DEPARTMENT OF CHEMISTRY

UNIVERSITY OF ESWATINI

JULY 2019 SUPPLEMENTARY/RE-SIT EXAMINATION

TITLE OF PAPER : **INTRODUCTION TO ANALYTICAL CHEMISTRY**

COURSE NUMBER : **C204/CHE 212**

TIME : **3 hours**

Important information:

1. This paper contains five (5) 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) Explain the difference between precision and accuracy and explain how each one of them is measured in a data set. (4)

b) List the three types of errors that can occur during a chemical analysis and describe their effects on the analytical results. (6)

c) The analysis of diesel for sulphur (S) content revealed the following replicate results:

427, 423, 401, 425, 431, 424, 422, 429, 418, 414 ppm

Calculate the following:

i. The median, spread (range) and variance of the set of results. (6)

ii. The coefficient of variation (CV) of the set of results. (2)

d) Describe the preparation of the following solutions:

i. 200 mL of a 1:3 H_2SO_4 aqueous solution from concentrated H_2SO_4. (2)

ii. Describe the preparation of 2.00 L of a 0.551 M aqueous $HClO_4$ solution from a concentrated solution which is 70.0% (w/w) $HClO_4$ and has a specific gravity of 1.664.

[Molar mass (g mol^{-1}): $HClO_4$ = 100.46] (5)

QUESTION TWO

a) Give a detailed explanation of the differences between the following terms

i. replicate and analyte

ii. Limit of detection and limit of quantification

iii. End point and Equivalence point (6)

a) The following data was obtained from the analysis of the sample in ppm.

26 25 24 26 15

i. Should the value '15' be considered part of the data at 95 % confidence level? (4)

ii. Using another method, the values obtained for the same analysis yields the following:

33 26 25 35 33

Do the means for the two methods differ significantly at 95 % confidence level? (5)

iii. Comment on the accuracy of the second method at 95 % confidence level, if the true value is 32 ppm. (5)

iv. Can the precision for the two methods be considered the same at 95 % confidence level? Explain. (5)

QUESTION THREE

a) Describe the following terms;
   i. amphiprotic solvent
   ii. Brønsted-Lowry acid
   iii. Brønsted-Lowry base
   iv. Autoprotolysis (4)

b) Use reaction equations to show that $H_2AsO_4^-$ can act as an amphiprotic substance in water. (2)

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:

$$CH_3NH_2(aq) + HCO_3^-(aq) \rightleftharpoons CH_3NH_3^+(aq) + CO_3^{2-}(aq) \quad (2)$$

d) An aqueous solution of barium hydroxide, $Ba(OH)_2$, has a pH of 13.041. Calculate the molar concentration of barium hydroxide in this solution. (Express your answer to 3 significant figures.) (4)

e) Calculate the pH (to 3 decimal places) of the following solutions, after writing suitable balanced reaction equations for any reactions that occur:
   i. A 0.250 M HBr solution. (3)
   ii. A 0.0450 M propanoic acid (CH_3CH_2COOH) solution.

$$[K_a(CH_3CH_2COOH) = 1.34 \times 10^{-5}] \quad (7)$$

f) Arrange the bases sodium acetate ($NaCH_3COO$), sodium hypochlorite (NaOCl) and sodium iodate ($NaIO_3$) in order of increasing strength. Give a reason for your answer. (3)

Acid	Ka
Acetic acid, CH_3COOH	1.75×10^{-5}
Hypochlorous acid, HOCl	3.0×10^{-8}
Iodic acid, HIO_3	1.7×10^{-1}

QUESTION FOUR

a) Calculate the pH of the following solutions, after writing a balanced reaction equations for any reactions that occur.

i. A solution obtained by mixing 15.0 mL of a 0.450 M HNO_3 solution with 10.00 mL of a 0.450 M $Ca(OH)_2$ solution and diluting the mixture with distilled water to a final volume of 50.0 mL. (8)

ii. A 0.0650 M sodium benzoate (NaC_6H_5COO) solution.

$[Ka(C_6H_5COOH) = 6.28 \times 10^{-5}]$ (7)

b) Define the term buffer. (3)

c) How many milliliters of a 0.200 M NaOH solution must be added to 50.0 mL of a 0.650 M CH_3COOH solution to obtain a buffer with a pH of 4.90? Show the relevant reaction equation. $[Ka(CH_3COOH) = 1.75 \times 10^{-5}]$ (7)

QUESTION FIVE

a) Consider the titration of 25 mL of 0.3 M HF with 0.3 M NaOH.[Ka(HF)= 6.6×10^{-4}]

i. Calculate the pH at the equivalence point (After adding 25 mL of 0.3 M NaOH (6)

ii. Choose an appropriate 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
Cresol purple	7.6 – 9.2
Phenolphthalein	8.3 – 10.0

b) The chromium in a 0.2200 g sample of an ore is oxidized to CrO_4^{2-} with Na_2O_2. The solution is acidified and treated with 0.7642 g of pure $FeSO_4$, resulting in the following reaction:

$$CrO_4^{2-}(aq) + 3Fe^{2+}(aq) + 8H^+(aq) \rightarrow Cr^{3+}(aq) + 3Fe^{3+}(aq) + 4H_2O(l)$$

After the reaction was complete, the excess Fe^{2+} was back-titrated with 9.74 mL of 0.01667 M $K_2Cr_2O_7$ to reach the end point.

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Calculate the weight percentage of Cr_2O_3 in the ore sample.

[Molar masses (g mol^{-1}): $FeSO_4$ = 151.908; Cr_2O_3 = 151.990]

(10)

c) In Question (b), a back-titration method was used to determine the chromium content in the sample. Give three reasons why back-titrations are often used instead of direct titrations. (3)

d) Why are potassium permanganate solutions filtered before they are standardized? (2)

e) Ce(IV) is also a strong oxidizing agent that can be used in redox titrations. List *two* disadvantages of using Ce(IV) over potassium permanganate in redox titrations. (2)

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 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	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 101.07	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	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 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	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)