UNIVERSITY OF SWAZILAND
FINAL EXAMINATION

MAY 2008

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 8 printed pages, including the cover and appendix.
		8. Additional material; 3 graph papers.

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

Question 1 [25]

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

Determination	% Aspirin (w/w)
1	94.25
2	97.63
3	92.33
4	91.55
5	88.45

Calculate the following parameters, using the data from the table:

i) Mean (2)
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) A 0.4512 g sample of primary-standard-grade Na_2CO_3 required 36.44 mL of an H_2SO_4 solution to reach an end point in the reaction;

$$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$$

What is the molarity of the H_2SO_4 ? (4)

d) Using examples where appropriate, **briefly** explain the following terms as applied in analytical chemistry.

i) Co-precipitation
ii) Reagent blank
iii) Standard Reference Material (3)

Question 2 [25]

a) i) Using a hypothetical data set, explain the difference between accuracy and precision. (4)

ii) Write down the formula for the Gaussian curve in statistics and explain the meaning of any four (4) terms appearing in it. (5)

b) Two methods were used to measure the pH of a blood sample taken from a patient. The following results were obtained;

Potentiometrically	**pH**				
	4.76	4.93	5.63	4.78	4.81
Titration	5.24	6.63	4.91	5.62	5.95

i) The mean pH for 5 000 patients recorded over a two year period by the potentiometric method is 5.45. Is this particular patient's blood pH significantly different from other patient's pH measured by titration at the 95 % confidence level? (4)

ii) In the data set for the titration measurements above, would the value of 6.63 be considered an 'outlier'? Justify your reasoning. (4)

iii) Is the mean value of potentiometric measurements significantly different from that of the titration method at the 95 % confidence level? (5)

iv) Compare the precision of the two methods at the 95 % confidence level. (3)

Question 3 [25]

a) i) What is the difference between end-point and equivalence point in a precipitation titration? (4)

ii) Explain what is meant by a blank titration in precipitation titrations (2)

iii) Explain what is meant by a back titration in precipitation titrimetry, citing an example. (4)

b) A 0.050M $AgNO_3$ solution is used to titrate 25 mL of 0.10 M NaBr.

i) Given that the K_{sp} value for AgBr is 5.0×10^{-13}, calculate the pAg for the following added volumes of $AgNO_3$ solution;

20 mL 50 mL 70 mL
49 mL 51 mL (10)

ii) Plot the resulting titration curve. (5)

Question 4 [25]

a) Using examples, equations and illustrations explain the basic principles behind the application of the following techniques as used in analytical chemistry;

i) Gravimetric analysis
ii) Solvent extraction
iii) Complexometric titrations (12)

b) 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)

c) Calculate the pH of a 400 mL solution containing 0.28 M NH_4Cl and 0.07 M NH_3 in an acid/base type of titration, where $K_b = 1.76 \times 10^{-5}$.

The important reaction is;

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$ (4)

d) Briefly describe how Dichlorofluorescein functions as an indicator in Fajan's titrations. (4)

Question 5 [25]

a) Standard solutions of an element X were prepared in 100 mL volumetric flasks. The absorbances of the final solutions were measured 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 standard (mL)	Total Vol. (mL)	Absorbance
0	100.00	0.163
1.0	100.00	0.240
2.0	100.00	0.319
3.0	100.00	0.402
4.0	100.00	0.478

i) Calculate the final concentration of the added standard in each solution in **ppm.** (5)
ii) Using the **graphical method**, determine the concentration of element X, given that sample absorbance is at 0.430 (7)

b) i) In a bid to improve suppressed analytical signal, an analyst performs a standard additions procedure on soil samples for the analysis of Manganese. Outline the experimental procedure for performing standard additions, using diagrams where applicable to illustrate. (5)

ii) Briefly outline the four (4) main procedures to be employed during any analytical work as part of the quality control protocol. Use diagrams to illustrate your reasoning. (8)

Question 6 [25]

a) i) a bottle of commercial concentrated HCl has the following on its label: purity 37 % (weight percent composition) and specific gravity 1.18 g/mL. Calculate the molarity if the HCl. (5)

ii) A sample of salt water with a density of 1.02 g/mL contains 17.8 ppm nitrate, NO_3^-. Calculate the molarity of nitrate in water. (5)

b) 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)

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

	$V_1 = 2$	3	4	5	6	7	8	9	*10*	15	*20*	*30*
$V_2 = 2$	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. *Chem.* 63 (1991) 139.

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								

Atomic mass → 10.811
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 longest half-life.