

UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2006

**TITLE OF PAPER : INTODUCTORY ANALYTICAL
CHEMISTRY**

COURSE NUMBER: C204

TIME ALLOWED : 3 HOURS

**INSTRUCTIONS : ANSWER ANY FOUR(4) QUESTIONS.
EACH QUESTION CARRIES 25MARKS.**

**A periodic table and other useful data have been provided
together with this paper.**

**You are not supposed to open this paper until permission to do so has
been granted by the Chief Invigilator.**

Question 1 (25 marks)

- a) Differentiate between:
- I. Precision and accuracy
 - II. Determinate and indeterminate error
 - III. Constant determinate error and proportional determinate error. (6)
- b) Give the various types /categories of determinate errors commonly encountered during chemical analysis. Give an example in each case. Briefly discuss how these errors can be eradicated or reduced. (8)
- c)
- I. What do you understand by 'Tolerance of an equipment'? Give an illustrative example. (2)
 - II. Which would you prefer for use during an analysis that requires some degree of high accuracy – an A class pipette or B class pipette? Why? (2)
- d) Given the following data sets

A	2.31	2.33	2.30	2.30
B	11.74	11.82	11.79	11.80
C	56.33	56.21	56.27	56.16

- I. Which of the data sets has the best precision and why?
- II. Is the most precise set of data necessarily the most accurate? Justify your answer.

(7)

Question 2 (25 marks)

- a) Differentiate between:
- I. Sample mean, and population mean.
 - II. Sample standard deviation and population standard deviation.
 - III. What step/s should be taken during laboratory analyses to make the sample mean to be as close as possible to the population mean? (5)

- b) Give an expression for the confidence limits for the true mean of a given set of data. Offer an explanation (i.e. the meaning) for this expression and define all the terms in the expression. (3)
- c) The following data (in ppm CaCO_3), were obtained during the analysis of a drinking water sample for total hardness: 227.1, 228.6, 226.9, 228.3 and 226.4
Calculate:
- I. The mean value
 - II. The median value
 - III. The range of the data
 - IV. The standard deviation
 - V. The standard deviation of the mean
 - VI. The variance
 - VII. The % RSD (Relative Standard Deviation)
 - VIII. The confidence interval at 95% confidence level (17)

Question 3(25 marks)

- (a). Define the following terms in connection with the true value of an experimental measurements, assuming there is no systematic error.
- (i). Confidence limit
 - (ii). Confidence level. (2)
- (b). What happens to the confidence interval of a given experimental value when $s \rightarrow \sigma$? How can this be achieved during analysis? (2)
- (c). A spectrophotometer whose accuracy is being evaluated gave the following absorbance readings for a particular solution at a wavelength of 350.0 nm.
- 0.638, 0.639, 0.639, 0.638, 0.640, 0.639, 0.640.
- If the true absorbance is 0.640:
- (i). Estimate the percent error in the absorbance. (3)
 - (ii). Determine whether there is a significant difference between the experimental mean and the true value at the 99% confidence level. (6)
- (d). A new method for the analysis of SO_2 was being evaluated by comparing the results on using it with that of the standard method. The results of the concentrations of SO_2 (in $\mu\text{L}/\text{m}^3$), by the two methods are tabulated below:

New Method	Standard Method
21.30	23.54
25.72	23.09
24.62	24.25
21.54	21.62
22.31	24.27
21.54	21.62
20.51	22.20

- (i). Determine the pooled mean and the pooled standard deviation for the two data sets. (7)
- (ii). Employ the paired t-test to determine whether there is a significant difference between the two methods at the 95% confidence level. (4)
- (iii). Comment on the accuracy/reliability of the new method. (1)

Question 4 (25 marks)

- (a). What do you understand by the following?
 - (i). Standard addition method of analysis.
 - (ii). Internal standard method of analysis. (2)
- (b). State any advantage/s of Standard addition method over the external standardization method. (2)
- (c). Briefly describe how you would employ the multiple point internal standard method for the analysis of Fe in a given sample, using Mn as the internal standard. (8)
- (d). In using the internal standard method to determine Ca, the following absorbance readings were obtained:

Ca (mg/L)	A_{422}	Cu(mg/L)	A_{324}
1.00	0.086	1.00	0.142
2.00	0.177	2.00	0.292
3.00	0.259	3.00	0.438
4.00	0.350	4.00	0.576

- (i). Calculate the average relative absorbance (A_{324}/A_{422}) produced by equal concentrations of Cu and Ca in mg/L. (5)
- (ii). Using Cu as an internal standard for the Ca determination, a sample containing 2.47mgCu/L gave an absorbance, $A_{324} = 0.269$ and $A_{422} = 0.218$. Determine the concentration of Ca in the sample in mg/L. (8)

Question 5 (25 marks)

- (a) Given 100.00 ml of CCl_4 , a separatory funnel and other items for the extraction of a solute X in a 100.00ml aqueous sample give a detailed procedure for this experiment (7)
- (b) A 250-mg sample of an organic compound (FW = 84) is dissolved in 200 ml of H_2O . The aqueous phase is extracted with 50 ml of benzene and allowed to reach equilibrium. The analysis of the aqueous phase now shows that it contains only 63 mg of the organic compound. Calculate K_D . (12)
- (c) The observed distribution ratio, D, for the extraction of UO_2^{2+} (as the nitrate complex) from 8 M HNO_3 into ether is 1.86. Calculate the percentage remaining in the aqueous phase after three extractions with equal volume of ether? (6)

Question 6 (25 marks)

- (a). Describe the process of homogeneous precipitation. Give three of its advantages. Illustrate this principle with a specific example, citing a precipitation for which it has been employed. (7)
- (b). What is meant by "digestion of a precipitate"? Briefly describe what happens in the process of digesting a precipitate and give two advantages of this step during gravimetric analysis. (6)
- (c). What is peptization? How can it 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 303.7 mg:
- Calculate the % Ca in the sample.
 - Suppose the precipitate was ignited at a higher temperature to Calcium Oxide, calculate its weight.(i.e. the weight of the CaO)
 - If two balance readings were used for each measured weight, and there was a constant error of 0.1mg 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 $\nu = N - 1 =$ 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 <i>Observations</i>	Confidence level		
	Q90	Q95	Q99
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.

TABLE 4

Quantity	Symbol	Value	General data fundamental constants
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	$F = eN_A$	$9.6485 \times 10^4 \text{ C mol}^{-1}$	
Boltzmann constant	k	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$	
Gas constant	$R = kN_A$	$8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$	
Planck constant	h $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34} \text{ J s}$ $1.054\,57 \times 10^{-34} \text{ J s}$	
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 of 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 permeability†	μ_0	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^2$	
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$ $4\pi \epsilon_0$	$8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24} \text{ J T}^{-1}$	
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27} \text{ J T}^{-1}$	
Electron g value	g	2.002 32	
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11} \text{ m}$	
Rydberg constant	$R_\infty = m_e e^4/8h^3 c$	$1.097\,37 \times 10^5 \text{ cm}^{-1}$	
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$	
Gravitational constant	G	$6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$	
Standard acceleration of free fall†	g	$9.806\,65 \text{ m s}^{-2}$	

† Exact (defined) value.

f	p	n	μ	m	c	d	k	M	G	Prefixes
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																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA I	IIA II	IIIB III	IVB IV	VB V	VIB VI	VII VII	VIII VIII	VIII VIII	VIII VIII	IB IX	IIB X	IIIA III	IVA IV	VA V	VIA VI	VIIA VII	VIIIA VIII
1	H 1.008 1	He 4.003 2																
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	Co 58.933 27	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	Ag 107.87 47	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	*Ln 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	Au 196.97 79	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	Hs (262) 105	Unh (263) 106	Uns (264) 107	Uno (265) 108	Uue (266) 109	Uun (267) 110								

TRANSITION ELEMENTS

Atomic mass
Symbol
Atomic No.

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	1	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				