

**UNIVERSITY OF SWAZILAND
FINAL EXAMINATION**

MAY 2007

- TITLE OF PAPER** : **INTRODUCTION TO ANALYTICAL CHEMISTRY**
- COURSE NUMBER** : **C 204**
- TIME** : **3 HOURS**
- Important information** :
1. Each question is worth 25 marks.
 2. Answer any **four (4)** questions in this paper.
 3. Candidates who show **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 and useful data.
 7. This paper contains 10 printed pages, including the cover and appendix.
 8. 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) Calculate the formula weights of the following compounds and round off to the correct significant figures.
i) $\text{Ca}_3(\text{PO}_4)_2$ ii) $(\text{NH}_4)_2\text{CO}_3$ iii) CH_3COOH (3)
- b) i) Distinguish between systematic and random error, using examples to illustrate. (4)
ii) Distinguish between precision and accuracy, using examples to illustrate your explanation. (4)
- c) The following data were obtained for the analysis of caffeine in coffee.

DETERMINATION	Caffeine (ppm)
1	100
2	95
3	167
4	90
5	97

- i) Determine the confidence interval for the data set at the 95 % confidence level. (10)
ii) Explain what this confidence interval means to the analyst. (2)
iii) Calculate the coefficient of variation. (2)

Question 2 [25]

- a) i) Write down the equation that describes the 'bell-shaped' curve in chemometrics and explain all the terms appearing in it. Draw this curve. (5)
ii) In the curve in a (i) locate the mean, and standard deviation (2)
iii) Under what conditions in analytical sampling will the population variance be the same as the sample variance? (1)
- b) i) What are the main classes of determinate error? In each class give an example of the source of that error. (6)
ii) During a gravimetric analysis of Ni, there was a constant loss of 1.5 mg of Ni due to its solubility. Calculate the % error due to this loss for the following weights of Ni in a given sample.
a) 50 mg b) 250 mg (6)
- c) 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 ha has an excess of the toxic element Arsenic from the application of a certain herbicide. Briefly **outline** the steps you would undertake for a quantitative analysis of soil samples in the affected plantation. Your explanation should include, but not restricted to,
i) Sampling protocol
ii) Quality control

iii) Data analysis and interpretation

(5)

Question 3 [25]

a) What are the assumptions that are made in the establishment and application of the least squares method? (2)

b) The phosphorus content in a urine sample was analysed by employing a spectrophotometric method. The data for the standards and samples are given below:

Standard	1	2	3	4	Urine sample
P (mg/L)	1.00	2.00	3.00	4.00	x
Absorbance	0.205	0.410	0.615	0.820	0.625

Employ the least squares regression method to:

i) Calculate the slope, intercept and concentration, x, of phosphorus in the urine sample. (12)

ii) Plot the best straight line, i.e. the best least square line. (5)

c) An analysis is carried out in soil to determine the concentration of Zn at the RSSC. The data is shown in the table below. Using this information, advice the analyst on the quality of the data obtained.

Replicates	Concentration (ppm)
1.	329
2.	333
3.	345
4.	326
5.	322
Mean	331
Std Deviation	9

Your advice should include:

i) An Analytical Quality Control (AQC) chart showing all the necessary analytical control limits at the 95 % confidence interval. (5)

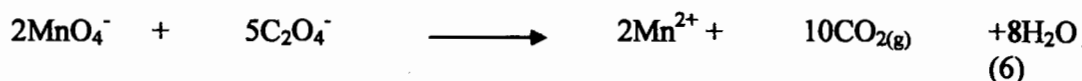
ii) An interpretation of the implications of the resulting chart. (1)

Question 4 [25]

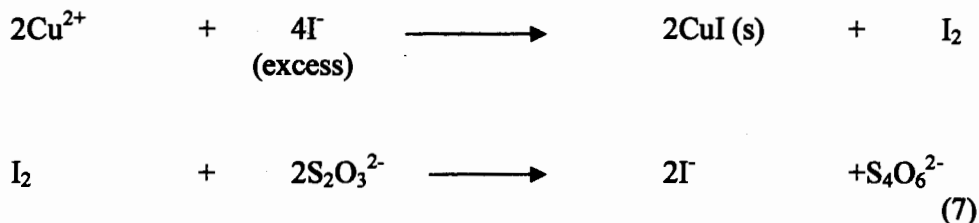
- a) Explain the role of a blank titration in the determination of chlorine in water samples. (2)
- b) List any four (4) desirable properties of a primary standard, and name one which is commonly used in chlorine determinations. (5)
- c) A 25.00 mL 0.100 M NaCl solution is titrated with 0.500M AgNO₃. Calculate the pAg value at the following stages of the titration, given that for AgCl, K_{sp} = 1.8 x 10⁻¹⁰.
- i) After the addition of 0.5 mL
 - ii) At the equivalence point
 - iii) At 5 mL past the equivalence point (6)
 - iv) Plot the titration curve (2)
- d) In the Mohr titration of Cl⁻, Br⁻ and CN⁻ in samples,
- i) State the reagents needed to identify the end point (2)
 - ii) Explain, using chemical equations the colour changes leading to the end point. (2)
 - iii) What is likely to cause 'titration error' in Mohr titration? (2)
 - iv) Explain how the 'titration error' is minimized experimentally. (2)
- e) Use the Le Chatelier's principle to explain why the pH should be strictly controlled. (2)

