Chem. 312, Spring 2007. Practice Exam # 1. Name: Solutions

If you bring solutions to class on Wednesday February 28th, it will count towards 10% of the real exam (if this would help). It will not count if your real exam score would be lowered by the inclusion of your score for the practice exam. No partial credit is available, so just provide a list of answers. Read everything before doing anything.

1. Imagine you are the manager of an analytical laboratory. A potential client comes to ask you to provide analytical support for the manufacture of tablets containing selenomethionine (the analogue of the amino acid methioinine in which the sulfur atom has been replaced by selenium) and vitamin E that are to be used in a clinical trial of the anti-cancer properties of these compounds. List five of the questions that you would ask this person that would help you decide whether your lab could take on this project and allow you to calculate how much to charge. (10 points).

1. What are the analytes?
2. What are the concentrations of the analytes?
3. What else is in the tablets?
4. How many samples will you send?
5. How quickly do you want the results?

2. You are writing instructions so that your lab staff can determine the total selenium content of a single tablet. You need them to prepare 1000.0 mL of a standard solution containing 5.00 x10^2 ppm of selenium from solid anhydrous sodium selenate, which is readily soluble in water. What mass of the solid do you tell them to weight out? (atomic weights: Na 22.989768, Se 78.96, O 15.9994, H 1.0079). (10 points).

500 ppm is 500 mg L^{-1} so 500 mg is needed.

$\therefore$ mass of Na_2SeO_4 needed $= 500 \times \frac{188.937136}{78.96}$ mg

$= 1196.410436$ mg

$= \underline{1.20 \text{ g}}$ (3 digits) (I would accept 4)

3. For sample preparation, you propose weigh one tablet, which is then transferred to a Teflon vessel to which is added 10 mL of concentrated nitric acid. The vessel is sealed and heated in a microwave oven until the organic matter has been mostly converted to carbon dioxide and water, and the inorganic constituents have been dissolved. Any selenium will have been oxidized to selenate. The vessel is cooled, carefully opened and the contents transferred to a 50-mL flask and made up to volume. To validate the method, you ask one of your staff to analyze a standard reference yeast material containing 1250 ± 25 μg kg^{-1} of selenium, where the ± term is the 95% confidence interval. The following 5 replicate values are obtained: 1150, 1250, 1180, 1160 and 1260 μg kg^{-1}. What can you deduce about the accuracy of your proposed method? ($t_{95\%,\ n=5}$ = 2.78, $Q_{95\%,\ n=5}$ = 0.72)? (10 points). Give reasons for your answer (10 points). Comment on the precision of the method (5 points).

First check for outliers with Q test. $Q_{calc} = \frac{10}{110}$ obviously $< Q_{tab}$

$\therefore$ no outliers.

Use calculator: $\bar{x} = 1200\ \mu g\ kg^{-1}$, $s = 51.48\ \mu g\ kg^{-1}$

$95\%\ CI = \frac{ts}{\sqrt{n}} = \frac{2.78 \times 51.48}{\sqrt{5}} = 64.00\ \mu g\ kg^{-1}$

So result of analysis is $1200 \pm 64\ \mu g\ kg^{-1}$ as this interval includes 1250, the procedure is accurate.

The relative standard deviation is 4.29%, this is acceptable for determinations in the 5 - 50 ppb concentration range.

You cannot compare the 95% CI as you don't know the value for n in the calculation of the $\pm 25\ \mu g\ kg^{-1}$

4. You find a titrimetric procedure for the determination of selenate in which the titrant forms an insoluble compound with selenate. You get one of your staff to set up the automated microtitrator instrument for this analysis and to check that it is possible to determine to determine 250.0 μg of selenium. What volume of the stock 5.00 x10^2 ppm solution is taken for the test? (10 points).

500 ppm is 500 $\mu g\ mL^{-1}$ so to get 250 μg you need 0.500 (3 digits) mL. I will accept 0.5000 (4 digits).

5. For this titration a buffer solution at pH 3.76 is needed. You choose acetic acid (CH_3COOH, K_a 1.74 x 10^{-5} molecular weight 60.05) and sodium acetate as the buffer components. What masses of each compound do you tell your assistant to weigh out to make 1.00 L of the buffer? (15 points)

$$pH = pK_a + \log \frac{[acetate]}{[acetic\ acid]}$$

If $K = 1.74 \times 10^{-5}$ $pK_a = 4.76$

$\therefore 3.76 = 4.76 + \log \frac{[acetate]}{[acetic\ acid]}$

$\therefore \log \frac{[acetate]}{[acetic\ acid]} = -1$. So choose a value of $[CH_3COOH]$.

If the concentration of CH_3COOH is 1 M then the concentration of CH_3COO^- must be 0.1 M.

$\therefore$ mass CH_3COOH needed = 60.05 g (in one liter).

mass CH_3COONa needed = 82.03 g

(60.05 - 1.0079 + 22.9898)

6. Your assistant adds the acetic acid, then the fire alarm goes off and he forgets to add the sodium acetate. What is the pH of the solution? (15 points)

What is the pH of a 1M CH_3COOH solution.

$$K_a = \frac{[H^+][A^-]}{[HA]} = 1.47\times10^{-5} = \frac{x^2}{1-x}.$$

Solve for x: (method of successive approximations

gives $x = 3.83\times10^{-3}$ $\therefore$ $pH = 2.42$.

7. Back to Q 4. If the reaction between the precipitating agent (titrant) and selenate has a 2:1 stoichiometry and the titrant concentration is 1.00 x 10^{-3} M, what volume of titrant should have been added when the equivalence point is reached? Selenate is the analogue to sulfate (the sulfur atom has been replaced by a selenium atom), so the formula of sodium selenate is Na_2SeO_4. (15 points).

$$\# \text{ mol Se} = \frac{250\times10^{-6}}{78.96} = 3.16616\times10^{-6}$$

$\therefore$ # mol reagent needed $= 2\times 3.16616\times10^{-6}$

$\therefore$ volume of reagent sol^n $= \dfrac{2\times3.16616\times10^{-6}}{1.00\times10^{-3}}$ L

$= 6.33$ mL (3 digits)