

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, October 3rd

1. A student prepares a combined standard solution by weighing out 252.6 mg of KNO_3 and 148.5 mg of $\text{NaH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, dissolving in deionized water to a final mass of 102.234 g. After mixing, 1.022 g of this solution was transferred to a clean dry container and diluted with deionized water to a final mass of 250.654 g. Calculate the final concentration NO_3^- -N and PO_4^{3-} -P in ppb.

Strategy: This question involves a series of gravimetric dilutions. Since we are asked for the final concentrations as mass ratio (i.e., $\mu\text{g}/\text{kg}$ of nitrate-nitrogen and phosphate-phosphorus, respectively), we can convert the mass of solids dissolved into a corresponding mass of the elements N and P. Dividing by the mass of solution and taking into account the dilutions yields the final result.

Solution:

In the stock standard solution we have;

$$\frac{\mu\text{g NO}_3^- \text{-N}}{\text{kg soln}} = \frac{252.6 \mu\text{g}}{102.234 \text{g}} \times \frac{1000 \text{ mg}}{1 \text{ mg}} \times \frac{14.007 \text{g/mol}}{101.103 \text{g/mol}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 3.423_1 \times 10^5 \text{ ppb NO}_3^- \text{-N}$$

and

$$\frac{\text{mg PO}_4^- \text{-P}}{\text{kg soln}} = \frac{148.5 \text{ mg}}{102.234 \text{ g}} \times \frac{1000 \text{ mg}}{1 \text{ mg}} \times \frac{30.974 \text{ g/mol}}{173.977 \text{ g/mol}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 2.586_1 \times 10^5 \text{ ppb PO}_4^- \text{-P}$$

After diluting 1.022 g of this stock to a final mass of 250.654 g, we have;

$$\frac{(3.423_1 \times 10^5 \text{ ppb NO}_3^- \text{-N})(1.022 \text{ g})}{250.654 \text{ g}} = 1395.7 \text{ ppb NO}_3^- \text{-N}$$

and

$$\frac{(2.586_1 \times 10^5 \text{ ppb PO}_4^- \text{-P})(1.022 \text{ g})}{250.654 \text{ g}} = 1054.4 \text{ ppb PO}_4^- \text{-P}$$

2. A method to measure the soluble organic carbon in seawater includes oxidation of the organic materials to CO_2 with $\text{K}_2\text{S}_2\text{O}_8$, followed by gravimetric determination of the CO_2 trapped by a column of NaOH -coated asbestos. A water sample weighing 6.234 g produced 2.378 mg of CO_2 . Calculate the concentration of organic carbon in seawater as ppm C.

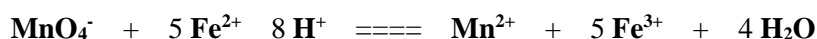
Strategy: This question involves a gravimetric determination of the carbon dioxide released upon the combustion dissolved organic carbon. Since we are asked for the final concentration of carbon as mass ratio (i.e., ppm C = mg of carbon per kilogram of seawater sample), we can convert the mass of CO_2 trapped into a corresponding mass of carbon. Dividing by the mass of the sample yields the final concentration as ppm C.

Solution:

$$\frac{\text{mg C}}{\text{kg sample}} = \frac{2.378 \text{ mg CO}_2}{6.234 \text{ g seawater}} \times \frac{12.011 \text{ g/mol}}{44.010 \text{ g/mol}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = \frac{104.1 \text{ mg C}}{\text{kg}} = 104.1 \text{ ppm C}$$

3. The amount of iron in a meteorite was determined by redox titration using **KMnO₄** as the titrant. A 0.4185 g sample of the meteorite was dissolved in acid and the liberated **Fe³⁺** was quantitatively converted to **Fe²⁺** using a reducing column. Titrating this solution with 0.02500 M **KMnO₄** requires 41.27 mL to reach the end-point. Determine the wt% of **Fe₂O₃** in the sample.

Strategy: This question involves a volumetric determination of the iron content by titrating with a standard solution of permanganate ion. The number of moles of analyte (**Fe²⁺**) is determined by the number of moles of titrant added multiplied by the stoichiometric ratio of analyte to titrant (from the balanced chemical equation below). We can then convert the number of moles of **Fe²⁺** to the number of moles of **Fe₂O₃**. Multiplying by the FW and dividing by the sample mass yields the desired mass ratio. Multiplying by 100 gives a wt%.