Question 5 [25]

- a) i) Distinguish between a primary standard and a secondary standard. (4)
ii) Give four (4) essential requirements for a primary standard for titration purposes. (4)
- b) What are the desirable properties of a standard solution meant for titrimetric method of analysis? (4)
- c) A 0.6000 g pure sodium oxalate Na₂C₂O₄ was weighed, dissolved in an acid and titrated with a Potassium Permanganate solution, KMnO₄. The volume of the permanganate added to reach end-point was 34.00 mL. Calculate the molarity of the KMnO₄. The equation for the reaction is;



d) During the standardization of sodium thiosulphate solution, 0.2500 g of pure copper metal was dissolved and treated with excess KI. The liberated iodine required 44.90 mL of the solution of sodium thiosulphate to reach the end-point. Calculate the molarity of the sodium thiosulphate. The pertinent reactions are:



Question 6 [25]

a) Describe the process of homogenous precipitation. Give three (3) of its advantages. Illustrate this principle with a specific example, citing a precipitate for which it has been employed. (7)

b) What is meant by 'digestion of a precipitate'? Briefly describe what happens in the process of digestion a precipitate and give two (2) advantages of this step during gravimetric analysis. (6)

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

d) The Ca in a limestone sample was precipitated as Calcium oxalate, which was ignited to calcium carbonate weighing 123.4 mg. if the limestone sample weighed was 303.7 mg,

- i) Calculate the % Ca in the sample.
- ii) Suppose the precipitate was ignited at a higher temperature to calcium oxide (CaO), calculate its weight (the weight of the CaO).
- iii) If two (2) balance readings were used for each measured weight and there was constant error of 0.1 mg for every balance reading, estimate the relative weighing error (in %), in weighing the calcium carbonate. (10)

Table 1(A)
Values of t for ν Degrees of Freedom for Various Confidence Levels

ν	Confidence Level			
	90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

^a $\nu = N - 1 = \text{degrees of freedom.}$

Table 1(B) Values of t for Various Levels of Probability

Degrees of Freedom	Factor for Confidence Interval				
	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
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	1.90	2.36	3.50	5.40
8	1.40	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	1.80	2.20	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
x	1.29	1.64	1.96	2.58	3.29

TABLE 2Values of *F* at the 95% Confidence Level

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
$\nu_2 = 2$	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

TABLE 3Rejection Quotient, *Q*, at Different Confidence Limits*

No. of Observations	Confidence level		
	Q ₉₀	Q ₉₅	Q ₉₉
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
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372

*Adapted from D. B. Rorabacher, *Anal. Chem.* 63 (1991) 139.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Elementary charge	e	$1.602\,177 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_A e$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = N_A k$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Planck constant	h	$6.626\,08 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34} \text{ J s}$
Avogadro constant	N_A	$6.022\,14 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u	$1.660\,54 \times 10^{-27} \text{ Kg}$
Mass		
electron	m_e	$9.109\,39 \times 10^{-31} \text{ Kg}$
proton	m_p	$1.672\,62 \times 10^{-27} \text{ Kg}$
neutron	m_n	$1.674\,93 \times 10^{-27} \text{ Kg}$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi\epsilon_0$	$1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c \epsilon_0^2$	$1.097\,37 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	g	$9.806\,65 \text{ m s}^{-2}$
Gravitational constant	G	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	$1 \times 10^{-7} \text{ J}$
1 eV	=	$1.602\,2 \times 10^{-19} \text{ J}$	1 eV/molecule	=	96 485 kJ mol ⁻¹

