

CHEMISTRY 311 - Mid Term

ANSWER ALL QUESTIONS IN BOOKLETS PROVIDED. SHOW ALL WORK.
TOTAL MARKS 40.

1. a) What volume of a 50.0 $\mu\text{g/L PO}_4^{3-}$ - P stock solution is required to prepare 250.0 mL of a 1.00 $\mu\text{g/L PO}_4^{3-}$ - P standard solution? [2]

b) A researcher needs to analyze water samples for phosphorous down to levels of 0.050 μM . A supplier of an Ion Chromatograph (IC) reports a detection limit of 5 ppb PO_4^{3-} . Does the IC meet the detection limit requirements of the researcher? [2]

a) $C_1 V_1 = C_2 V_2$

$$\therefore V_1 = \frac{C_2 V_2}{C_1} = \frac{(1.00 \mu\text{g/L})(250.0 \text{ mL})}{(50.0 \mu\text{g/L})} = 5.00 \text{ mL}$$

b) $0.050 \mu\text{M} \longrightarrow ? \text{ ppb } \text{PO}_4^{3-}$

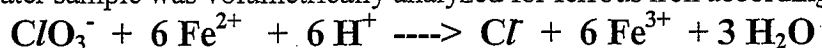
$$0.050 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times \frac{95. \text{ g}}{\text{mol}} \times \frac{1 \text{ mol } \text{PO}_4^{3-}}{1 \text{ mol P}} \times \frac{10^6 \mu\text{g}}{\text{g}}$$

$$= 4.75 \frac{\mu\text{g } \text{PO}_4^{3-}}{\text{L}}$$

rounds off to $5 \frac{\mu\text{g } \text{PO}_4^{3-}}{\text{L}}$

\therefore Yes

2. A wastewater sample was volumetrically analyzed for ferrous iron according to;



- a) If a 100. mL wastewater sample required 0.84 mL of 0.100 N KClO_3 titrant to reach the end point, what is the concentration of Fe^{2+} in units of mg/L Fe^{2+} ? [2]
 b) If the titration was carried out in a class A, 50.0 mL burette (individual reading error ± 0.02 mL), what is the relative uncertainty in the final answer? [2]
 c) What procedural modifications can you suggest to reduce the relative uncertainty in this determination? [2]
 d) What mass of potassium chlorate, KClO_3 , (molar mass 122.5 g mol^{-1}) is required to prepare 2.00 L of the titrant solution? [2]

$$\begin{aligned} \text{a) } N_1 V_1 &= N_2 V_2 & N_2 &= \frac{N_1 V_1}{V_2} = \frac{(0.100 \text{ N})(0.84 \text{ mL})}{(100. \text{ mL})} \\ & & &= 8.4 \times 10^{-4} \text{ N} \end{aligned}$$

$$EW_{\text{Fe}^{2+}} = \frac{MW}{K(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+})}$$

$$\begin{aligned} K &= \text{\#mols } e^- \text{ transferred per mole } \text{Fe}^{2+} \text{ reacted} \\ &= \frac{1 \text{ mole } e^-}{1 \text{ mol } \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}} & \therefore EW_{\text{Fe}} &= MW_{\text{Fe}} = 55.85 \frac{\text{g}}{\text{equiv}} \end{aligned}$$

$$\begin{aligned} \therefore \text{Conc. } \text{Fe}^{2+} &= 8.4 \times 10^{-4} \frac{\text{equiv}}{\text{L}} \times 55.85 \frac{\text{g}}{\text{equiv}} = 0.0469 \frac{\text{g}}{\text{L}} \\ &= 46.9 \frac{\text{mg}}{\text{L}} \text{Fe}^{2+} \quad \text{or} \quad 47 \frac{\text{mg}}{\text{L}} \text{Fe}^{2+} \end{aligned}$$

$$\text{b) } V_t = V_f - V_i \quad [(0.02)^2 + (0.02)^2]^{\frac{1}{2}} = 0.0283$$