Solution:

$$\begin{aligned} \text{wt\% Fe}_2\text{O}_3 &= \frac{\text{mass Fe}_2\text{O}_3}{\text{mass sample}} = \frac{n_{\text{Fe}_2\text{O}_3}}{0.4185 \text{ g sample}} \times \frac{159.688 \text{ g}}{1 \text{ mol}} \times \left(n_{\text{Fe}} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \right) \times \frac{159.688}{1 \text{ mol}} \\ &= \frac{\left(n_{\text{MnO}_4} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4} \right) \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \times \frac{159.688 \text{ g}}{1 \text{ mol}}}{0.4185 \text{ g}} \\ &= \frac{(M_{\text{MnO}_4} \times V_{\text{MnO}_4}) \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \times \frac{159.688 \text{ g}}{1 \text{ mol}}}{0.4185 \text{ g}} \\ &= \frac{0.02500 \text{ mol/L} \times 0.04127 \text{ L} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \times \frac{159.688 \text{ g}}{1 \text{ mol}}}{0.4185 \text{ g}} \\ &= 0.9842 \text{ or } \mathbf{98.42\%} \end{aligned}$$

4. The *Total Hardness* of a water sample can be determined volumetrically using ethylenediamine tetraacetate (EDTA), which forms a 1:1 complex with Ca^{2+} and other divalent metal cations. Calculate the *Total Hardness* and express as ppm CaCO_3 , if a 50.00 ± 0.05 mL water sample required 3.22 ± 0.03 mL of a $(1.330 \pm 0.005) \times 10^{-3}$ M EDTA titrant to reach a *Calmagite* end-point. Estimate the uncertainty in your answer by propagation of the reported errors, given that only one analytical determination was made.

Strategy: This question involves a volumetric determination of the divalent metal cations (M^{2+}), which is then expressed as a mass of CaCO_3 that would give an equivalent amount of Ca^{2+} . Since we are asked for the uncertainty in the final concentration and we do not have any replicate determinations to estimate the precision, we must propagate the various reading errors or other associated uncertainties through the calculation.

Note:

For addition and subtraction, the absolute errors are additive.

For multiplication and division, the relative errors are additive.

See further Section 3.4 of the Textbook.

Solution:

$$\begin{aligned}
 \frac{\text{mg CaCO}_3}{\text{kg sample}} &= \frac{n_{\text{CaCO}_3}}{V_{\text{sample}}} \times \frac{100.087 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1.000 \text{ kg}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \\
 &= \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample}}} \times \frac{100.087 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1.000 \text{ kg}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \\
 &= \frac{(1.330 \pm 0.005) \times 10^{-3} \text{ mol/L} \times (3.22 \pm 0.03) \text{ mL}}{(50.00 \pm 0.05) \text{ mL}} \times \frac{100.087 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1.000 \text{ kg}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \\
 &= 8.5727 \frac{\text{mg CaCO}_3}{\text{kg}} \pm \left(\sqrt{\left(\frac{0.005}{1.330}\right)^2 + \left(\frac{0.03}{3.22}\right)^2 + \left(\frac{0.05}{50.00}\right)^2} \right) \\
 &= 8.5727 \frac{\text{mg CaCO}_3}{\text{kg}} \pm (0.0101) \\
 &= \mathbf{8.57_3 (\pm 0.08) \text{ ppm CaCO}_3}
 \end{aligned}$$

5. A *Standard Reference Material* is certified to contain 94.6 ppb of a persistent organic pollutant. The results of five replicate analysis are 98.6, 98.4, 97.2, 94.6 and 96.2 ppb. Quantify the precision and accuracy of this determination.

Strategy: This question involves quantitative measures of both precision and accuracy. Precision is measure of 'reproducibility' and is best assessed by calculating the *sample standard deviation* and converting this to a *relative standard deviation* and a *confidence interval* (typically at the 95% confidence level). Accuracy is measured by comparing the experimental mean to the accepted value and calculating a *% difference* (also known as the % bias).

Solution:

The sample standard deviation is given by;

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}}$$

For the given data set;

$$N=5, \quad \bar{x} = 97.0 \text{ ppb}, \quad s = 1.655 \text{ ppb}$$

and the relative standard deviation (RSD) = $(1.655/97.0) \times 100\% = 1.7\%$

The confidence interval is given by;

$$CI = \frac{(t)(s)}{\sqrt{N}} = \frac{(2.776)(1.655 \text{ ppb})}{\sqrt{5}} = 2.055 \text{ ppb}$$

where $t = 2.776$ at $N-1 = 4$ degrees of freedom and the 95% confidence level.

Consequently, we can be 95% confident that our experimental value is **97.0 +/- 2.1 ppb** (i.e., is between 94.9 and 99.1 ppb).

