CHEMISTRY 311 - ASSIGNMENT 2

*Hand-in your answers in a **neat and organized format** to the appropriate number significant figures, showing chemical equations and calculations where appropriate.*
Due date: Tuesday, Oct. 16th, 2018

1. Propagate the indeterminate readings errors associated with the volumetric analysis of dissolved oxygen using class A analytical laboratory glassware (100.0 +/- 0.08 mL sample, 0.0200 +/- 0.0001 N sodium thiosulfate and 5.00 +/- 0.03 mL of titrant) and compare that to the same using a digital titrator in the field (20.0 +/- 1 mL sample, 0.200 +/- 0.004 N sodium thiosulfate and 100 +/- 2 uL of titrant added).

2. A Method Detection Limit (MDL) can be estimated according to a procedure described in U.S. EPA Method 300.0 by analyzing at least seven replicates with a concentration close to the estimated method detection limit. The MDL is then calculated as (t) x (SD) where t = Student's t value for a 99% confidence level with n - 1 degrees of freedom and SD is the sample standard deviation. Check for outliers using the Grubb's test at the 95% confidence level and estimate the method detection limit for the measurements of a 2.5 ppb NO_3^- - **N** standard solution by ion chromatography.

| 2.8 | 1.7 | 2.4 | 2.9 | 2.1 | 4.0 | 2.3 | 2.6 | 1.8 | 2.7 |

3. Carbon dioxide in the atmosphere was analyzed by bubbling air into a 100.0 mL volume of 5.00 x 10^{-2} M barium hydroxide 'trapping solution' at a flowrate of 0.8 L/min for 90. mins at 12.0 °C and 1.00 atm. The remaining **Ba(OH)₂** was then back-titrated with 34.32 mL of 0.1600 M **HCl** (see further the CHEM 311 Lab Manual).
a) Determine the concentration of **CO₂** in the air sample as a mole ratio x 10^6 (ppm$_v$).
b) If all glassware used for the volumetric measurements was class A, what do you suspect is the largest source of indeterminant error in the method described.
c) If the air sampled was uncontaminated outdoor air, do you suspect that your answer is exhibiting a bias?

4. The following data were collected during a study of the concentration of zinc in samples drawn from several locations in Lake Erie (all concentrations in ppm).

Location	Conc Zn^{2+} at air-water	Conc Zn^{2+} at sediment-water
1	0.430	0.415
2	0.266	0.238
3	0.567	0.390
4	0.531	0.410
5	0.707	0.605
6	0.716	0.609

Determine if there is a significant difference between the concentration of **Zn** at the air-water interface and the sediment-water interface at the 95% confidence level.

5. The following calibration data are provided for a series of external aqueous standards of Cd^{2+} that had been buffered at a pH of 3.7 and 4.6, respectively.

[Cd²⁺] ppb	15.4	30.4	44.9	59.0	72.7	86.0
Signal (pH = 4.6)	4.8	11.4	18.2	26.6	32.3	37.7
Signal (pH = 3.7)	15.0	42.7	58.5	77.0	101	118

a) Use Excel to derive the best-fit lines using the method of least squares and indicate how much more sensitive this method is at the lower pH.
b) Using the Excel Spreadsheet for least squares analysis described in the textbook (Section 4.9), report the standard deviation of the slope and the intercept.
c) A single sample buffered at pH 3.7 was analyzed for cadmium yielding a signal of 66.3. Report the concentration of Cd^{2+} in the sample and the 95% confidence interval.

6. A combined standard solution was prepared to contain 25.0 uM caffeine and 5.0 uM of an appropriately chosen internal standard. Analysis of this combined standard gave signals for the caffeine and internal standard of 0.155 and 0.233 (arbitrary units), respectively. A 1.00 mL aliquot of internal standard solution was added to a 10.0 mL sample to yield a 10.0 uM solution of the internal standard in the diluted sample. Analysis of the spiked sample yields signals for the analyte and internal standard of 0.274 and 0.198, respectively.
a) What considerations go into choosing an appropriate internal standard?
b) Is the analytical technique in this case more sensitive to caffeine or the internal standard?
c) Report the concentration of caffeine in the sample in units of ppm.

7. The following data were obtained in a determination of chromium in water. The protocol was to run a blank, a 20.00 mL sample, and then the sample with one and two 250. uL standard addition spikes containing each 150. ng/mL of **Cr**. Three replicates were measured for each sample.

Solution	Volume of **Cr** spike (uL)		Instrument Readings	
		#1	#2	#3
Blank	0.00	0.005	0.009	0.003
Sample	0.00	0.086	0.088	0.085
Addition 1	250.	0.179	0.191	0.188
Addition 2	500.	0.305	0.310	0.318

a) Assuming that the volume of the spike was negligible, calculate the mean concentration of **Cr** in ng/mL in the sample.
b) Determine the magnitude of the error introduced in part a) and indicate if this is a determinant or indeterminant error.