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

Table 5 : PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS																						
	IA	IIA	IIIA	IVA	V	VI	VII	VIII	VIII	VIII	IX	X	XI	XII	IIIA	IVA	V	VIA	VIIA	VIIIA	IIc	Z	
1	H 1.008 1																						
2	Li 6.941 3	Be 9.012 4																					
3	Na 22.990 11	Mg 24.305 12																					
4	K 39.098 19	Ca 40.078 20	Sc 44.956 21	Ti 47.88 22	V 50.942 23	Cr 51.996 24	Mn 54.938 25	Fe 55.847 26	Ni 58.69 28	Cu 63.546 29	Zn 65.39 30	Ga 69.723 31	Ge 72.61 32	As 74.922 33	Se 78.96 34	Br 79.904 35	Kr 83.80 36						
5	Rb 85.468 37	Sr 87.62 38	Y 88.906 39	Zr 91.224 40	Nb 92.906 41	Mo 95.94 42	Tc 98.907 43	Ru 101.07 44	Rh 102.91 45	Pd 106.42 46	Cd 112.41 48	In 114.82 49	Sn 118.71 50	Sb 121.75 51	Te 127.60 52	I 126.90 53	Xe 131.29 54						
6	Cs 132.91 55	Ba 137.33 56	*La 138.91 57	Hf 178.49 72	Ta 180.95 73	W 183.85 74	Re 186.21 75	Os 190.2 76	Ir 192.22 77	Pt 195.08 78	Hg 200.59 80	Tl 204.38 81	Pb 207.2 82	Bi 208.98 83	Po (209) 84	At (210) 85	Rn (222) 86						
7	Fr 223 87	Ra 226.03 88	**Ac 227 89	Rf (261) 104	Hn (262) 105	Unh (263) 106	Uns (262) 107	Uno (265) 108	Uue (266) 109	Uun (267) 110													

Atomic mass
Symbol
Atomic No.

TRANSITION ELEMENTS

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

*Lanthanide Series

**Actinide Series

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

TABLE 6
INTERNATIONAL ATOMIC MASSES

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227	Mercury	Hg	80	200.54
Aluminum	Al	13	26.981539	Molybdenum	Mo	42	95.94
Americium	Am	95	243	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.757	Neon	Ne	10	20.1797
Argon	Ar	18	39.948	Neptunium	Np	93	237
Arsenic	As	33	74.92159	Nickel	Ni	28	58.6934
Astatine	At	85	210	Niobium	Nb	41	92.90638
Barium	Ba	56	137.327	Nitrogen	N	7	14.00674
Berkelium	Bk	97	247	Nobelium	No	102	259
Beryllium	Be	4	9.012182	Osmium	Os	76	190.2
Bismuth	Bi	83	208.98037	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.42
Bromine	Br	35	79.904	Phosphorus	P	15	30.9737622
Cadmium	Cd	48	112.411	Platinum	Pt	78	195.08
Calcium	Ca	20	40.078	Plutonium	Pu	94	244
Californium	Cf	98	251	Polonium	Po	84	210
Carbon	C	6	12.011	Potassium	K	19	39.0983
Cerium	Ce	58	140.115	Praseodymium	Pr	59	140.90765
Cesium	Cs	55	132.90543	Promethium	Pm	61	145
Chlorine	Cl	17	35.4527	Protactinium	Pa	91	231.03588
Chromium	Cr	24	51.9961	Radium	Ra	88	226
Cobalt	Co	27	58.93320	Radon	Rn	86	221
Copper	Cu	29	63.546	Rhenium	Re	75	186.207
Curium	Cm	96	247	Rhodium	Rh	45	102.90550
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.4678
Einsteinium	Es	99	252	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.36
Europium	Eu	63	151.965	Scandium	Sc	21	44.955910
Fermium	Fm	100	257	Selenium	Se	34	78.96
Fluorine	F	9	18.9984032	Silicon	Si	14	28.0855
Francium	Fr	87	223	Silver	Ag	47	107.8682
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.989768
Gallium	Ga	31	69.723	Strontium	Sr	38	87.62
Germanium	Ge	32	72.61	Sulfur	S	16	32.066
Gold	Au	79	196.96654	Tantalum	Ta	73	180.9479
Hafnium	Hf	72	178.49	Technetium	Tc	43	98
Helium	He	2	4.002602	Tellurium	Te	52	127.60
Holmium	Ho	67	164.93032	Terbium	Tb	65	158.92534
Hydrogen	H	1	1.00794	Thallium	Tl	81	204.3833
Indium	In	49	114.82	Thorium	Th	90	232.0381
Iodine	I	53	126.90447	Thulium	Tm	69	168.93421
Iridium	Ir	77	192.22	Tin	Sn	50	118.710
Iron	Fe	26	55.847	Titanium	Ti	22	47.88
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.9055	Uranium	U	92	238.0289
Lawrencium	Lr	103	262	Vanadium	V	23	50.9415
Lead	Pb	82	207.2	Xenon	Xe	54	131.29
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.967	Yttrium	Y	39	88.90585
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.39
Manganese	Mn	25	54.93805	Zirconium	Zr	40	91.224
Mendelevium	Md	101	258				