DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

JUNE 2014 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 [25]

a) 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. (2)

b) In a bid to improve suppressed analytical signal, an analyst performs a standard additions procedure on soil samples for the analysis of Mn. Outline the experimental procedure for performing standard additions, using diagrams where applicable to illustrate. (7)

c) Using appropriate illustrations compare external calibration curves with standard addition methods and their use in elemental analysis. Clearly explain how an external calibration curve is obtained. (4)

d) Give two disadvantages of using standard addition compared to external calibration (3)

QUESTION 2 [25]

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

b) 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)

c) 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 AgNO3

ii) At equivalence point

iii) At 26.0 mL

iv) Plot the titration curve (10)

d) Explain what is meant by standardization in titration and give one example of a primary standard used in acid-base titration. (3)

QUESTION 3 [25]

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 by calculating the correlation coefficient, r.

ii) Use the method of least squares regression analysis of the data to calculate the slope, intercept, and concentration of the unknown. (15)

c) i) Draw the Gaussian curve. (2)

ii) Indicate clearly the position of 1σ (1)

iii) Indicate clearly the position of μ (1)

iv) State the percentage of the area under a normalized Gaussian curve covered by $\mu \pm 2\sigma$ (2)

d) Explain the difference between accuracy and precision (2)

QUESTION 4 [25]

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 K_b for the equilibrium;

$CN^- + H_2O \leftrightarrow HCN + OH^-$ (3)

d) i) What is the difference between 'end point' and 'equivalence point' in precipitation titrimetry? (2)

ii) For the standardization of sulphuric acid, 0.4512 g sample of primary-standard grade sodium carbonate required 36.44mL of an H_2SO_4 solution to reach an end point. What is the molarity of the H_2SO_4? (4)

QUESTION 5 [25]

a) 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	k49
20	61

Assuming that no interferences are present, determine the Cu concentration within the sample in ppb using the graph method if the sample measured was prepared by diluting to volume 1 ml of sample extract into a 10 mL volumetric flask.

(10)

b) 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. (5)

c)

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

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

d) Explain the term 'Homogeneous precipitation'. What necessitates this method and what are its unique advantages? (4)

QUESTION 6 [25]

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

ii) Explain three (3) different ways which can be used to detect systematic errors. (3)

b) An atomic absorption method for the determination of copper content in fuels yielded a pooled standard deviation of s_{pooled} = 0.32 μg Cu/mL ($s \rightarrow \sigma$). 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. (3)

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

c) A standard method for the determination of carbon monoxide (CO) level in gaseous mixture is known from many hundred measurements to have a standard deviation of 0.21 ppm CO. A modification of the method yields a value for s of 0.15 ppm CO pooled from a data set with 12 degrees of freedom.

i) Does the modification give more precise measurements than the original method at 95 % confidence level? (3)

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

d) 150.0 mL of 0.2105 M nitric acid was added in excess to 0.5 Kg sample with calcium carbonate. The excess acid was back titrated with 0.1055 M sodium hydroxide. It required 75.5 mL of the base to reach the end point.
Calculate the percentage (w/w) of calcium carbonate in the sample. (7)

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	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ 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 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 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								

TRANSITION ELEMENTS

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

*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.