UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION

JULY 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. Diagrams must be large and clearly labelled accordingly.

5. This paper contains an appendix of chemical constants and useful data.

6. This paper contains 10 printed pages, including the cover and appendix.

7. Special materials: 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) $Ca_3(PO_4)_2$ ii) $(NH_4)_2CO_3$ iii) CH_3COOH (3)

b) Distinguish the following terms;

i) Precision and accuracy
ii) Random and systematic errors
iii) Sample mean and population mean (6)

c) 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
ii) Median
iii) Standard deviation
iv) Variance (10)

d) If the 'true value' of the aspirin in the table is 96.55 % (w/w), calculate the;

i) Mean error
ii) % error
ii) ‰ error (6)

Question 2 [25]

a) The following data was obtained from the analysis of a sample, in ppm;

26 25 24 26 15

i) Should the value '15' be considered part of the data at the 95 % confidence level? (4)

ii) Using another method, the values obtained for the same analysis yields the following:

33 26 25 35 33

Do the two methods give the same result at the 95 % confidence level? (5)

iii) Comment on the precision of the second method at the 95 % confidence limit, if the 'true' value is 32 ppm. (2)

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

c) 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. (9)

Question 3 [25]

a) Using appropriate illustrations, compare calibration curves with standard additions methods and their use in elemental analysis.

i) Clearly explain how a normal calibration curve is obtained. (4)

ii) Clearly explain how one uses the standard additions method to determine concentration. (5)

iii) Under what conditions does the standard additions method provide more accurate analytical information than the calibration curve method? (3)

b) The following data were obtained for the procedure;

ADDITIONS	ABSORBANCE
1	0.106
2	0.153
3	0.208
4	0.257
0	0.049

i) Calculate the slope using the least squares linear regression. (4)

ii) Calculate the y-intercept using the least squares linear regression. (4)

iii) State the equation of the curve. (2)

iv) Plot the calibration curve. (3)

Question 4 [25]

a) Explain the meaning of the following terms as used in precipitation titrations, giving examples as appropriate;

i) Blank titration (2)

ii) Back titration (4)

iii) End point (2)

iv) Equivalence point (2)

b) A 20mL solution of 0.100 M NH_3 is titrated with 0.200 M HCl.

i) Calculate the pH of the ammonia solution at the following volumes of HCl added.

0 mL 1 mL 9.0 mL 9.99 mL 10 mL
10.01 mL 11 mL. (7)

ii) Plot the resulting titration curve and indicate on it the value of K_b for the NH_3/NH_4 system. (4)

iii) Suggest a suitable indicator for the titration. (2)

c) Explain the term 'replicate measurements'. Why is it a necessary step in laboratory analysis of a sample? (2)

Question 5 [25]

a) In precipitation reactions,

i) Explain the role of a primary standard. (2)
ii) List three (3) desirable properties of the substance listed in (i) above. (3)

b) In the laboratory, the determination of chlorine by the Fajan's titration in samples of a sewage treatment plant,

i) Name a common adsorption indicator in these titrations. (2)
ii) Use diagrams to explain how the indicator named in (i) above works. (3)
iii) Using the diagrams in (ii) above, explain the role of a pH 10 buffer in Fajan's titrations. (2)
iv) Explain how a blank is prepared in these titrations, and also why it is included. (2)

c) i) Plot the titration curve expected from the titration of 25.0 mL of 0.08 M KSCN with 0.04 M Cu^+ (Ksp, CuSCN is 4.8×10^{-15}) as titrant after the following volumes have been added,

0.10 mL 49.0 mL 50 mL, 55 mL (8)

ii) With reference to the titration system in c (i) above, quantitatively sketch the shape of the titration curve for each of the following concentrations of KSCN,

0.008 M 0.08 M 0.8 M,

on the same diagram. (3)

Question 6 [25]

a) List four (4) advantages of gravimetric analysis. (4)

b) i) What is coprecipitation? (2)

ii) Briefly discuss the different types of coprecipitation and state how each of them can be minimized. (5)

c) A given sample of $Zr(HPO_4)_2$ weighing 628 mg was ignited to ZrP_2O_7. Calculate the weight of the new product. (4)

d) A sample containing 8 % Fe_3O_4 was reacted and then precipitate as $Fe(OH)_3$. The $Fe(OH)_3$ (s) was ignited to Fe_2O_3, which weighed 150 mg. Determine the weight of the sample used. (6)

e) Explain the basic principles of gravimetric analysis. (4)

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											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.

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 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
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 .1(A)

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

	Confidence Level			
ν	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