DEPARTMENT OF CHEMISTRY

UNIVERSITY OF ESWATINI

MAY 2019 MAIN EXAMINATION

TITLE OF PAPER :   INTRODUCTION TO ANALYTICAL CHEMISTRY

COURSE NUMBER: C204/C212

TIME   :   3 hours

Important information: 1. This paper contains 6 questions.

2. Each question is worth **25** marks

3. Answer any **4** questions in this paper

4. Marks for **ALL** procedural calculations will be awarded

5. Start each question on a fresh page of the answer sheet

6. Diagrams must be large and clearly labelled accordingly

7. This paper contains an appendix of chemical constants

8. Report all numerical answers to the *correct number of significant figures* and with appropriate units.

You are not supposed to open this paper until permission has been granted by the chief invigilator

QUESTION ONE

a) Distinguish the following terms using examples to illustrate. (5)
   i. Systematic and random errors
   ii. Precision and accuracy

b) Glucose levels are routinely monitored in patients suffering from diabetes. The glucose concentrations in a patient with mildly elevated glucose were determined in different months by the spectrophotometric analytical method. The following results were obtained during a study to determine the effectiveness of the diet.

| Time	Glucose concentration (mg/L)
Month 1	1108, 1122,1075,1099,1115,1083,1100
Month 2	992,975,1022,1001,991
Month 3	788,805,779,822,800
Month 4	799,745,750,774,777,800,758

   i. Calculate a pooled standard deviation of the method for the first two months (month 1 and month 2). (5)
   ii. Is the mean glucose level obtained in month 3 significantly different from that obtained in month 4 at 95 % confidence level? (5)
   iii. Determine the 95 % confidence interval for the mean value for month one (1). (4)
   iv. What is the meaning of the results obtained in a (iii) above? Explain (2)
   v. How many replicate measurements in a month are needed to decrease the confidence interval in b (ii) to 1100.3±10.0 mg/L of glucose? (4)

QUESTION TWO

a) Describe the preparation of the following solutions:
   i. 250.0 mL of a 0.275 M NaOH solution from a concentrated commercial reagent, which is 50.0% (w/w) NaOH and has a specific gravity of 1.53.
   [Molar mass (gmol^{-1}): NaOH = 39.997] (6)
   ii. 1.5 L of a 0.075 M H_2SO_4 solution from a concentrated reagent, which is 96.5% (w/w) H_2SO_4 and has a specific gravity of 1.84.

   [Molar mass (gmol^{-1}): H_2SO_4 = 98.079] (5)

b) Explain the difference between the equivalence point and the end point in a titration.

(2)

c) The arsenic in 0.9885 g of a pesticide sample was determined by converting the arsenic to AsO_4^{3-} and treating it with 50.00 mL of a 0.05162 M $AgNO_3$ solution to precipitate all the AsO_4^{3-} as Ag_3AsO_4:

$$3Ag^+(aq) + AsO_4^{3-}(aq) \rightarrow Ag_3AsO_4(s)$$
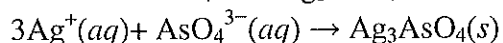
The excess $AgNO_3$ was back-titrated with 11.18 mL of a 0.09965 M KSCN solution to reach the end point:

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$$
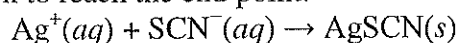
Calculate the weight percent As_2O_3 in the pesticide sample. [Molar mass (g mol^{-1}):197.841]

(6)

d) A 100.00 mL sample of bottled spring water was treated to convert any iron present to Fe^{2+}. The Fe^{2+} was titrated with a 0.001163 M $K_2Cr_2O_7$ solution and required 15.67 mL to reach the end point:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$
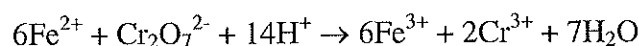
Calculate the concentration of Fe (in ppm) in the bottled spring water sample.

