MURANG'A UNIVERSITY OF TECHNOLOGY

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF APPLIED SCIENCES

UNIVERSITY ORDINARY EXAMINATION

2017/2018 ACADEMIC YEAR

EXAMINATION FOR MASTER OF SCIENCE IN CHEMISTRY

ACH 615: ADVANCED ANALYTICAL CHEMISTRY I

DURATION: 3 HOURS

DATE: 24TH AUGUST, 2018

TIME: 9.00 – 12.00 NOON

Instructions to Candidates:

1. Answer **Any Four** questions.
2. Mobile phones are not allowed in the examination room.
3. You are not allowed to write on this examination question paper.

QUESTION ONE (25 marks)

a) State the difference between qualitative and quantitative analysis (2 marks)

b) List the steps in a chemical analysis (5 marks)

c) Dust falls on a city at a rate of 65mgm^{-2}day^{-1}, major metallic elements in the dust include Al, Mg, Cu, Zn, Mn and Pb. Lead accumulates at a rate of 0.03mgm^{-2}day^{-1}. How many metric tonnes of Pb fall on the 535 square kilometers of the city in a year (3 marks)

d) How many milliliters of 3.00M H_2SO_4 are required to react with 4.35g of solid containing 23.2 wt% $Ba(NO_3)_2$ if the reaction is $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(s)$ (3 marks)

e) The concentration of an alkane $C_{20}H_{42}$ (FM 282.55) in a particular sample of rain water is 0.2 ppb. Assume that the density of rain water is 1.00g/mL. Find the molar concentration of $C_{20}H_{42}$ (3 marks)

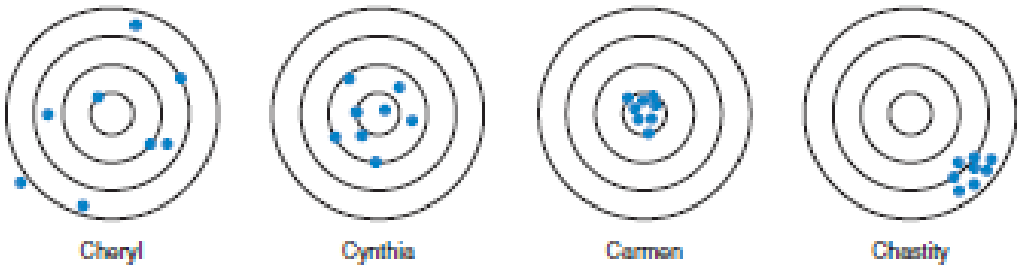
f) The efficiency of a GC column is measured by a parameter called plate height H (mm), which is related to the gas flow rate ($\mu, mL/\text{min}$) by the Van Deemter equation

H = A + B/μ + Cμ where A,B,C are contants.

Prepare an Excel spread sheet with a graph showing values of H as a function of μ

μ = 4,6,8,10,20,30,40,50,60,70,80,90,100. mL/min. use the values of A = 1.65mm,

B = 25.8mm. mL/min and C=0.0236mm.min/mL (10 marks)



Cheryl Cynthia Carmel Chastity shot the targets above at a girl scout camp. Match each target with the proper description

i. Accurate & precise
ii. Accurate & not precise
iii. Precise & not accurate
iv. Neither precise nor accurate (2 marks)

QUESTION TWO (25 marks)

a) i. Explain the difference between systematic and random errors (2 marks)

ii. State whether the error is systematic or random (2 marks)

I. A 25mL transfer pipet consistently delivers 25.031± 0.009mL

II. Four consecutive 20.0 µL injections of a solution into a chromatograph were made and the area of a particular peek was 4383, 4410, 4401 and 4390 units.

iii. Find the absolute and % relative uncertainty of and express each answer with a reasonable number of sig. figures

9.23 (± 0.2) – 4.1(±0.1) = ? (4 marks)

iv. Traces of toxic synthetic hexachlorohexanes in North Sea sediments were extracted by a known process and by two new procedures and measured by chromatography

Method	Concentration found (pg/g)	Standard deviation (pg/g)	No. of Replications
Conventional	34.4	3.6	6
Procedure A	42.9	1.2	6
Procedure B	51.1	4.6	6

I. State the units of concentration in full (1 mark)

II. Is the standard deviation of procedure B significantly different from that of the conventional method? Explain. (3 marks)

b) Lithium Isotope ratios are important to medicine geology, astrophysics and chemistry. Measurements of $^{6}Li/^{7}Li$ ratio in a standard reference material are given here. Do the two methods give statistically equivalent results? Explain (6 marks)

Method 1	**Method 2**
0.082601	0.08183
0.082621	0.08186
0.082589	0.08205
0.082617	0.08206
0.082598	0.08215
	0.08208

c) Consider the following equilibrium

1. $Ag^{+} + Cl^{-} \rightleftharpoons Ag\,Cl(aq)$ $K=2.0 \times 10^{3}$
2. $AgCl(aq) + Cl^{-} \rightleftharpoons AgCl_2^{-}$ $K=9.3 \times 10^{1}$
3. $AgCl(s) \rightleftharpoons Ag^{+} + Cl^{-}$ $K= 1.8 \times 10^{-10}$

i. Calculate the numerical value of the equilibrium constant for the reaction.

