CHEMISTRY 311 - ASSIGNMENT 1

Hand-in your answers in a neat organized format to the appropriate number significant figures, showing chemical equations and calculations where appropriate.

Due date: Tuesday, September 25th

1. Calculate the mass of primary standards (**$NaNO_3$** and **$KH_2PO_4 \cdot 3H_2O$**) required to prepare 250.0 mL of a combined standard solution containing 100.0 μg/L of **NO_3^--N** and 10.00 μg/L of **PO_4^{3-}-P**. Are there any practical challenges that limit the precision of the reported concentrations of your combined standard solution? If so, how might you suggest modifying your procedure.

2. Sodium sulfite (**Na_2SO_3**) is sometimes used to remove excess chlorine from disinfected water supplies, especially if they are going to be used for fish rearing.
a) Write a balanced redox reaction in which the final products are sulfate and chloride ion.
b) Calculate the mass of sodium sulfite required to react with the residual chlorine in 26 m^3 of supply water containing 1.2 mg/L **Cl_2**?
Note that sodium sulfite also reacts with dissolved oxygen, so adding too much to a fish tank can have dire consequences, so it is important to get the math and chemistry right on this one.

3. A mineral is analyzed for it's calcium content as follows. A 1.032 g finely ground sample was dissolved in 25 mL of hot 4 M **HCl** and diluted with 175 mL of **H_2O**. This solution was heated to a boil and 50 mL of a hot solution containing 2.0 g of **$(NH_4)_2C_2O_4$** was slowly added to precipitate **CaC_2O_4**(s) as the monohydrate. The solution was neutralized by adding 6 M **NH_3** and slowly cooled. After decanting the supernatant solution, the solid was transferred to a filter crucible and washed with several portions of cold 0.1% **$(NH_4)_2C_2O_4$** . The crucible was dried at 105ºC for 1 hr and then heated at 500ºC in a furnace for an additional 2 hr. The mass of the precipitate was recorded to be 0.154 g.

$$Ca^{2+} + C_2O_4^{2-} \xrightarrow{105^oC} CaC_2O_4 \cdot H_2O(s) \xrightarrow{500^oC} CaCO_3(s)$$

a) Determine the concentration of calcium in the mineral sample in mg/g.
b) Provide three desired properties of a precipitate in gravimetric analysis.

4. The alkalinity of a freshwater sample is a measure of its acid neutralizing ability and is primarily due to the presence of hydrogen carbonate ion (**HCO_3^-**). The *Total Alkalinity* is determined by titrating a water sample with a standardized acid to a methyl orange endpoint (pH ~ 4.5). What volume of 0.0280 N **H_2SO_4** titrant is required to titrate a 25.0 mL water sample with a known alkalinity of 120. ppm of **$CaCO_3$**? Does your result suggest a problem with the methodology? If so, how could you modify the procedure to reduce the relative uncertainty in your analytical result?

5. The analysis of a *Reference Material* for lead in blood samples with a certified concentration of 12.6 ng/mL was analyzed by graphite furnace atomic absorption (GFAA) spectroscopy. The results of six replicate analysis are listed below. Check for potential outliers using the Grubb's test at the 95% confidence level. Incorporating the removal of outliers (if any), quantify the precision and accuracy of the GFAA method to analyze lead in blood samples.

12.9 11.2 10.6 12.1 13.0 11.5 ng/mL

6. In the standardization of hydrochloric acid, high purity sodium carbonate is dried and weighed into a flask and dissolved in water before being titrated with **HCl**.

Mass of $\mathbf{Na_2CO_3}$ (±0.1 mg)	Volume of **HCl** delivered (±0.03mL)
126.0	23.77
105.4	19.51
122.8	22.85
112.5	20.06

a) What is the balanced chemical reaction that occurs.
b) Write a general mathematical expression for the millimolar concentration of **HCl** in terms of the mass of $\mathbf{Na_2CO_3}$ (mg) and the volume of **HCl** titrant (mL).
c) What is the absolute and relative uncertainty in the calculated concentration based on the propagation of the reported reading errors for titration of 105.4 mg of $\mathbf{Na_2CO_3}$?
d) Calculate the mean concentration, standard deviation and relative standard deviation based on the data from the four trials.

7. A field portable volumetric analysis method for *Dissolved Oxygen* using a Hach Digital Titrator™ is based on the Winkler titration, whereupon the dissolved oxygen is converted to an equivalent amount of iodine which is then titrated with sodium thiosulfate. The volume of titrant added is recorded with a digital counter (corresponding to the delivery of 1.25 μL) and can be converted to an analyte concentration with an appropriate 'digit multiplier'.
a) Calculate the concentration of the thiosulfate titrant required such that the 'digit multiplier' for the titration of a 60. mL sample is 0.10 ppm $\mathbf{O_2}$ per digit.
b) What mass of $\mathbf{Na_2S_2O_3.5H_2O}$ would be required to prepare 100. mL of this titrant?

8. The concentration of cyanide ($\mathbf{CN^-}$) in a copper electroplating bath can be determined by a complexation titration with $\mathbf{Ag^+}$, forming the soluble $\mathbf{Ag(CN)_2^-}$ complex. In a typical analysis a 5.00 mL sample from an electroplating bath is transferred to a 250 mL Erlenmeyer flask and treated with 100 mL of $\mathbf{H_2O}$, 5 mL of 20% w/v **NaOH** and 5 mL of 10%w/v **KI**. A sample was titrated with 0.2012 M $\mathbf{AgNO_3}$, requiring 17.36 mL to reach the end-point as signaled by the appearance of a yellow precipitate of **AgI**.
a) Suggest the appropriate lab glassware to be employed for transferring each of the sample, water, sodium hydroxide and potassium iodide solutions, respectively.
b) What is the molarity of a 10% w/v **KI** solution and why is it added?
c) Report the concentration of cyanide in the electroplating bath as parts per million of $\mathbf{CN^-}$.

BONUS. The *Kjeldahl procedure* was used to analyze a 5.00 mL of a solution containing 390 mg of a food sample. The liberated $\mathbf{NH_3}$ was collected in 50.00 mL of 0.0336 M **HCl**, and the remaining acid was *back-titrated* with 12.34 mL of 0.1046 M **NaOH** for complete titration.
a) What chemistry is involved in the *Kjeldahl procedure*?
b) What is the mass percent of nitrogen in the sample?