[Molar mass (g mol^{-1}): Fe = 55.847]

(6)

QUESTION THREE

a) Define the term weak electrolyte and give an applicable example. (2)

b) Use reaction equations to show that HPO_4^{2-} can act as an amphiprotic substance in water. (3)

c) Identify the Brønsted-Lowry acid and base on the left hand side of the following equation, and also identify the conjugate acid and base on the right hand side:

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

(2)
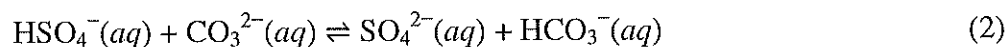
d) Calculate the pH (to 3 decimal places) of the following solutions, after writing suitable balanced reaction equations for any reactions that occur:

i. A solution obtained by mixing 0.365 g of $Ba(OH)_2$ solid with 60.0 mL of a 0.0650 M HCl solution.

[Molar mass (g mol^{-1}): $Ba(OH)_2$ = 171.342] (5)

ii. A 0.0750 M $NaNO_2$ solution. [$K_a(HNO_2)$ = 7.1 × 10^{-4}] (5)

e) Define the term buffer. (2)

3

f) With the help of Handerson's Hasselbalch equation, calculate the volume of a 0.550 M nitrous acid (HNO_2) solution needed to be added to 1.50 L of a solution containing 0.850 g of sodium nitrite ($NaNO_2$) to produce a buffer of pH 3.70?

[Molar mass ($gmol^{-1}$): $NaNO_2$ = 68.996]

[$K_a(HNO_2) = 7.1 \times 10^{-4}$]   (6)

QUESTION FOUR

a) What are the assumptions that are made in the establishment and application of the least squares method?   (2)

b) A calibration graph was prepared as part of a validation procedure for a new method to determine an active constituent of a sunscreen by UV spectrophotometry. The following data was obtained as shown in the table below.

Analyte concentration (mg/L)	Absorbance
0	0.095
20	0.227
40	0.409
60	0.573
80	0.786
100	0.955
120	1.123
Unknown	0.350

    i.   Check the linearity of the data.

    ii.   Use the least squares regression analysis of the data to calculate the concentration of the unknown (You don't need to draw a graph).   (15)

c) In a bid to improve suppressed signal, an analyst uses the method of standard addition procedure on soil samples for the analysis of manganese. Outline the experimental procedure for performing method of standard addition, using diagrams where applicable to illustrate.   (6)

d) What are the advantages of using the method of standard addition, over the external calibration?   (2)

QUESTION FIVE

a) Consider the titration of 15.00 mL of a 0.500 M methyl amine (CH_3NH_2) solution with a 0.300 M HCl solution. [$K_a(CH_3NH_3^+) = 2.3 \times 10^{-11}$]

    iii.   Calculate the pH after the addition of 10.00 mL of the HCl solution.   (7)

    iv.   Calculate the pH at the equivalence point (after addition of 15 Ml of HCl) (10)

v. Choose a suitable indicator for this titration from the table below and motivate your answer. (2)

Indicator	pH transition range
Methyl red	4.2 – 6.3
Bromothymol blue	6.2 – 7.6
Phenolphthalein	8.3 – 10.0

b) Define a primary standard and list five desirable properties of a primary standard. (6)

QUESTION SIX

a) Differentiate between a galvanic and an electrolytic cell. (2)

b) Using an example, differentiate between an oxidizing and a reducing agent. (3)

c) The standard hydrogen electrode (SHE) is the electrode against which all electrode potentials are referenced.

    i. Draw the SHE and label all the components. What is the role of platinum? Why is it a suitable metal for this role? (3)

    ii. State the function of a salt bridge . (2)

d) Given the electrochemical reaction shown, if the standard reduction potential of $Zn^{+2} \rightarrow Zn$ is -0.76 V, and the standard reduction potential of $Cu^{2+} \rightarrow Cu$ is 0.34 V. What is E° for the following electrochemical cell? (3)

$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$$

e) List four (4) factors that should be considered when selecting an oxidizing agent in redox titrations. (4)

f) Which are the two (2) disadvantages of potassium dichromate as an oxidizing agent in redox titrations as compared to permanganate? (3)

a) You have just been employed as an Analytical Chemist at Royal Eswatini Sugar Corporation, in charge of soil chemistry analysis. It is alleged that a certain plantation within an area of 1 hectare has an excess of toxic element Arsenic from the application of a certain herbicide. Briefly explain the steps you would undertake for quantitative analysis of soil in the affected plantation. Limit your explanation;

    i. Sampling

    ii. Sample preparation.