$$\frac{0.0283}{0.84} = 0.0337 \quad (\text{or } 3.37\%)$$

$$(0.0337)(46.9 \text{ mg/L}) = 1.58 \text{ mg/L}$$

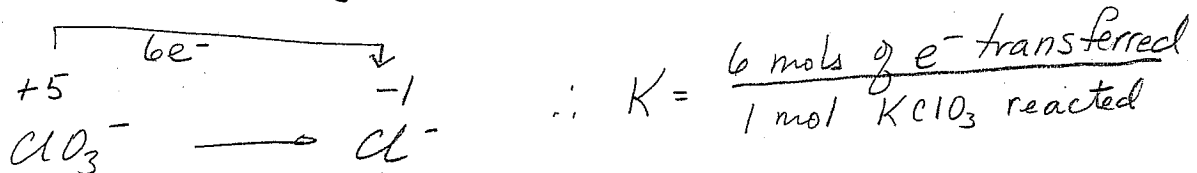
$$\therefore 46.9 \pm 1.6 \frac{\text{mg}}{\text{L}} \quad \text{or} \quad 47 \pm 2 \frac{\text{mg}}{\text{L}} \text{Fe}^{2+}$$

c) dilute titrant
larger sample volume
smaller (more precise) buret

$$d) (2.00 \text{ L})(0.100 \text{ N}) = 0.200 \text{ equiv of } \text{KClO}_3$$

$$\text{mass } \text{KClO}_3 = \# \text{equiv.} \times \text{EW}$$

$$\text{EW} = \frac{\text{MW}}{\text{KClO}_3 \rightarrow \text{Cl}^-}$$



$$\therefore \text{EW} = \frac{122.5 \text{ g/mol}}{6 \text{ equiv/mol}} = 20.42 \text{ g/equiv}$$

$$0.200 \text{ equiv} \times 20.42 \text{ g/equiv} = 4.083 \text{ g } \text{KClO}_3$$

3. A *Standard Reference Material* is certified to contain 94.6 ppm of an organic contaminant in soil. Your analysis gives values of 98.6, 98.4, 97.2, 94.6 and 96.2 ppm. Do your results differ from the expected result at the 95% confidence level? [3]

$$\mu \text{ (true value)} = 94.6 \text{ ppm}$$

$$\bar{x} = 97.0 \text{ ppm} \quad s = 1.65 \text{ (use calculator)}$$

$$n = 5$$

$$\frac{ts}{\sqrt{N}} = \frac{(2.78)(1.65)}{\sqrt{5}} = 2.06 \text{ at } 95\%$$

$$|\bar{x} - \mu| = \frac{ts}{\sqrt{N}}$$

rearrange and solve for t_{calc}

$$t_{\text{calc}} = \frac{|\bar{x} - \mu| \sqrt{N}}{s} = \frac{(2.4)(\sqrt{5})}{1.65} = 3.25$$

Since $t_{\text{calc}} > t (df=4)$

then results are significantly different

4. During the field analysis of total hardness using a Hach Digital Titrator™ method a 100. mL sample is titrated with a 0.800 M ethylenediaminetetraacetate (EDTA⁴⁻), which forms a 1:1 complex with Ca²⁺. A student inadvertently adds one drop (~50 μL) of titrant to the sample before carrying out the titration. Estimate the sign and the magnitude of the error introduced in ppm CaCO₃. [4]

$$\begin{aligned} \# \text{ mols Ca}^{2+} \text{ consumed by addition of 50 } \mu\text{L} \\ \text{of EDTA} \\ = (50 \times 10^{-6} \text{ L})(0.800 \text{ M}) = 4.0 \times 10^{-5} \text{ mols} \end{aligned}$$

$$\therefore [\text{Ca}^{2+}] = \frac{4.0 \times 10^{-5} \text{ mols}}{0.100 \text{ L}} = 4.0 \times 10^{-4} \frac{\text{mol}}{\text{L}} \text{ Ca}^{2+}$$

