UNIVERSITY OF SWAZILAND
FINAL EXAMINATION

MAY 2010

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 rewarded.
		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; 2 graph papers.

You are not supposed to open this paper until permission has been granted by the chief invigilator.

Question 1

a) The following results were obtained for the analysis of aspirin in 100 g aspirin tablets:

Determination	% Aspirin (w/w)
1	226.4
2	228.3
3	226.9
4	228.6
5	243.8
6	227.5
7	226.6
Average	**229.7**

i) The mean is calculated by a first year student and presented as 229.7 (w/w). Using your knowledge of data reproducibility and applying the necessary statistical tool at the 95 % interval, would you say that the mean is correct? If not, determine the correct mean for the data. [6]

Hence, calculate the following parameters, using the data from the table:

ii) Median [2]
iii) Standard deviation [4]
iv) Variance [2]

b) Using the same data set in (a);

i) Determine the confidence interval for the data set at the 95% confidence level. [4]
ii) Explain what this confidence interval means to the analyst. [2]

iii) Explain what the standard deviation calculated in (a) above means to the analyst. [2]

c) Under what abnormal conditions are the following techniques applied in analytical chemistry;

a) Standard additions?
b) External standards?
c) Back titration? [3]

Question 2

a) The concept of CRM and or SRM is widely used by industry for their AQC measures. Briefly explain;
   i) What are CRMs or SRMs? [2]
   ii) What is their central role in analytical chemistry? [2]
   iii) How are they certified? [4]

b) Distinguish the following terms;
   i) Precision and accuracy
   ii) Random and systematic errors
   iii) Sample mean and population mean [3]

c) A second year BSc student is on trial, suspected of second degree burglary. Broken pieces of glass were found on his jacket, which he claims were from broken glassware from the C204 laboratory sessions. Laboratory glassware is a special borosilicate glass and so determination of the boron content of the glass in the jacket and also from the crime scene was done. Each analysis was replicated 5 times. The results from the analyses are presented in the table below;

Boron concentration (ppm)	
From Crime scene	From Jacket
14.0	15.4

The population or pooled standard deviation for the test was found to be 0.7 ppm. Would you be 99 % confident that indeed the student committed the said offence? [6]

d) Calcium (Ca) in a 200 mL sample of natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO was 26.7134 g. Calculate the concentration of Ca in water in g/100ml. [5]

e) Give three (3) essential properties that a solvent must possess if it is to be successfully used as an extraction solvent. [3]

Question 3

a) The pain reliever phenacetin is soluble in cold water to the extent of 1.0g in 1310 mL and soluble in diethyl ether to an extent of 1.0g in 90 mL.

i) Determine the approximate distribution coefficient for phenacetin in those 2 solvents. [3]

ii) If 150 g of phenacetin were dissolved in 100 mL of distilled water, how much ether would be required to extract 90 % phenacetin in a single extraction? [5]

iii) What percentage of the phenacetin would be extracted from the aqueous solution in part (ii) above by two 25 mL portions of ether? [5]

b) Because crude oil from various sites will have differences in composition, it is often possible to determine the source of a crude oil sample by measurement of the concentration of minor constituents such as anthracene. Replicate analyses of an anthracene sample from a commercial supplier were done and gave a mean value of 123 ppb. The same analysis was performed on an unknown sample from the Nhlambeni community along the Lusushwana River, downstream the Matsapa Industrial site. The sample is suspected to be from the petroleum storage tanks in the Matsapa Industrial area. The results are presented in the table below;

Sample ID	Concentration (ppb)
1	134
2	135
3	137
4	137
5	133

Would you be 95 % confident that the unknown sample is from the Matsapa industrial site storage tanks? [4]

c) List any four (4) desirable properties of a primary standard, and name one which is commonly used in chlorine determinations. [5]

d) Using litmus as an indicator and applying Le Chatelier's Principle,

i. Write the net ionic equation for the system at equilibrium, [1]

ii. Explain the net effect of adding hydroxide ions, [1]

iii. Explain the net effect of adding hydrogen ions, [1]

to the observed colour changes.

Question 4

a) Given that a linear relationship exists between the concentration and the absorbance of the permanganate ion given below;

C_{MnO4^-}	1.00	5.00	10.00	20.00	25.00	Unknown
Absorbance	0.030	0.147	0.301	0.577	0.738	0.217

i) Using the data as far as possible, plot the 'best straight line'. [3]
ii) Use the least squares regression analysis of the data to **calculate** the slope, intercept, and concentration of the unknown sample. [12]

b) A 1.00 L sample of polluted water was analysed for the presence of Pb^{2+}, by adding an excess of Na_2SO_4 to precipitate 229.8 mg of the lead as $PbSO_4$. What is the concentration of the Pb in the water sample in mg/L? [2]

c) In the process of assessing responsibility for a chemical spillage on the drainage lines to the Usushwana River, two possible suspected industries are identified. Fluorescence spectrometer is used to determine the relative concentrations of the samples from the suspected industries and the samples from the Usushwana River. These are compared, and the results are presented below;

Sample Identity	Mean	Std deviation	No. of samples
Suspect 1	2.31	0.07	4
Suspect 1	2.67	0.09	5
Polluted sample	2.45	0.08	6

Which of the two suspected industries would you say, with 95 % certainty, is responsible for the oil spill in the river? [8]

Question 5

a) Total hardness of water may also be determined using complexometry. Briefly explain the chemistry involved in the reaction vessel during this determination. Your explanation should include discussion on;

i) The preferential adsorption of the EDTA to the cations in solution, [2]
ii) The necessary equations, [2]
iii) How the end-point is attained, [4]
iv) Indicator name, other than Eriochrome Black T. [1]

b) Standard solutions of an element X were mixed with an unknown sample containing the element. The absorbance of the final solution was taken with an Atomic Absorption Spectrophotometer (AAS). The added standard has a concentration of 1 mg/L

(ppm) and is added incrementally at 1.0 mL. Absorbance readings obtained are tabulated below;

Vol. 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. [4]

ii) Using the graphical method, determine the concentration of element X, given that sample absorbance is at 0.430 [7]

c) Calculate the pH of a 0.05M solution of HF, given that $K_a = 1.0 \times 10^{-3}$. [5]

Question 6

a) i) Briefly describe how Dichlorofluorescein functions as an indicator in Fajan's titrations. [4]

ii) In the determination of chloride ions in waste water, explain why dextrin is added to the solutions prior to the Fajan's titrations. [1]

b) The precision of a colorimetric method for the creatinine content in serum was being evaluated by employing the same procedure and performing several sets of analyses on different samples. The following absorbance data were obtained

Sample 1	Sample 2	Sample 3
0.810	0.702	0.681
0.880	0.699	0.661
0.826	0.724	0.665
0.865	0.751	

(i) Calculate the pooled mean and the pooled standard deviation. [5]

(ii) Are there any significant differences between data sets 1 & 2; 1 & 3 and 2 & 3? Justify your reasoning with the necessary calculations. [12]

(iii) Comment on the precision of the instrument. [3]

Table .1(A)

Values of t for ν Degrees of Freedom for Various Confidence levels

	Confidence Level			
V	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

	Factor for Confidence Interval				
Degrees of Freedom	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	5.19	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 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. *Chem.* 63 (1991) 139.

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	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	8.314 51 J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		6.2364×10 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		
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 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}
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
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	9.806 65 m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^2 Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ 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 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	(220) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

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

TRANSITION ELEMENTS

*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 lowest half-life