    iii. Quality control

(6)

$$s_{pooled} = \sqrt{\frac{s_1^2(N_1 - 1) + s_2^2(N_2 - 1)}{N1 + N2 - 2}}$$

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{N_1 N_2}{N_1 + N_2}}$$

$$m = \frac{n \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}$$

$$r = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left[n \sum x_i^2 - \left(\sum x_i\right)^2\right]\left[n \sum y_i^2 - \left(\sum y_i\right)^2\right]}}$$

TABLES

TABLE 1: Table of Acid and Base Strength

Ka	Acid		Conjugate Base	
	Name	Formula	Formula	Name
Large	Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
$3.2 * 10^9$	Hydroiodic acid	HI	I-	Iodide
$1.0 * 10^9$	Hydrobromic acid	HBr	Br-	Bromide
$1.3 * 10^6$	Hydrochloric acid	HCl	Cl-	Chloride
$1.0 * 10^3$	Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
$2.4 * 10^1$	Nitric acid	HNO_3	NO_3^-	Nitrate ion
--------	Hydronium ion	H_3O+	H_2O	Water
$5.4 * 10^{-2}$	Oxalic acid	$HO_2C_2O_2H$	$HO_2C_2O_2^-$	Hydrogen oxalate ion
$1.3 * 10^{-2}$	Sulfurous acid	H_2SO_3	HSO_3^-	Hydrogen sulfite ion
$1.0 * 10^{-2}$	Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion
$7.1 * 10^{-3}$	Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
$7.2 * 10^{-4}$	Nitrous acid	HNO_2	NO_3^-	Nitrite ion
$6.6 * 10^{-4}$	Hydrofluoric acid	HF	F -	Fluoride ion
$1.8 * 10^{-4}$	Methanoic acid	HCO_2H	HCO_2^-	Methanoate ion
$6.3 * 10^{-5}$	Benzoic acid	C_6H_5COOH	C_6H_5COO-	Benzoate ion
$5.4 * 10^{-5}$	Hydrogen oxalate ion	$HO_2C_2O^{2-}$	$O_2C_2O_2^{2-}$	Oxalate ion
$1.8 * 10^{-5}$	Ethanoic acid	CH_3COOH	CH_3COO	Ethanoate (acetate) ion
$4.4 * 10^{-7}$	Carbonic acid	CO_3^{2-}	HCO_3^-	Hydrogen carbonate ion
$1.1 * 10^{-7}$	Hydrosulfuric acid	H_2S	HS-	Hydrogen sulfide ion
$6.3 * 10^{-8}$	Dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	Hydrogen phosphate ion
$6.2 * 10^{-8}$	Hydrogen sulfite ion	HS^-	S^{2-}	Sulfite ion
$2.9 * 10^{-8}$	Hypochlorous acid	$HClO$	ClO^-	Hypochlorite ion
$6.2 * 10^{-10}$	Hydrocyanic acid	HCN	CN^-	Cyanide ion
$5.8 * 10^{-10}$	Ammonium ion	NH_4^+	NH_3	Ammonia
$5.8 * 10^{-10}$	Boric acid	H_3BO_3	$H_2BO_3^-$	Dihydrogen carbonate ion
$4.7 * 10^{-11}$	Hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion
$4.2 * 10^{-13}$	Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	Phosphate ion
$1.8 * 10^{-13}$	Dihydrogen borate ion	$H_2BO_3^-$	HBO_3^{2-}	Hydrogen borate ion
$1.3 * 10^{-13}$	Hydrogen sulfide ion	HS-	S^{2-}	Sulfide ion
$1.6 * 10^{-14}$	Hydrogen borate ion	HBO_3^{2-}	BO_3^{3-}	Borate ion
---------	water	H_2O	OH-	Hydroxide

$K_w = 1 \times 10^{-14}$

Table 4: Z- Table

Confidence Level , %	z
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

Table 3: T- Table

VALUES OF *t* FOR VARIOUS LEVELS OF PROBABILITY					
Degrees of Freedom	Factor for Confidence Interval				
	80%	90%	95%	99%	99.90%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.3	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.6	8.6
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.9	2.36	3.5	5.4
8	1.4	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.8	2.2	3.11	4.44
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14

Table 5: F- Table

Critical values of F at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Table 2: The Q- Table

Number of Observations	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.943
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.83	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 121.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (?)	111 Rg (?)							

Lanthanides

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 152.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97

Actinides

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)