Converting to ppm CaCO₃

$$\begin{aligned} 4.0 \times 10^{-4} \frac{\text{mol}}{\text{L}} \text{ Ca} \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol Ca}} \times \frac{100,000 \text{ mg}}{1 \text{ mol CaCO}_3} \\ = 40 \frac{\text{mg}}{\text{L}} \text{ CaCO}_3 = 40 \text{ ppm CaCO}_3 \end{aligned}$$

Since this is the conc. of Ca²⁺ removed by the 1 drop addition ∴ the experimental result will suffer a negative bias

$$- 40 \text{ ppm CaCO}_3$$

5. The following procedures may be included in a sampling and analysis programme.

Indicate the rationale for THREE of the procedure. [3]

- a) The sample is filtered (0.45 μm) and 2 mL/L of HNO_3 is added
- b) A *spike* of isotopically labelled analyte is added prior to sample preparation steps
- c) Every 15th lab analysis is of a *certified reference material*
- d) A deionized water *blank* is collected at the sampling site and transported to the lab for analysis

a) filtered to sample for dissolved analyte
nitric acid added to preserve dissolved metals

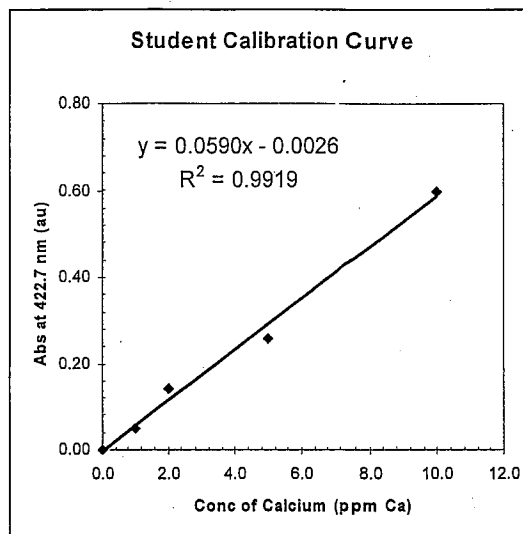
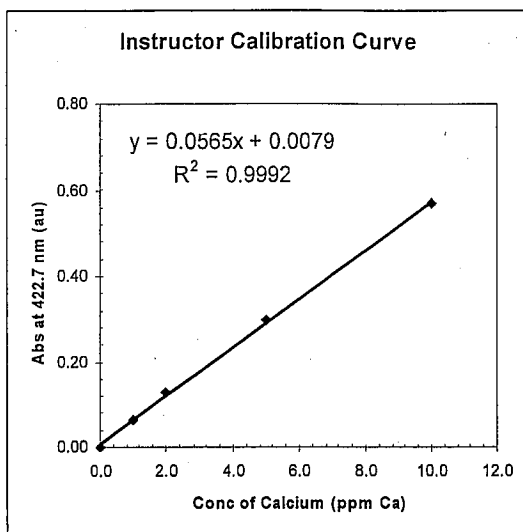
b) to measure recovery in preparation steps
and/or for internal calibration

c) quality control to check method
and prepare quality control chart/s.

d) field blank to check for contamination
during sampling, storage and transport

6. In the determination of Calcium by flame atomic absorption spectroscopy, the following calibration curves were obtained. [3]

- Determine the concentration of Calcium for an unknown sample with an absorbance of 0.440 au.
- Comment on the relative precision and accuracy of results generated using these curves.



$$a) \quad y = mx + b$$

\uparrow \uparrow
 abs. conc.

$$\therefore x = \frac{y-b}{m}$$

$$= \frac{0.440 - 0.0079}{0.0565}$$

$$= 7.65 \text{ ppm Ca}$$

b) Instructor calibration curve is more precise as can be seen visually with less scatter (also R^2 closer to 1.000)

Cannot determine which calibration curve will yield more accurate result without data for an SRM / CRM.

