{14.7}{7.42}\sqrt{3} = 3.43$

$t = 3.43 > t_{95\%}(df = 10) \rightarrow 2.228 \therefore$

Mean values are statistically different @ 95% confidence

4. A 30.00 mL solution containing an unknown amount of I^- was treated with 50 mL of a 0.3650 M solution of $AgNO_3$. The precipitate of AgI that resulted was filtered off, and the filtrate solution (plus a little Fe^{+3}) was titrated with 0.2870 M KSCN. When 37.60 mL had been added, the solution turned red. What was the molar concentration of I^- in the original 30.00 sample? (show work for partial credit) (10)

$0.365 \times 50\,ml = 18.25$ mmoles Ag^+ total

$0.2870 \times 37.60\,ml = 10.79$ mmoles $SCN^- = Ag^+$ moles left

7.46 mmoles Ag^+ used to ppt I^-

$\therefore \frac{7.46\,mmoles}{30.00\,ml} = 0.2487M\ I^-$

5. In spectroscopic methods, briefly explain how ensemble averaging can be used to increase the S/N ratio, and thereby improve the detection limits of the method. How many measurements would need to be made to enhance the S/N by a factor of 10? (10)

Ensemble averaging is a method where the spectrum is obtained n times and averaged. The noise is the standard deviation of the signal, and it is random. Hence, if you average n spectra, the noise will tend to cancel out since it is random, but the real signal component (e.g., absorption bands, etc.) are truly additive, and hence when you take the average of n spectra, you improve the S/N by $\mathbf{n^{1/2}}$. Therefore, to improve the S/N by a factor of 10, n must be equal to 100

6) Calculate a) the pH of a solution containing 0.0035 M KOH? (5)

$$[H^+] = \frac{10^{-14}}{3.5\times10^{-3}} = 2.86\times10^{-12}$$

$$pH = -\log(2.86\times10^{-12}) = \boxed{11.54}$$

b) the pH of a water solution that contains 0.035 M of phenylacetic acid, which has a pKa value of 4.31. (show work for partial credit) (10).

$$pKa = 4.31; \therefore Ka = 4.90\times10^{-5}$$

$$4.90\times10^{-5} = \frac{x^2}{F-x}; \quad \text{assume } F \gg x$$

$$F = 0.035$$

$$4.90\times10^{-5} = \frac{x^2}{0.035}$$

$$x^2 = 1.715\times10^{-6}$$

$$x_1 = 1.310\times10^{-3}$$

$$4.90\times10^{-5} = \frac{x^2}{0.035 - 1.31\times10^{-3}}$$

$$\rightarrow x_2 = 1.285\times10^{-3}$$

$$4.90\times10^{-5} = \frac{x^2}{0.035 - 1.285\times10^{-3}}$$

$$x_3 = 1.285\times10^{-3}$$

5

$$[H^+] = 1.285\times10^{-3}$$

$$pH = -\log 1.285\times10^{-3} = \boxed{2.89}$$

7. A recent graduate of U of M was fortunate enough to obtain a job at a new start-up company in Ann Arbor, name Criticare. This company's first product was going to be a small portable spectrophotometric meter and single-use disposable that would be able to detect the levels of total hemoglobin (Hb) in a single drop of whole blood (obtained by finger prick), very similar to a very successful product already on the market (developed and sold by HemoCue Inc., with sales of over $35 million/year). The U of M grad was assigned the task of determining the optimal path-length specification that would be required in the disposable plastic cuvette into which the drop of blood would wick (to be manufactured by injection molding). The student knew the following: a) the normal range of Hb in blood is 11-19 g/dl (grams per 100 mL); b) Hb has a molecular weight of 43,500 (on average); c) the molar absorptivity of cyanmethemoglobin (the species that would be formed by the dry reagents in the cuvette) is 25,000 $M^{-1}cm^{-1}$ at 540 nm; d) the proposed instrument would have an LED light source centered at this wavelength; and e) the most precise absorbance measurements can be made when the measured absorbance value is close to 0.5. Hence, since the student had taken Chem 241, he/she decided that it would be best if the cuvette were designed to yield this absorbance value (and thus optimal precision) at the average normal concentration of Hb in blood. What pathlength in millimeters (mm) should this former student propose to the engineers designing the disposable cuvette? (show work for partial credit) (10).

$$\text{Avg Hb} = \frac{11+19}{2} = 15\ g/dl = 150\ g/L$$

$$\text{Molarity} = \frac{150\ g}{43{,}500} = 3.45 \times 10^{-3}\ M$$

$$A = \varepsilon b c;\quad 0.5 = 25{,}000\,(b)\,3.45 \times 10^{-3}$$

$$b = 0.0058\ cm$$

$$= \boxed{0.058\ mm}$$

Bonus Question:

In an single-use immunochromatography test strip that can be used to test for pregnancy by detecting the presence of the protein hormone human chorionic gonadotropic (hCG), what is the name for the type of immunoassay method that makes use of two different antibodies that selectively bind to two different sides of the same analyte protein, that enables the method to work so well! (3)

Sandwich immunoassay