The % difference (bias) between our experimental mean and the accepted value is given by;

$$\% \text{ bias} = \left(\frac{97.0 - 94.6}{94.6} \right) \times 100\% = 2.5\%$$

As we can see, the precision of the analysis of this sample was better than 2% as reported by the RSD. The accuracy of the determination is somewhat suspect as there is an apparent positive bias of +2.5%. It should be noted however, that the lack of precision limits our ability to be confident that this bias is real as the accepted value is only slightly below our experimental value.

6. A field portable volumetric analysis method for *Total Alkalinity* using a Hach Digital Titrator™ is based on the neutralization of bases in a water sample with the protons of a standardized sulfuric acid titrant (H_2SO_4). The volume of titrant added is recorded with a digital counter which corresponds to the delivery of 1.25 μL and can be converted to an analyte concentration with an appropriate ‘digit multiplier’. Calculate the ‘digit multiplier’ for the titration of a 25 mL sample with 0.1600 N H_2SO_4 titrant cartridge to yield the total alkalinity in units of ppm as CaCO_3 .

Strategy: This question involves the volumetric determination of *Total Alkalinity* using a digital titrator. We are told that 1 digit counter = 1.25 μL of titrant added and need to calculate a ‘multiplier’ that converts # of digits to the *Total Alkalinity* as ppm CaCO_3 . So, let’s calculate of concentration of analyte in a 25.0 mL sample as if the end point was reached after adding 1 digit of the specified 0.1600 N sulfuric acid. Since the concentration of the titrant is given as *Normality*, we can say that the #equivalents of titrant = #equivalents of analyte (or any unit of concentration that is equivalent to the amount of analyte).

$$N_{\text{analyte}} = \frac{N_{\text{titrant}} \times V_{\text{titrant}}}{V_{\text{analyte}}}$$

Solution:

$$N_{\text{analyte}} = \frac{0.1600N \times 1.25 \times 10^{-6} \text{L}}{25.0 \times 10^{-6} \text{L}} = 8.00 \times 10^{-6} N$$

Converting this to ppm CaCO_3 gives;

$$\frac{8.00 \times 10^{-6} \text{equiv}}{\text{L}} \times \frac{50,000 \text{ mg}}{\text{equiv}} \times \frac{1 \text{ L}}{1.00 \text{ kg}} = 0.400 \text{ ppm } \text{CaCO}_3$$

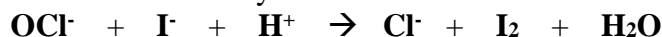
This means that each digit (i.e., $1.25 \times 10^{-6} \text{L}$) of this titrant added to a 25.0 mL sample corresponds to 0.400 ppm of CaCO_3 in the sample. Consequently, the # of digits required to reach the endpoint can be multiplied by (**0.40 ppm CaCO_3 /digit**) to obtain the *Total Alkalinity* as ppm CaCO_3 .

7. The following method is reported in *Standard Methods for the Examination of Water and Wastewater* for the analysis of sodium hypochlorite (**NaOCl**) in bleach.

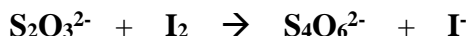
- a 20.00 mL sample of bleach is diluted to 100.0 mL.
- a 25.00 mL aliquot of the diluted sample is then transferred into a flask and treated with an excess acidic iodide solution.
- the iodine thus formed, is titrated with a standard thiosulfate solution.

The chemistry is outlined below (unbalanced equations):

Excess iodide is reacted with the analyte in an acidic solution.



The resulting iodine (**I₂**) is then titrated with a standardized solution of sodium thiosulfate.



If 12.62 mL of a 0.00400 N thiosulfate solution was required to reach the end point, what is the concentration of the original bleach solution as wt% and ppm as **Cl₂**?

Strategy: This question involves a volumetric determination of the concentration of **NaOCl** in a bleach solution. Since the concentration of the titrant is given in units of *Normality*, we will solve this using equivalents and not worry about balancing the chemical equations. We will determine the *Normality* of **NaOCl** in the titrated solution, account the dilution and convert to a wt% and ppm **Cl₂** in the original solution.

Solution:

$$N_{\text{analyte}}^{\text{dilute}} = \frac{N_{\text{S}_2\text{O}_3} \times V_{\text{S}_2\text{O}_3}}{V_{\text{analyte}}^{\text{dilute}}} = \frac{(0.00400 \text{ equiv/L}) \times (12.62 \text{ mL})}{25.00 \text{ mL}} = 2.01_9 \times 10^{-3} \text{ equiv/L}$$

$$N_{\text{analyte}}^{\text{original}} = \frac{N_{\text{analyte}}^{\text{dilute}} \times V_{\text{analyte}}^{\text{dilute}}}{V_{\text{analyte}}^{\text{original}}} = 2.01_9 \times 10^{-3} \text{ equiv/L} \times \frac{100.0 \text{ mL}}{20.00 \text{ mL}} = 0.0100_9 \text{ equiv/L}$$

