



# MURANG'A UNIVERSITY OF TECHNOLOGY

**SCHOOL OF PURE & APPLIED SCIENCES**

DEPARTMENT OF PHYSICAL & BIOLOGICAL SCIENCES

UNIVERSITY POSTGRADUATE EXAMINATION

2018/2019 ACADEMIC YEAR

**SECOND YEAR SECOND SEMESTER EXAMINATION FOR  
M.SC. CHEMISTRY**

ACH 615 - ADVANCED ANALYTICAL CHEMISTRY I

DURATION: 3 HOURS

DATE: APRIL 25 2019

TIME: 2.00 – 5.00 PM

**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) Differentiate the terms precise and accurate. (2marks)
- (b) List the key steps in a chemical analysis (5marks)
- (c) Using a hypothetical HPLC chromatogram sketch, show how the lipids present in a chocolate sample can mask the signal of caffeine as an analyte of interest. (2marks)
- (d) Find the molarity of 37% wt% HCl (density of HCl = 1.19/cc) (3marks)
- (e) A solution contains 12.6ppm calcium nitrate dissolved, which dissociates into the nitrate and calcium ions. Find the concentration of ions in moles/litre. (2marks)
- (f) The density of water varies with temperature and this can be computed by the formula:

$$\text{Density (g/mL)} = a_0 + a_1T + a_2T^2 + a_3T^3. \text{ Where } T \text{ is temperature (}^\circ\text{C)}, a_0 = 0.99989, \\ a_1 = 5.3322, a_2 = -7.5899 \times 10^{-6}, a_3 = 3.671 \times 10^{-8}$$

Using MS Excel spreadsheets compute the density of water for the following temperatures ( $^\circ\text{C}$ ), 0, 5, 10, 15, 20, 25, 30, 35 (11 marks)

*(Export your spreadsheet into word then save it indicating your Reg. number, then print)*

### **QUESTION TWO (25MARKS)**

- (a) Differentiate interpolation from extrapolation with respect to a calibration curve.(3marks)
- (b) State any three requirements of a lab notebook record. (3marks)
- (c) Using any data in the appendix explain the relationship between tolerance and calibration. (3marks)
- (d) Using the error computation formula in the appendix solve the problem below:

We can measure the concentration of HCl solution by reaction with pure sodium carbonate.  $2\text{H}^+ + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$ .

A volume of  $27.35 \pm 0.04\text{ml}$  of HCl solution was required for complete reaction with  $0.9674 \pm 0.009\text{g}$  of  $\text{Na}_2\text{CO}_3$  (FM.  $105.988 \pm 0.001$ ). find the molarity of the HCl and its absolute uncertainty. (10marks)

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

<u>Method I</u>	<u>Method II</u>
0.082601	0.08183
0.082621	0.08186
0.082589	0.08205
0.082617	0.08206
0.082598	0.08215
0.08208	

**QUESTION THREE (25 MARKS)**

- (a) State whether the following errors are systematic or random.
- A 25ml transfer pipette consistently delivers 25.03±0.009ml. (1mark)
  - Four consecutive 200µL injections of a solution into a GC were made and the area of a particular peak was 4383, 4410, 4401, 4390 units. (1mark)
- (b) Find the absolute and percentage relative uncertainty and express each answer with a reasonable number of significant figures  $9.23 (\pm 0.2) - 4.1 (\pm 0.1) = ?$  (4marks)
- (c) 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. Using the data in the appendix and MS Excel
- Find the mean and standard deviation for the following spiked data and prepare a control chart. (8marks)
  - State whether or not the observations meet each of the following criteria for stability of a control chart. (2marks)
- (d) Consider the following equilibrium:
- $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl (aq)} \quad k = 2 \times 10$
  - $\text{AgCl (a)} + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^- \quad k = 9.3 \times 10^{-1}$
  - $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad k = 1.8 \times 10^{-10}$
- Calculate the numerical value of the equilibrium constant for the reaction (4marks)
- $$\text{AgCl (aq)} \rightleftharpoons \text{AgCl (s)}$$
- (e) Calculate the concentration of AgCl(aq) in equilibrium with undissolved solid AgCl(s) (3marks)
- (f) State any two sources of experimental errors in a titration. (2marks)

#### **QUESTION FOUR (25 MARKS)**

(a) Using EXCEL, Spreadsheets solve the problem. Presented are Mass spectrum signals of CH<sub>4</sub> in Hydrogen.

(b)

<b>CH<sub>4</sub> vol %</b>	0	0.062	0.122	0.246	0.971	1.921
<b>Signal mV</b>	9.1	47.5	95.6	193.8	812.5	1671.9

- (i) Subtract the blank from all the signals. (2marks)
- (ii) Using the method of LEAST SQUARES find the slope and intercept and their uncertainties. (8marks)

(b) Low concentrations of Ni-EDTA near the detection limit gave the following counts in an MS Measurement: 175, 104, 164, 193, 131, 189, 155, 133, 159, 176.

Ten measurements of a blank hold a mean of 45 counts. A sample of 100 $\mu$ M, Ni-ETDA gave 1797 counts. Estimate the detection limit. (5marks)

(c) Traces of toxic synthetic hexachlorohexanes in the North Sea sediments were extracted by a known process and by two new procedures (A and B) and measured by chromatography.

<b>Method</b>	<b>Concentration found</b>	<b>Std dev</b>	<b>replicates</b>
Conventional	34.4	3.6	6
Procedure A	42.9	1.2	6
Procedure B	51.1	4.6	6

**I-** Is the standard deviation of procedure B significantly is different from that of the conventional procedure or not? (3marks)

**II-** Is the mean concentration found by procedure B significantly different from that of the conventional procedure? (3marks)

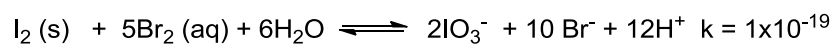
(d) What is the relationship between:

- (i) Standard deviation and accuracy
- (ii) Standard deviation and precision (4marks)

**QUESTION FIVE (25 MARKS)**

- (a) For numbers 116.0, 97.9, 114.2, 106.8, 108.3:
- (i) Find Mean, standard deviation, range and 90% confidence interval for the mean  
(*You may use a calculator and NOT MS excel*) (10marks)
  - (ii) Using the Q-test decide whether the value 97.9 should be discarded. (3marks)

- (b) Suppose 1 litre of solution is prepared such that it contains 0.0010mol Br<sub>2</sub>(aq), 0.0050mol IO<sub>3</sub><sup>-</sup>, 0.002mol Br<sup>-</sup>, 1.0 mol H<sup>+</sup> and excess solid I<sub>2</sub> and that the reaction equation is:



Calculate the concentration when the solution comes to equilibrium:

- (i) By considering stoichiometry. (5marks)
  - (ii) By Excel spreadsheets. (5marks)
- (c) Why end point is considered a point past the equilibrium? (2marks)