UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2006

TITLE OF PAPER	**:**	**INTRODUCTORY ANALYTICAL CHEMISTRY**
CCOURSE NUMBER	**:**	**C204**
TIME	**:**	**THREE HOURS**
INSTRUCTIONS	**:**	**Answer any FOUR questions. Each question carries 25 marks.**

A periodic table, other useful tables and data have provided with this paper.

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Question 1 (25 marks)

(a) Calculate the formula weights of the following compounds and round off to the correct significant figures.

(i) $Pb(NO_3)_2$ (ii) KCl (iii) $Ca_3(PO_4)_2$ (6)

(b) Given the following expression, calculate the relative and absolute errors in %A, giving your answers with appropriate number of significant figures.

$$\%A = \frac{(0.1137 \pm 003) \times (74.116 \pm 0.005) \times (38.04 \pm 0.02)}{(800.0 \pm 0.21)}$$ (5)

© Use an illustrative example to show that a set of data from replicate experimental measurements could be very precise without being accurate. (2)

(d) The (%w/w) in the alloy of a metal X, determined by potentiometric titration method yielded the following results:

16.887; 16.997; 16.857; 16.728; 16.883; 16.840; 16.968; 16.992.

Calculate:

(i) The mean, (ii) The median. (iii) The standard deviation, (iv) The variance, (v) The %RSD, (vi) The confidence interval at 95% confidence level. Explain what the confidence interval means. (12)

Question 2 (25 marks)

Given the following data set:

	Set A	Set B
N	**10**	**12**
Mean, x	**34.65**	**35.78**
Standard deviations, s	**0.82**	**0.71**

Determine:

(i) The pooled mean

(ii) The pooled standard deviation. (5)

(b) (i) What is a Gaussian error curve? (1)

(ii) Give four of the main features of a normalized Gaussian curve. (4)

(iii) What % of the area under a normalized Gaussian curve is covered by the following:

$\mu + 1\sigma$ $\mu \pm 2\sigma$ $\mu \pm 3\sigma$ (3)

(iv) State the equation that describes a Gaussian curve, and define the parameters involved. Under what condition is this equation applicable? (4)

© The ideal gas law expression given below can be employed for the determination of the formula weight (FW), of a gas.

$$F.W. = \frac{mRT}{PV}$$

Where:

m	=	(0.118 ± 0.002)g
T	=	(298.2 ± 0.005) K
P	=	(0.724 ± 0.005)atmos
V	=	(0.250 ± 0.005) L
R	=	(0.082056 ± 0.000001)

(i) Determine the compound's formula weight. (2)

(ii) Calculate the absolute error and the cumulative % relative error in the formula.. (6)

<u>Question 3 (25 maarks)</u>

(a) Explain the following terms/statements:

(i) A normal calibration curve, (2)

(ii). Matrix marching (during external standardization) (2)

(b). Briefly describe the steps to be taken when employing the multiple point standard addition method for the analysis of iron in a given water sample by a spectroscopic method. (6)

©. Standard solution of an element, X. were mixed with an unknown sample containing X. The absorbance of the final solution was taken with an Atomic Absorption Spectrophotometer. The added standard solution is 1.0 ppm in X (i.e. 1.00 mg/L in X). Absorbance readings obtained are tabulated below:

Vo. of Unknown (mL)	Vol.of Standard (mL)	Total Vol. (mL)	Absorbance
10.00	0	100.00	0.163
10.00	1.0	100.00	0.240
10.00	2.0	100.00	0.319
10.00	3.0	100.00	0.402
10.00	4.0	100.00	0.478

(i) Calculate the final concentration of the added standard in each solution in ppm, (5)

(ii) Employing the multiple point (Graphical) method, determine the concentration of X in the unknown. (10)

Question 4 (25 marks)

(a) State the Nernst's distribution law. Give its mathematical expression and define all the parameters in it. (3)

(b) Distinguish distribution coefficient, K_D, from distribution ratio, D. Illustrate this difference with an example. (4)

© For the extraction of a weak acid, HB, whose anion, B^-, does not penetrate the organic phase and assuming that HB is monomeric in both phases:

(i) State the expression for its distribution ratio, D, of HB and define all the parameters in it. (3)

(ii) Hence identify the factors that influence the value of D. (3)

(d). (i) The distribution ratio for X between CCl_4 and H_2O is 19. If 50 mL of an aqueous solution of 0.25 M X is shaken with 100 mL of CCl_4, calculate the percentage of X remaining in the water. (6)

(ii) If the aqueous solution is now extracted with two 50 mL portions of CCl_4 instead of one 100-mL portion, calculate the % of Y remaining in the aqueous phase. Assume no volume changes during the extraction. (6)

Question 5 (25 marks)

(a) (I) What is digestion of a precipitate and why is this step essential during gravimetric analysis of a sample? (3)

(ii) What steps are involved during the digestion process? (2)

(iii) Explain the difference between digestion and postprecipitation. (2)

(b). Give three of the ideal characteristics of a good analytical precipitate.. (3)

©. (i) What is coprecipitation? (1)

(ii) Briefly discuss the different types of coprecipitation that exist and state how each of them can be minimized. (6)

(b) A sample comprising Al and Mg, and weighing 3.084 g was dissolved and diluted to 100 mL in a volumetric flask. A 250 – mL portion of it was taken and treated with 8-hydroxyquinoline to precipitate all the Al and Mg. After drying, the precipitate weighed 1.7748g. Another 25.00 mL portion of the sample was taken and treated with ammonia to precipitate only $Al(OH)_3$. The latter precipitate was ignited and weighed 0.1167 g. Calculate the % Al and % Mg in the sample. (8)

Question 6 (25 marks).

(a) Distinguish between the following:

(i) The equivalent point and the end point of a titration. . (2)

(ii) A primary standard and a secondary standard for volumetric titrimetry. (2)

(b) Give four of the essential requirements for a primary standard for volumetric titrimetry. (4)

© Describe how you would prepare:

(i) 1.00L of 0.0750 M $AgNO_3$ from the solid reagent. (3)

(ii) 300.00 mL of 4.00% (w/v) aqueous $BaCl_2$ from a 0.500 M $BaCl_2$. (3)

(iii), 1.00L of a solution that is 50.00 ppm in Na^+, starting with solid Na_2SO_4 (4)

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

$$2Cu^{2+} + \underset{\text{(excess)}}{4I^-} \rightarrow 2CuI_{(s)} + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$ (7)

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 2

Values *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. i9	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 3

Rejection Quotient, Q, at Different Confidence Limits*

No. of	Confidence level		
Observations	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
S	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.. *Chcm.* 63 (1991) 139.

TABLE 4

General data 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	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ 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}

TABLE 5 : 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										Atomic mass → Symbol → Atomic No. →	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 *Ln 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

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	0	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				