$AgCl(s) \rightleftharpoons AgCl(aq)$ (2 marks)

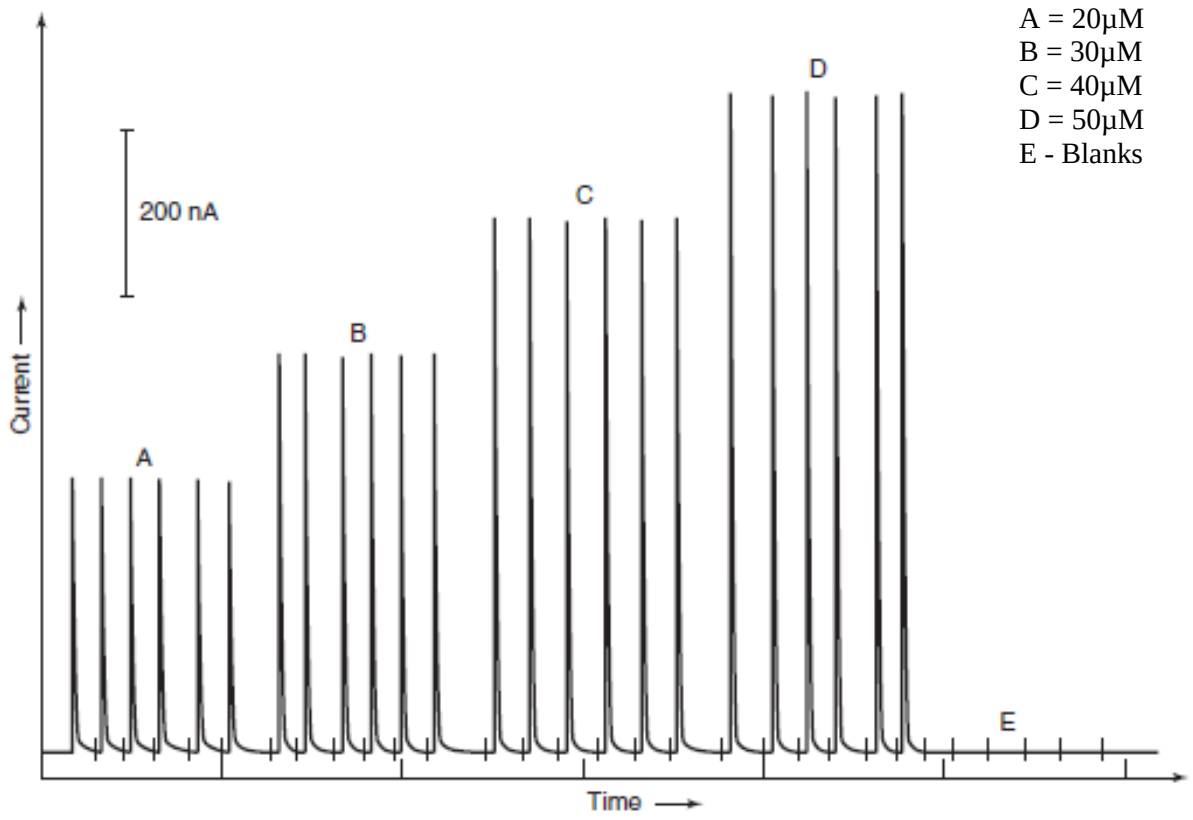
ii. Calculate the concentration of AgCl(aq) in equilibrium with undisolved solid AgCl(s)

(2 marks)

d) State when standard additions and internal standards instead of a calibration curve are desirable and why (3 marks)

QUESTION THREE (25 marks)

a) The figure below gives replicate measurements of As(III) concentration by an electrochemical method



Electrochemical analysis of As(III). Replicate samples correspond to (A) 20 µM, (B) 30 µM, (C) 40 µM, (D) 50 µM As(III), and (E) blanks. *[From I. G. R. Gutz, O. L. Angnes, and J. J. Pedrotti, "Adaptation of Poly(tetrafluoroethylene) Tips to Mercury Drop Electrodes and Evaluation by Flow Injection Analysis," Anal. Chem.* ***1993,*** *65, 500.]*

i. Using a millimeter ruler measure each peak height in the nearest 0.1mm

Noting that the length that corresponds to 200 nA in the figure, make a Table showing the observed current (nA) for each concentration (µM) of As(III)

The blanks appear to be near 0, so we shall disregard them in this problem.

ii. Construct a calibration curve with 24points (A-D) and find the slope and intercept and their uncertainties using the method of least squares (9 marks)

iii. Calculate the concentration (and uncertainty) of As(III) in an unknown that gave a mean of 50lnA in six measurements (3 marks)

b) Why is it desirable in the method of standard addition to add a small volume of concentrated standard rather than a large volume of a dilute standard (2 marks)

c) Low concentrations of Ni-EDTA near the detection limit gave the following counts in a MS measurement.

