UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION

JULY 2009

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 attract additional marks.
		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: 3 graph papers.

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

Question 1 [25]

a) Define the following terms as applied in analytical chemistry;

i) Qualitative analysis ii) Replicate measurement

iii) Population mean iv) Analytical interference

v) Data validation [5]

b) Give three of the most important sources of determinate error in chemical analysis. [3]

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 [2]

ii) Median [2]

iii) Standard deviation [4]

iv) Variance [2]

d) The percentage carbohydrate content of a glycoprotein is determined to be 12.6, 11.9, 13.0, 12.7 and 12.5, in replicate analyses.

i) Find the 50 % and 95 % confidence intervals for the carbohydrate content. [4]

ii) Comment on the implications of your results to the true mean. [3]

Question 2 [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) Give the two scenarios when it is appropriate to apply the Student's t-test. In each case, give the relevant equation. [6]

c) You are developing a procedure for determining traces of Cu in biological samples. A standard reference material (SRM) is taken through the analysis to validate your method, and the analysis is replicated 5 times. The mean of the data is obtained at 10.8 ppm with a standard deviation of ± 0. 7ppm. The SRM has a value of 11.7 ppm. Does your method give a statistically correct value at the 95 % confidence interval? [7]

d) Applying the Principles of Von Weimarn equation, state the steps you would take to minimise relative super-saturation and thereby enhance or promote the formation of a good analytical precipitate. [4]

e) In order to standardise a HCl solution, it was titrated with 0.1165 g of a primary standard Na_2CO_3 to a methyl red end-point by boiling the carbonate solution near the end-point to remove CO_2. Calculate the molarity of the acid if 21.44 mL acid was required for the titration. [5]

Question 3 [25]

Riboflavin (Vitamin B2) was determined in a cereal sample by measuring its fluorescence intensity in 5 % acetic acid solution. A calibration curve was prepared by measuring the fluorescence intensity of a series of standards of increasing concentrations. The following data were obtained.

Standard	**1**	**2**	**3**	**4**	**5**	**Sample**
(µg/mL)	0.000	0.100	0.200	0.400	0.800	x
Intensity	0.0	5.8	12.2	22.3	43.3	15.4

a) Use the method of least squares to obtain the best straight line for the calibration curve and to calculate the concentration of riboflavin in the sample solution. [12]

b) Calculate the correlation coefficient for the data. [4]

c) What are the three most important features of a good analytical precipitate in gravimetry? [3]

d) An ore was analysed for the Mn content by converting the Mn to Mn_3O_4 and weighing it. If a 1.52 g sample yielded Mn_3O_4 weighing 0.126 g, what is the percent Mn in the sample? [6]

Question 4 [25]

a) The iron content in a blended bulk ore material is about 5 % (wt/wt), and the relative standard deviation of sampling, Ss, is 0.021. How many samples should be taken in order to obtain a relative standard deviation, R, of 0.016 in the results at the 95% confidence level (i.e. the standard deviation, Sx, for the 5% iron content is 0.08 % (wt/wt)? [5]

b) Explain the role of a blank titration in the determination of chlorine in water samples. [2]

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

d) A 25.00 mL 0.100 M NaCl solution was titrated with 0.500M $AgNO_3$. Calculate the pAg value at the following stages of the titration, given that for AgCl, $K_{sp} = 1.8 \times 10^{-10}$.

i) After the addition of 0.5 mL
ii) At the equivalence point
iii) At 5 mL past the equivalence point [6]

iv) Plot the titration curve [2]

e) In the Volhard titration method,

i) state the reagents needed to identify the end point [2]
ii) explain, using chemical equations the colour changes leading to the end point. [2]
iii) give one limitation of this method. [1]

Question 5 [25]

a) 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]

b) Distinguish between the following terms;

i) Sample and population mean
ii) End-point and equivalence point
iii) Occlusion and Surface adsorption [6]

c) Using equations as far as possible, briefly explain why pH is an important parameter that needs to be controlled in Mohr titration. [4]

d) Explain the role of a primary standard. [2]

Question 6 [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 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) 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]

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

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

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	(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.