DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

JULY 2016 SUPPLEMENTARY EXAMINATION

TITLE OF PAPER	:	**INTRODUCTION TO ANALYTICAL CHEMISTRY**
COURSE NUMBER	:	**C204**
TIME	:	**3 HOURS**

Important Information :

1. Each question is worth 25 marks.
2. Answer any **four (4)** question in this paper
3. Marks for **ALL** procedural calculations will be awarded.
4. Start each question on a fresh page of the answer sheet.
5. Diagrams must be large and clearly labelled accordingly.
6. This paper contains an appendix of chemical constants.
7. Additional material : graph paper.

You are not supposed to open this paper until permission has been granted by the Chief Invigilator

QUESTION 1 [25 MARKS]

a) A young scientist determined the amount of Riboflavin (Vitamin B 2) in a cereal sample by measuring its fluorescence intensity in 5% acetic acid solution. A calibration curve was prepared by measuring the fluorescence intensities of a series of standards of increasing concentrations. The concentration of the standard was found to be 10.0 ppm. Explain in detail **TWO** ways which the young scientists can use to show that the method and instrument used for measurements gives accurate results. (Give a detailed explanation how this would be achieved) (6)

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

26	25	24	26	15

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

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

33	26	25	35	33

Do the two methods give the same result at the 95% confidence level? (5)

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

iv) Can the precision of the two methods be considered the same? Explain. (5)

QUESTION 2 [25 MARKS]

a) You have just been employed as an analytical chemist at RSSC, in charge of soil chemistry analysis. It is alleged that a certain plantation with an area of 1ha has an excess of toxic element Arsenic from the application of a certain herbicide. Briefly outline the steps you would undertake for quantitave analysis of soil in the affected plantation. Explanation should include, but not restricted to,

i) **Sampling**

ii) **Quality control**

iii) **Method validation**

iv) **Data analysis and interpretation**
(6)

b) An atomic absorption method for the determination of copper content in fuels yielded a pooled standard deviation of spooled = 0.32 μg Cu/mL (s → σ). The analysis of the oil from a reciprocating aircraft engine showed a copper content of 8.53 μg Cu/mL.

i) Calculate the 99% confidence limits for the result based on a mean of four (4) analyses. (4)

ii) Explain in your own words what the confidence limits calculated in (i) mean (2)

iii) How many replicate measurements are necessary to decrease the 99% confidence for the analysis to ± 0.20 μg Cu/mL? (3)

c) One of the challenges in the quantification of elements is the problem of interferences. Explain what is meant by interferences giving a specific example and a solution on how this interference can be eliminated in analytical chemistry. (4)

d) What is 0.21ppm CO in mol/L (2)

e) Using examples differentiate between quantitative and qualitative analysis in analytical chemistry. (4)

QUESTION 3 [25 MARKS]

a) Calculate the pH of an aqueous buffer solution made from 0.150M NH_4Cl and 0.100M NH_3. [3]

b) Find the pH at each of the following points in the titration of 25 mL of 0.3 M HF with 0.3 M NaOH.

The initial pH

After adding 10 mL of 0.3 M NaOH

After adding 12.50 mL of 0.3 M NaOH

After adding 25 mL of 0.3 M NaOH

After adding 26 mL of 0.3 M NaOH [9 marks]

Draw the titration curve and clearly show the equivalence point and buffer region. (5 marks)

c) How will the titration curve drawn in (b) differ from that of the titration of 0.3M HCl with 0.3M NaOH? Include sketch diagrams to explain. [4]

d) One of the challenges in the quantification of elements is the problem of interferences. Explain what is meant by interferences giving a specific example and a solution on how this interference can be eliminated in analytical chemistry. [4]

QUESTION 4 [25 MARKS]

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 sun cream by UV spectrophotometry. The following data were obtained;

Analyte Concentration (mg/cm3)	0	20	40	60	80	100	120	Unknown
UV absorbance at 325 nM	0.095	0.227	0.409	0.573	0.786	0.955	1.123	0.350

i) Check for the linearity of the data.

ii) Use the method of least squares regression analysis of the data to calculate the concentration of the unknown.

(15 Marks)

c) In a bid to improve suppressed analytical signal, an analyst performs a standard additions procedure on soil samples for the analysis of manganese. Outline the experimental procedure for performing standard additions, using diagrams where applicable to illustrate. (5)

d) What are the advantages of using standard addition over external calibration? (3)

QUESTION 5 [25 MARKS]

a) A student was asked to determine the concentration of ammonia, a volatile substance, in a commercially available cloudy ammonia solution used for cleaning. First the student pipetted 25.00 mL of the cloudy ammonia solution into a 250.0 mL conical flask. 50.00 mL of 0.100 mol L^{-1} $HCl_{(aq)}$ was immediately added to the conical flask which reacted with the ammonia in solution. The excess (unreacted) HCl was then titrated with 0.050 mol L^{-1} $Na_2CO_{3(aq)}$. 21.50 mL of $Na_2CO_{3(aq)}$ was required.

i) Calculate the concentration of the ammonia in the cloudy ammonia solution. (6)

ii) The method in (a) is known as back titration. Give four (4) purposes of back titration i.e. cases which would require the use of back titration instead of direct titration. (4)

a) In titrimetry;

i) Differentiate between primary standard and a secondary standard for titrimetric analysis (2)

ii) Explain what is meant by standardization and give one example of a primary standard used in acid-base titration to standardize HCl and one to standardize NaOH which you have used in the laboratory during your C204 experiments. (4)

iii) Give four (4) desirable properties for a primary standard used for titration purposes. (4)

b) Describe how 2.00L of 0.0500M $AgNO_3$ can be prepared from a primary grade solid of $AgNO_3$. (5)

QUESTION 6 [25 MARKS]

a) The concept of CRM and or SRM is widely used by industry for their quality control measures. Briefly explain;

i) What are CRM or SRMs (2)

ii) What is their central role in analytical chemistry? (2)

How are they certified? (4)

b) Distinguish between sample mean and population mean (2)

c) In the determination of chlorine by Fajan's titration in samples,

i) Name the common adsorption indicator used in this titration. (2)

ii) What is the reason for the addition of dextrin before titration? (2)

d) An iron ore was analysed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron (III) was precipitated as the hydrous oxide $Fe_2O_3.xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3.

Calculate

i) The % Fe in the sample

ii) The % Fe_3O_4 in the sample. (6)

e) i) What is meant by 'digestion of a precipitate'? Briefly describe what happens in the process of digesting a precipitate and give **two** (2) advantages of this step during gravimetric analysis. (3)

ii) What is peptization? How can this phenomenon be avoided during gravimetric analysis (2)

APPENDIX

Useful Formulas

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

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

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 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

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 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 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	3.57	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

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)