175, 104, 164, 193, 131, 189, 155, 133, 151, 176

Ten measurements of a blank hold a mean of 45 counts. A sample 1.00 µM Ni-ETDA gave 1797 counts. Estimate the detection limit of Ni-EDTA (5 marks)

If 0.250MNH_3 solution is prepared by diluting 8.45 (±0.04)mL of 28.0 (±0.5) wt% NH_3 [density 0.899 (±0.003)g/mL] upto 500.0 (±0.2)mL. Calculate the uncertainty in 0.250M. The molecular mass of NH_3 17.0305g/mol has negligible uncertainty relative to other uncertainties in this problem (6 marks)

QUESTION FOUR (25 marks)

a) A trainee in a medical lab will be released to work on her own when her results agree with those of an experienced worker at the 95%

Confidence level. Results for a blood urea nitrogen analysis are shown below

Trainee	$\bar{x}$ = 14.5 mg/dL	S = 0.5 mg/dL	n = 6 samples
Experienced worker	$\bar{x}$ = 13.9 mg/dL	S = 0.4 mg/dL	n = 5 samples

Should the trainee be released to work alone? Explain (5 marks)

b) Volatile compounds in human blood serum were measured by trap GC-MS. For quality control, serum was periodically spiked with a constant amount of 1, 2-dichlorobenzene and the concentration (ng/g = ppb) was measured.

i. Find the mean and standard deviation for the following spiked data and prepare a control chart (8 marks)

ii. State whether or not the observations (Obs) meet each of the criteria for stability of a control chart

Day	Obs ppb	Day	Obs ppb	Day	Obs ppb	Day	Obs ppb
0	1.05	84	1.03	154	0.89	251	0.79
1	0.70	91	1.13	156	0.72	259	0.94
3	0.42	101	1.64	161	1.18	262	0.77
6	0.95	104	0.79	167	0.75	277	0.85
7	0.55	106	1.07	175	0.76	282	0.72
30	0.68	112	0.60	182	0.93	286	0.68
70	0.83	113	0.80	185	0.72	288	0.86
72	0.97	119	0.81	189	0.87	290	1.04
76	0.60	125	0.84	199	0.85	294	0.85
80	0.87	128	0.83	212	1.03	296	0.59
		134	0.88	218	0.90	300	0.83
		147	0.89	220	0.86		
		149	0.72	237	1.05		

c) The formation of tetrafluoroethylene from its elements is very exothermic

$2F_2\ (g) + 2C(s) \rightleftharpoons F_2C = CF_2\ (g)$

tetrafluoroethylene

i. If a mixture of F_2 and graphite C and C_2F_4 is at equilibrium in a closed container, will the reaction go to the right or left if F_2 is added (1 mark)

ii. If a tetrafluoroethylene eating bacteria is added what happens to the equilibrium (1 mark)

iii. If the reaction vessel is crushed to $^1/_8$ of its volume, how will the equilibrium shift (1 mark)

iv. What happens to the magnitude of the equilibrium constant when the vessel is heated, explain (2 marks)

d) Verify the following calculations

$\sqrt{3.1415(\pm 0.0011)} = 1.7724_3(\pm 0.0003_1)$ (2 marks)

e) Rewrite the number 3.12356 ($\pm 0.16789\%$) in the forms:

i. Number ($\pm$ absolute uncertainity) (1½ marks)

ii. Number (± percent relative uncertainty) (1½ marks)

With appropriate number of digits

QUESTION FIVE (25 marks)

a) To prepare a solution of NaCl, you weigh out 2.634 (± 0.002)g and dissolve it in a volumetric flask whose volume is 100.00 (± 0.08)mL. Express the molarity of the solution, along with its uncertainty with appropriate number of digits (5 marks)

b) During gravimetric analysis, you forgot to dry the filter crucibles before collecting the precipitate. After filtering the product you dry the product and crucible thoroughly before weighing them

i. Is the mass of the product always high or always low. Explain (2 marks)

ii. What type of error is this? (1 mark)

c) The ratio of the number of atoms of the isotopes ^{69}Ga and ^{71}Ga in eight samples from different sources was measured in an effort to understand differences of the atomic mass of gallium

Sample	$^{69}Ga/Ga^{71}$
1	1.52660
2	1.52974
3	1.52592
4	1.52731
5	1.52894
6	1.52804
7	1.52685
8	1.52793

Find the

i. Mean

ii. Standard deviation

iii. Variance (8 marks)

d) Using Excel, solve the problem. Here are MS signals for methane CH_4 in hydrogen gas

CH4 Vol.%	0	0.062	0.122	0.245	0.486	0.971	1.921
Signal mV	9.1	47.5	95.6	193.8	387.5	812.5	1671.9

i. Subtract the blank value (9.1) from all other values (2 marks)

ii. Use the method of least squares to find the slope and intercept and their uncertainties (5 marks)