DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

JUNE 2015 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)** 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

a) 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.(4)

ii) What is peptization? How can this phenomenon be avoided during gravimetric analysis (3)

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. (5)

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

c) i) What is meant by coprecipitation in gravimetry? (2)

ii) Briefly describe three (3) different types of coprecipitation. (3)

d) Explain how the particle size of a precipitate can be controlled with reference to relative supersaturation. (3)

QUESTION 2

a) A 50.0 mL of 0.0500M NaCl is titrated with 0.1000M $AgNO_3$. Calculate the pCl 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 AgNO3

ii) At equivalence point

iii) At 26.0 mL

Plot the titration curve (8)

b) 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;

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

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

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

c) 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? (2)

ii) Write down all the reactions which take place during this titration. (4)

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

QUESTION 3

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

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

(ii) What specifications should be met by the SHE? (2)

(iii) State the function of the salt bridge and explain how it works. (2)

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

ii) Calculate the potential of the following cell and indicate the reaction that would occur spontaneously if the cell were short circuited.

Pt | U^{4+} (0.200M), UO_2^{2+} (0.0150 M), H^+ (0.0300 M) || Fe^{2+} (0.0100 M), Fe^{3+} (0.0250 M) | Pt

The two half reactions are;

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ E° = +0.771 V

$UO_2^{2+} + 4H^+ + 2e^- \leftrightarrow U^{4+} + 2H_2O$ E° = +0.334 V (6)

c) What is a buffer solution? What equation is used to calculate the pH of a buffer solution? (3)

d) Draw the titration curve for the titration of 20 mL, 0.1 M CH3COOH titrated with 0.1 M NaOH. Show calculations (6)

QUESTION 4

a) The following data was obtained in the analysis of copper using flame atomic absorption spectroscopy.

conc, ppm	% transmittance
5.1	78.1
17.0	43.2
25.5	31.4
34.0	18.8
42.5	14.5
51.0	8.7

Following calibration, a sample of unknown copper concentration was analysed. The measured transmittance was 35.6%.

i) Report the concentration using the graph method. (3)

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

b) The calibration method used in (a) is known as external calibration. Standard addition can is an alternative calibration method which can also be used to determine the concentration of copper in a sample.

i) Outline the experimental procedure for performing standard additions, using diagrams where applicable to illustrate. (7)

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

iii) What is the disadvantage of using the standard addition method? (1)

QUESTION 5

a) 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 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 estimate of the standard deviation for the method the first two months (month 1 and month 2). (5)

ii) Is the mean glucose level obtained in month 3 significantly the same as that obtained in month 4 at 95% confidence level? (5)

iii) Determine the 95% confidence interval for the mean value for month 1. Assume that s = 19 is a good estimate of σ. (4)

iv) What is the meaning of the results obtained in a (ii).Explain (2)

v) How many replicate measurements in month 1 are needed to decrease the confidence interval in b (ii) to 1100.3 ± 10.0 mg/L of glucose? (4)

b) Two barrels of wine were analysed for their alcohol content to determine whether they were from different sources. On the basis of six analyses, the average content of the first barrel was established to be 12.61% ethanol. Four analyses of the second barrel gave a mean Of 12.53% alcohol. The 10 analyses yielded a pooled standard deviation S_{pooled} of 0.070%. Do the data indicate a difference between the wines? (5)

QUESTION 6

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? (3)

b) i) Distinguish between systematic and random errors, using examples to illustrate. (4)

ii) Suppose that 0.50 mg of precipitate is lost as a result of being washed with 200 mL of wash liquid. If the precipitate weighs 500 mg, calculate the relative error. (2)

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

d) Describe the principle of "indirect titration" in analytical chemistry.(2)

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

f) 0.500g sample containing Na_2CO_3 is analysed by adding 50.0ml of 0.100M HCL, a slight excess, boiling to remove CO_2, and then back-titrating the excess acid with 0.100M NaOH . If 5.6ml NaOH is required for the back titration, what is the percent Na_2CO_3 in the sample? (5)

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

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

Ka	Acid		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

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

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	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{5}$ 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

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

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																	4.001 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	TRANSITION ELEMENTS										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								

*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.