Chem. 312, Spring 2007, In-class Exam # 1. **Name:**

Time allowed: one hour. Read everything before doing anything. Answer all the questions in any order that seems logical. 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 for messy work). There are six questions in total. If you need more space, use the backs of the pages.

1. Imagine you are the manager of an analytical laboratory. A potential client comes to ask you to provide information about the arsenic content of the fresh chickens sold in a national supermarket chain. A recent journal article suggests that there may be cause for concern (Lasky, T; Sun, WY; Kadry, A; Hoffman, MK "Mean total arsenic concentrations in chicken 1989-2000 and estimated exposures for consumers of chicken" *Environmental Health Perspectives,* **2004**, *112*,18-21). 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. (15 points)

1. What are you going to do with the result?
2. What is the likely concentration of arsenic in the chickens?
3. How precise ie what ± term?
4. How often are samples to be analyzed?
5. How many samples will arrive at once.

2. It is considered safe to consume up to 2 μg of arsenic per kg of body weight per day. Should we be concerned about the arsenic content of chicken meat? (5 points) Give reasons for your answer. (5 points) You might want to leave this question till you have answered some of the others.

Suppose the chicken standard is typical. Then if a typical serving was 5 oz of chicken then the amount of arsenic in a 5 oz portion would be $500 \times \frac{5}{2.2 \times 16} = 71\ \mu g$. An average person might weigh 150 lb = 68 kg, so the safe limit would be 136 μg.

To exceed the safe limit a 68-kg person would need to consume 9.6 oz of chicken (with this level of contamination). We should not be concerned about As in chicken meat.

3. You are writing instructions so that your lab staff can determine the total arsenic concentration (i.e. the sum of the concentrations of all chemical forms of arsenic) in a sample of chicken breast. You need them to prepare 250.0 mL of a standard solution containing 1,000 ppm of arsenic from solid anhydrous arsenic(III) oxide, which is readily soluble in water. What mass (in g) of the solid do you tell them to weight out? (atomic weights: As 74.922, O 15.9994, arsenic (III) oxide, 197.84). (10 points) Later on in the procedure you want this stock solution to be diluted so that a range of standards is available to calibrate the atomic absorption spectrometer to be used to determine the arsenic. The first step is to prepare an intermediate concentration standard by diluting 100 μL of the 1,000-ppm solution to 100 mL in a calibrated flask. The next step is, with a variable volume micropipet, to add appropriate volumes of this intermediate standard to a series of 50-mL calibrated flasks. What is the concentration (in ppb) of the intermediate standard? (5 points) What volume is needed to prepare a 5.00 ppb solution? (5 points)

0.3301 g, 1000 ppb, 250 μL 20

1000 ppm = 1000 mg L^{-1} ∴ in 250 mL you need 250 mg

As formula of oxide is As_2O_3 (see Q 6)

∴ mass needed = $\frac{250 \times 197.84}{2 \times 74.922}$ mg = 0.3301 g

Diluting 100 μL → 100 mL is 1000-times dilution, so the intermediate standard is 1000 ppb.

If x mL are taken $5 = 1000 \times \frac{x}{50}$ ∴ x = 0.250 mL or 250 μL.

4. You decide to check the accuracy of the concentration of the1,000 ppm stock solution by titration with standard tetraoxomangante(VII), (aka permanganate, MnO_4^-) solution. In this titration the arsenic(III) is oxidized to arsenic(V) and the permanganate is reduced to manganese(II). If the concentration of the permanganate is 0.01000 M, what volume is needed to titrate a 25.0 mL portion of the standard if the solution was prepared accurately. (10 points). The Roman numerals indicate the oxidation number of the element. Oxygen has oxidation number -2 in all of the compounds used in this work, except the hydrogen peroxide, thus the formula of arsenic(III) oxide is As_2O_3.