7. A blood serum sample was analyzed for potassium by flame atomic emission spectrometry (FAES) using the method of standard additions. In FAES, the signal obtained is directly proportional to analyte concentration. A 0.500 mL aliquot of serum was placed in each of two 5.00 mL volumetric flasks. In one flask, a 20.0 μL spike of 0.0500 M KCl was added. Both flasks were then filled and mixed by inversion. The signal for the unspiked flask was 32.1 a.u. and for the spiked flask 58.6 a.u. respectively. What is the potassium concentration in the original sample? [4]

$$\frac{A_x}{A_{x+s}} = \frac{[X]_f}{[X]_f + [S]_f}$$

note that both the unspiked and spiked sample are diluted

$$[X]_f = [X]_i \cdot \frac{V_i}{V_f} \quad \begin{array}{l} \leftarrow 0.500 \text{ mL} \\ \leftarrow 5.00 \text{ mL} \end{array}$$

$$[S]_f = [S]_i \cdot \frac{V_i}{V_f} = \frac{(0.0500 \text{ M})(20.0 \times 10^{-6} \text{ L})}{(5.00 \times 10^{-3} \text{ L})} = 2.00 \times 10^{-4} \text{ M} = 2.00 \text{ mM}$$

$$\frac{32.1}{58.6} = \frac{[X]_f}{[X]_f + (2.00 \text{ mM})}$$

$$0.5478 [X]_f + 0.1095 \text{ mM} = [X]_f$$

$$[X]_f (1 - 0.5478) = 0.1095 \text{ mM}$$

$$[X]_f = \frac{0.1095 \text{ mM}}{(1 - 0.5478)} = 0.2423 \text{ mM}$$

$$\therefore [X]_i = 2.423 \text{ mM}$$

8. An HPLC analysis of a combined standard of 25.0 μM ValiumTM (MW = 284.5 g/mol) and 10.0 μM nitro-diazepam (internal standard) gave signal areas of 4322 a.u. and 1458 a.u., respectively. When a 100. mg hair sample was digested (dissolved), and analyzed for Valium, the digest (15.00 mL) was spiked with 100.0 μL of 20.0 mM nitro-diazepam, and subjected to HPLC analysis. The signal areas obtained for Valium and nitro-diazepam were 152 a.u. and 110 a.u., respectively. Determine the Valium concentration in the digest sample (μM) and the original hair sample (mg/g). [5]

$$F = \frac{4322 / 25 \mu\text{M}}{1458 / 10 \mu\text{M}} = 1.186 \quad \text{from combined standard soln.}$$

from spiked sample;

$$1.186 = \frac{152 / [X]_f}{110 / [S]_f}$$

$$\text{where } [S]_f = \frac{(100.0 \times 10^{-6} \text{ L})(20.0 \text{ mM})}{(15.0 \times 10^{-3} \text{ L})} = 0.1333 \text{ mM}$$

$$\therefore \frac{152}{[X]_f} = \frac{(1.186)(110)}{0.1333 \text{ mM}}$$

So $[X]_f = 0.1550 \text{ mM}$ in digest

$$\text{mass Valium in 100. mg hair} = 0.1550 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times \frac{284.5 \text{ g}}{\text{mol}} \times 15.0 \times 10^{-3} \text{ L} = 6.613 \times 10^{-4} \text{ g}$$

$$\therefore \frac{0.6613 \text{ mg}}{0.100 \text{ g}} = 6.613 \frac{\text{mg}}{\text{g}}$$

9. Briefly describe the difference for any THREE of the following, providing common units of reporting in each case. [6]

- a) Turbidity versus Total Suspended Solids
- b) Total Alkalinity versus pH
- c) Total Dissolved Solids versus Specific Conductivity
- d) Dissolved Oxygen versus Oxidation Reduction Potential

(see notes & lab manual)