DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

MAY 2016 FINAL 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)** questions 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) During analysis it is important that a method blank be always included.

i) What is a method blank? [2]

ii) What is the purpose of a Method Blank? [2]

b) The following are three sets of data for the atomic mass of antimony from the work of Willard and McAlpine

Set 1 (Amu)	Set 2 (amu)	Set 3 (amu)
121.771	121.784	121.752
121.787	121.758	121.784
121.803	121.765	121.765
121.781	121.794	

i) Determine the mean and the standard deviation of each data set. [6]

ii) Determine the 95% confidence interval of set 1 if the standard deviation (s) is a good estimate of σ. [3]

iii) Determine whether the 121.803 value in the first data set is an outlier of that set at 95% confidence level. [3]

iv) Determine whether the precision of data set 1 is the same as that of data set 3. [4]

c) In analytical chemistry explain what is meant by the limit of detection of a method. Explain how this parameter is obtained. [5]

QUESTION 2 [25 MARKS]

a) i) List the four main types of determinate error. [2]

ii) Give a brief explanation/description of each of the types of determinate error you listed in (i) giving a specific example for each. [4]

iii) Explain two ways which can be used to detect determinate errors. [4]

b) The concentration of sodium was determined using flame emission. The data obtained for the external calibration is given below;

Sodium (ppm)	Emission Intensity
0.10	0.11
0.50	0.52
1.00	1.8
5.00	5.9
10.00	9.5
unknown	**4.4**

i) Use the graphical method to find the concentration of the unknown. [4]

ii) It was discovered that the emission intensities was influenced by a variety of factors, including flame temperature. In order to compensate for this variation an internal standard method was used where the same amounts of lithium was added to all the standards and sample. The following data was obtained

Sodium (ppm)	Emission Intensity	Li Emission Intensity
0.10	0.11	86
0.50	0.52	80
1.00	1.8	128
5.00	5.9	91
10.00	9.5	73
unknown	**4.4**	**95**

Determine the concentration of Na (graphically) using this data [6]

iii) Is there any difference between the plot made in **a (i)** and that in **a (ii)**. Explain (2)

iv) Give three characteristics of a good internal standard. [3]

QUESTION 3 [25 MARKS]

a) Define the terms *strong acid* and *weak acid.* Using hydrochloric and ethanoic acid as examples, write equations to show the dissociation of each acid in aqueous solution. [4]

b) Define the terms Brønsted-Lowry acid and Lewis base, and identify one example of each of these species in the equation from (a) above which is illustrating the dissociation of ethanoic acid. [4]

c) Suggest **two** methods, other than measuring pH, which could be used to distinguish between solutions of a strong acid and a weak acid of the same concentration. State the expected results. [4]

d) The pH values of solutions of three organic acids of the same concentration were measured.

acid X pH = 5

acid Y pH = 2

acid Z pH = 3

(i) Identify which solution is the least acidic. [1]

(ii) Deduce how the $[H^+]$ values compare in solutions of acids Y and Z. [2]

(iii) Arrange the solutions of the three acids in decreasing order of electrical conductivity, starting with the greatest conductivity, giving a reason for your choice. [2]

e) The CO in a 20.3 L sample of gas was converted to CO_2 by passing the gas over iodine pentoxide heated to 15 0 degrees Celsius.

$$I_2O_5\,(s) + 5CO\,(g) \rightarrow 5CO_2\,(g) + I_2\,(g)$$

The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M $Na_2S_2O_3$

$I_2 (g) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$

The excess $Na_2S_2O_3$ was back titrated with 2.16 mL of 0.00947 M I_2 solution.

i) Calculate the concentration in milligrams of CO (28.01 g/mol) per litre of sample. (6)

ii) The method used in e (i) is known as back titration; explain what is meant by back titration? (2)

QUESTION 4 [25 MARKS]

a) Gold was determined in a waste stream using voltammetry. The peak height of the current signal is proportional to concentration. A standard addition analysis was done by adding specific volumes of 10 ppm Au solution to the sample as shown in the table below. All solutions were made up to a final volume of 20 ml. The peak currents obtained from the analyses are also tabulated below

Volume of Sample / mL	Volume of Standard / mL	Peak Current / μA
5	0	8
5	2	16
5	5	25
5	10	41

i) Calculate the concentration of Au in the original sample using the least squares method. [10]

ii) What are the two assumptions made in the establishment and application of the least squares method? [4]

iii) Give the main advantage of using standard addition over external calibration. [1]

iv) Explain two disadvantages of using the standard addition method

v) What is 10 ppm Au in ppb? [2]

b) Describe a sampling situation in which a sampler can use judgemental sampling to collect his or her samples. What is the disadvantage and advantage of using this technique? [4]

c) Discuss another type of sampling technique used in analytical chemistry, giving one advantage and disadvantage. [4]

QUESTION 5 [25 MARKS]

a) In determining the amount of chlorine in unknown liquid samples, a gravimetric method was used. The method involved the addition of excess silver nitrate to the analyte. The excess silver nitrate was then back titrated using sodium thiocyanide and iron (III) was used as an indicator. At equivalence point

   i) What special name is given to this type of precipitation? [1]

   ii) Write down all the reactions which take place during this titration. [3]

   iii) What are the challenges of using this type of titration, and how can these problems be solved? Explain [4]

b)

   i) Explain the term 'Homogeneous precipitation'. [2]

   ii) Explain two ways in which homogeneous precipitation can be achieved during gravimetric analysis. Give a specific example for each. [4]

   iii) What are the unique advantages of homogenous precipitation when compared to direct precipitation? [3]

c) i) What is meant by co-precipitation in gravimetry? [2]

   ii) Briefly describe three (3) different types of co-precipitation. [3]

d) Explain how the particle size of a precipitate can be controlled with reference to relative super saturation. [3]

QUESTION 6 [25 MARKS]

a) Method validation is one of the key elements in the development of a method to be used for analysis. Method validation looks into the competence of the developed method to produce reliable data. Explain in detail four (4) different ways which one can use to validate his / her data. [10]

b) i) Find the pH in the titration of 25 mL of 0.3 M HF with 0.3 M NaOH after adding 10 mL of NaOH. [6]

ii) What name is given to the resultant solution in b (i)? [2]

c) i) A standard 0.0100 M solution Na^+ is required to calibrate a flame photometric method to determine the element. Describe how 500 mL of this solution can be prepared from a primary standard Na_2CO_3. [5]

ii) What is the concentration in c (i) in ppm? [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	2.18	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)