13.3 mL 10

1000 ppm = 0.0133472 M

∴ in 25 mL there are 3.3368×10^{-4} mol

Equation: $As^{3+} + Mn^{7+} \longrightarrow As^{5+} + Mn^{2+}$

2e loss, 5e gain

∴ $5As^{3+} + 2Mn^{7+} \longrightarrow 5As^{5+} + 2Mn^{2+}$ is the stoichiometry

∴ # mol permanganate needed = $\frac{2}{5} \times 3.3368 \times 10^{-4}$

If there is in x mL then the concentration is

$\frac{2}{5} \times \frac{3.3368 \times 10^{-4}}{x} \times 1000 = 0.01000$

∴ x = 13.3 mL (3 digits)

5. For sample preparation, you propose to transfer 500 mg of finely chopped chicken breast to a Teflon vessel to which is added 10 mL of concentrated nitric acid and 1.0 mL of 30% hydrogen peroxide solution. 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 arsenic will have been oxidized to arsenate. The vessel is cooled, carefully opened and the contents transferred to a 25-mL calibrated flask and made up to volume with water. To validate the method, you ask one of your staff to analyze a standard reference chicken breast material (from the National Chicken Council) containing 500 ± 15 $\mu g\ kg^{-1}$ of arsenic, where the ± term is the 95% confidence interval. The following 5 replicate values are obtained: 490, 485, 495, 490 and 470 $\mu g\ kg^{-1}$. What do 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 (20 points).

$\bar{x} = 486$ 95% CI = 12
$s = 9.62$

30

Apply Q test to check for outlier(s): 470 485 490 490 495 (range)

biggest gap

$Q_{calc} = \frac{15}{25} = 0.6 < Q_{tab}$ ∴ no outlier

Calculate $\bar{x}$ and s (use a calculator – you won't have time to work these out from the equations)

$\bar{x} = 486\ \mu g\ kg^{-1}$ and $s = 9.62\ \mu g\ kg^{-1}$

calculate 95% confidence interval, $\frac{ts}{\sqrt{n}} = \frac{2.78 \times 9.62}{\sqrt{5}}$

$= 12\ \mu g\ kg^{-1}$

Result is $486 \pm 12\ \mu g\ kg^{-1}$ and is to be compared with $500 \pm 15\ \mu g\ kg^{-1}$. There are not enough data to perform a t test, so just examine whether the mean of one data set falls within the 95% CI of the other data set.

As 486 is within 500 ± 15, the method is accurate (i.e. there is no evidence of a significant difference).

6. You would like to try a new alkaline extraction procedure for which you need a solution buffered at pH 10.0. You decide to make an ammonia/ammonium chloride buffer in which the ammonia concentration is 0.100 M. What mass of ammonium chloride is needed per liter of buffer if the pK_a of ammonia is 9.24. (atomic weight of ammonium chloride is 53.103 g mol^{-1}). (10 points) After making 1.00 L of the 0.100 M ammonia solution, what is the pH? (10 points).

20

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

$NH_4^+ \rightarrow NH_3 + H^+$ $pK_a = 9.24$

$$10.0 = 9.24 + \log \frac{0.1}{x} \quad \therefore \log \frac{0.1}{x} = 0.76 \quad \therefore \frac{0.1}{x} = 5.7543$$

$\therefore x = 0.017378$ mol L^{-1}

$\therefore$ mass NH_4Cl = 0.923 g (3 digits)

What is pH of 0.100 M NH_3 solution?

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

$pK_b = 4.76$ $K_b = 1.7378 \times 10^{-5}$

$$\therefore 1.7378 \times 10^{-5} = \frac{x^2}{0.1 - x}$$

1st iteration $x = 1.3183 \times 10^{-3}$

2nd iteration $x = 1.3095 \times 10^{-3}$

3rd iteration $x = 1.3096 \times 10^{-3}$

4th iteration $x = 1.3096 \times 10^{-3}$

$\therefore$ pOH = 2.88286

$\therefore$ pH = 11.117138

= 11.117 (3 digits to right of decimal point)

See pages 54 and 55 for rules on sig figs in logarithms.

Total points = 15 + 10 + 20 + 10 + 30 + 20 = 105.