DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

MAY 2014 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]

a) i) Distinguish between systematic and random error, using example to illustrate? (4)

ii) Distinguish between precision and accuracy, using examples to illustrate your explanation. (3)

b) What is meant by "occlusion in gravimetry? How can occlusion be minimized? (3)

c) What is meant by 'Peptization" in gravimetric analysis, and how is minimised? (3)

d) Explain two (2) cases when back titration is preferred instead of direct titration. (2)

e) Describe the principle of "indirect titration" in analytical chemistry. (3)

f) The phosphorus in 4.258 g of a plant food was converted to PO_4^{3-} and precipitated as Ag_3PO_4 through the addition of 50.00 mL of 0.0820 M $AgNO_3$. The excess $AgNO_3$ was back titrated with 4.46 mL of 0.0625M KSCN. Express the results of this analysis in terms of % P_2O_5. (7)

The chemical reactions are;

$P_2O_5 + 9H_2O \longrightarrow 2PO_4^{3-} + 6H_3O^+$

$2PO_4^{3-} + 6Ag^+ \longrightarrow 2Ag_3PO_4\ (s)$

$Ag^+ + SCN \longrightarrow AgSCN\ (s)$

QUESTION 2 [25]

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)

iii) How are they certified? (4)

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

c) Riboflavin (Vitamin B 2) is determined 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 following data were obtained.

Riboflavin (μg/mL) (x_i)	Fluorescence Intensity (y_i)
0	0
0.1	5.8
0.2	12.2
0.4	22.3
0.8	43.3
Unknown	15.4

i) Using the data as far as possible, plot the 'best straight line'. (3)

ii) Use the method of least squares regression analysis of the data to calculate the slope, intercept, and concentration of the unknown. (12)

QUESTION 3 [25]

a) The standardized Gas Chromatographic (GC) method and a newly developed Enzymatic Method (EM) were employed separately to determine the alcohol content of a locally brewed wine. The results obtained (in % Ethanol) are as follows:

GC (% Ethanol): 13.0, 13.5, 13.3, 12.9

EM(Ethanol %) : 15.1, 13.3, 12.7, 12.6, 13.1

i) Determine the pooled mean and the pooled standard deviation for the two data sets. (6)

ii) Is there any significant difference in the precision of the two methods at 95% confidence level? (4)

b) A method for the determination of mercury by atomic absorption spectrometry gave values of 400, 385 and 382 ppm for a standard known to contain 400 ppm. Does the mean value differ significantly from the true value, or is there any evidence of systematic error (bias) at 95% confidence level? (5)

c) An analysis is carried out in water to determine the concentration of Cu in a river passing through the Matsapha industrial site. The instrument was calibrated via standard addition method, and the response obtained is listed below;

Standard Addition Concentration (mg/L)	Instrument Reading(Units)
0	12
3	16
5	27
10	37
15	49
20	61

Assuming that no interferences are present, determine the Cu concentration within the sample in ppb using the graphical method. (6)

d) i) Explain the advantage of using the standard addition method instead of external calibration method for elemental analysis? (2)

ii) What is the disadvantage of using the standard addition method? (2)

QUESTION 4 [25]

a) In the lab I get the following 4 numbers for the concentration of chloride in a sample: 0.1015, 0.0991, 0.1016, 0.1014 and 0.1017 M.

What is;

i) the mean

ii) the median

iii) the 95% confidence interval

iv) relative standard deviation for this data set. (12)

b) In 4(a) there is one value that looks like a ringer (an outlier). Use a suitable method to determine if this value can be rejected from the data set. (5)

c) In 4(a) I had you calculate a relative standard deviation. The relative standard deviation is usually regarded as a measure of the relative error on your mean. You also calculated a confidence interval, which is also a measure of the uncertainty of the mean. Compare and contrast these numbers. Which is the better measure of experimental uncertainty? (3)

d) In acid-base titrimetry,

i) Explain what a primary standard is and state two reasons why NaOH is not a suitable primary standard (3)

ii) Name a common primary standard for the standardization of NaOH (2)

QUESTION 5 [25]

a) A 50.0 mL of 0.0500M NaCl is titrated with 0.1000M $AgNO_3$. Calculate the pAg value at the following stages of the titration, given that for AgCl, Ksp = 1.82×10^{-10}.

i) After addition of 10.0 mL of $AgNO_3$

ii) At equivalence point

iii) At 26.0 mL

iv) Plot the titration curve (10)

b) 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)

c) What is the 0.0100 M Na^+ in ppm and ppb? (3)

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

i) Sampling

ii) Quality control

iii) Data analysis and interpretation (7)

QUESTION 6 [25]

a) What is the difference between galvanic and non-galvanic cells? Explain. (3)

b) With an aid of a diagram explain the function of the salt bridge and explain how it works (3)

c) Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using;

i) $E^\circ_{Ag+/Ag} = 0.799$ V [AgCl, Ksp = 1.82×10^{-10}]

ii) $E^\circ_{AgCl}/Ag = 0.222$ V (5)

d) 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)

e) 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)

f) What is coprecipitation? (2)

g) What are the properties of a "good" precipitate in gravimetry? (2)

APPENDIX

VALUES OF t FOR VARIOUS LEVELS OF PROBABILITY					
Number of Observations	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

CRITICAL VALUES FOR REJECTION QUOTIENT Q			
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

Confidence Levels for Various Values of z

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 4-5 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

USEFUL CONSTANTS

$K_w = 1.00 \times 10^{-14}$

K_a [HCN] = 6.20×10^{-10}

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} kg^{-2}
Standard acceleration of free fall†	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

TRANSITION ELEMENTS

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.