To convert this to wt% we need the mass of each equivalent of **NaOCl**, which is referred to as the Equivalent Weight (EW). Recall the $\text{EW} = \text{MW}/K$, where K is the number of equivalents/mol or in this case;

$$K = \frac{\# \text{ mols of } e^- \text{ transferred}}{\text{mol of NaOCl reacted}} = \frac{2 \text{ equiv}}{1 \text{ mol}}$$

since $\text{OCl}^- \rightarrow \text{Cl}^-$ (note the change in oxidation state on the chlorine goes from +1 \rightarrow -1). Therefore;

$$\text{EW}_{\text{NaOCl}} = \frac{74.45 \text{ g/mol}}{2 \text{ equiv/mol}} = 37.23 \text{ g/equiv (similarly EW}_{\text{Cl}_2} = 70.91/2 = 35.45 \text{ g/equiv)}$$

and

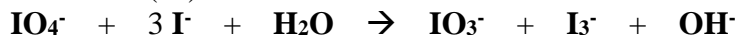
$$\text{wt\%} = \frac{\text{mass NaOCl}}{\text{mass solution}} \times 10^2 = \frac{(0.01009 \text{ equiv})(37.23 \text{ g/equiv})}{1 \text{ L}} \times \frac{1 \text{ L}}{1.00 \text{ kg}} \times 10^2 = 37.6 \%$$

$$\text{ppm Cl}_2 = \frac{\text{mass Cl}_2}{\text{mass solution}} \times 10^6 = \frac{(0.01009 \text{ equiv})(35.45 \text{ g/equiv})}{1 \text{ L}} \times \frac{1 \text{ L}}{1.00 \text{ kg}} = 3.5_8 \times 10^5 \text{ ppm Cl}_2$$

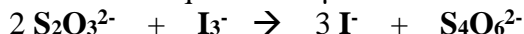
where a density of 1.00 kg/L has been assumed.

8. A 64.3 mg sample of a protein (MW = 58,600) was treated with 2.00 mL of 0.0487 M sodium periodate (NaIO_4) to selectively react with all of the serine and threonine residues.

The resulting solution was then treated with excess iodide ion to convert the unreacted periodate into triiodide ion (I_3^-).



A microtitration of the triiodide ion required 823 μL of 0.0988 M thiosulfate.



Calculate the total number of serine + threonine residues per molecule of protein.

Strategy: This question involves a *back titration*. The number of moles of serine and threonine residues is determined by the difference between the number of periodate ions initially present and the number remaining after some of them have reacted with the protein. The final answer is expressed as the ratio of the number of moles of serine + threonine to the number of moles of protein.

Solution:

$$\begin{aligned} \frac{\text{moles (serine+threonine)}}{\text{moles protein}} &= \frac{n_{\text{IO}_4^-}^{\text{reacted}}}{\text{mass protein}} = \frac{(n_{\text{IO}_4^-}^{\text{initial}} - n_{\text{IO}_4^-}^{\text{remaining}})}{\text{MW}_{\text{protein}} \cdot 64.3 \times 10^{-3} \text{ g}} \\ &= \frac{(M_{\text{IO}_4^-} \times V_{\text{IO}_4^-})^{\text{initial}} - n_{\text{S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mol IO}_4^-}{2 \text{ mol S}_2\text{O}_3^{2-}}}{1.0973 \times 10^{-6} \text{ moles}} = \frac{(M_{\text{IO}_4^-} \times V_{\text{IO}_4^-})^{\text{initial}} - (M_{\text{S}_2\text{O}_3^{2-}} \times V_{\text{S}_2\text{O}_3^{2-}}) \times \frac{1 \text{ mol IO}_4^-}{2 \text{ mol S}_2\text{O}_3^{2-}}}{1.0973 \times 10^{-6} \text{ moles}} \\ &= \frac{(0.0487 \text{ mol/L} \times 2.00 \times 10^{-3} \text{ L}) - (0.0988 \text{ mol/L} \times 823 \times 10^{-6} \text{ L}) \times \frac{1 \text{ mol IO}_4^-}{2 \text{ mol S}_2\text{O}_3^{2-}}}{1.0973 \times 10^{-6} \text{ moles}} \\ &= \frac{(9.74 \times 10^{-5} \text{ mols}) - \left((8.13 \times 10^{-5} \text{ mols}) \times \frac{1 \text{ mol IO}_4^-}{2 \text{ mol S}_2\text{O}_3^{2-}} \right)}{1.0973 \times 10^{-6} \text{ mols}} \\ &= 51.7 \rightarrow \mathbf{52 \text{ residues of serine + threonine per protein!}} \end{aligned}$$