UNIVERSITY OF SWAZILAND
FINAL EXAMINATION

MAY 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 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 9 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 in the replicate determination of the lead content in a blood sample (in ppm) using a conventional instrument;

0.752, 0.756, 0.752, 0.751, 0.760

Use the data as far as possible to calculate the following;

i) the variance [2]
ii) the relative standard deviation [4]
iii) the coefficient of variation [2]
iv) the spread [1]

b) A new instrument is purchased with promises of better precision and accuracy in determinations. The same blood sample used in (a) is analysed using the new instrument and the results are presented;

0.811, 0.751, 0.683, 0.827, 0.755

The normal, acceptable or true value of lead in blood is set at 0.755 ppm.

i) Is the mean value of the new instrument significantly different from that of the conventional instrument at the 95% confidence level? [5]
ii) Briefly **define** precision and **comment** on which of the two instruments is more precise. [2]
iii) Briefly **define** accuracy and **comment** on which of the two instruments is more accurate. [2]
iv) Based on your comments in (ii) and (iii) above, which instrument would you recommend and why? [2]

c) Define the meaning of determinant error in chemical analysis and give the likely sources from which they originate. [5]

Question 2 [25]

a) Calculate the pH of the following solutions, given that $K_w = 1.0 \times 10^{-14}$;

i) 0.1 M H_2SO_4 [2]
ii) 0.1 M NaOH [3]

b) 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
iv) $KMnO_4$ [4]

c) Distinguish between systematic and random error, using examples to illustrate. [4]

d) i) Distinguish between a primary standard and a secondary standard. [4]

ii) Give four (4) essential requirements for a primary standard for titration purposes. [4]

iii) What are the desirable properties of a standard solution meant for titrimetric method of analysis? [4]

Question 3 [25]

a) A Flame photometer was used to determine the Ca^{2+} concentration of a water sample. The instrument was calibrated via a standard additions method, and the responses obtained are listed below.

Standard addition concentration (mg/L)	Instrument reading (arbitrary units)
0	12
3	16
5	27
10	37
15	49
20	61

Assuming that no interferences are present, determine the Ca^{2+} concentration within the original sample. [8]

b) The distribution coefficient, K_D, of an organic salt between hexane and water is 90. A quantity of 0.1 mol of the salt is dissolved in 100 mL of water. Determine the number of moles of the salt that will remain within the aqueous phase following extraction by using;

i) 100 mL [4]

ii) four 25 mL aliquots [4]

of hexane to extract the salt from the aqueous phase.

c) Explain the difference between the following;

i) Mean and Median

ii) Standard deviation and variance [6]

d) Given that at 20°C only 0.24 g of an organic acid A dissolves in 100 mL of water, but 2.70 g of the same acid dissolves in 100 mL of ether. Calculate the value of the partition coefficient. [3]

Question 4 [25]

The analysis of sulphur in meteorites is used to classify and establish their origin. The following data was obtained for the analysis of sulphur in a meteorite found on the Antarctic ice shelf to try and determine its origin.

Replicate	Concentration (ppm)
1	6
2	5.8
3	12.3
4	6.3
5	6.1
6	5.9

a) A first year chemistry student calculated the mean of the data to be 7.01 ppm. Using your knowledge of data reproducibility and applying the necessary statistical tool at the 95% confidence interval calculate the correct mean of the data. [5]

b) Determine the 95 % confidence interval for sulphur in the meteorite, showing clearly all your calculations. [5]

c) The data from the analysis was not subjected to any quality control protocols.

i) Perform the necessary calculations and then plot a quality control chart for this data set and interpret the resulting chart with respect to the quality of the data. [5]

ii) The Standard Reference Material (SRM) for sulphur in meteorites shows a value of 5.58 ppm. Comment on the precision of this method at the 95% confidence interval. [5]

d) An independent analysis performed on another Asteroid (HC1998) revealed that it contained an average of 5.8 ppm sulphur after 6 trials with a deviation from the mean of 0.303. **Speculation** was rife that the Asteroid (HC1998) and the meteorite originate from the same parental body. Perform the necessary statistical manipulations (at the 95 % confidence level) to either confirm or reject the hypothesis. [5]

Question 5 [25]

a) 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

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. Your calculation should include the following important points;

i) The slope [3]
ii) The y-intercept, [3]
iii) The equation of the curve. [2]
iv) A plot of the calibration curve. [3]
v) The concentration of the sample. [2]

b) A certain barium halide exists as the hydrated salt $BaX_2.2H_2O$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.265 g) was dissolved in water (100 cm^3) and excess sulphuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of **X.** [5]

c) i) What is the difference between 'end point' and 'equivalence point' in precipitation titrimetry? [2]
ii) Explain what is meant by a blank titration in precipitation titration. [1]
iii) Explain what is meant by a back titration in precipitation titrimetry and the conditions which necessitate its application. [4]

Question 6 [25]

a) A 0.0500M $AgNO_3$ solution was used to titrate 25 mL of 0.100 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 $AgNO_3$;
20.00 mL 49.00 mL 50.00 mL 51 mL, 70.00 mL [10]
ii) Plot the titration curve. [3]

b) An organic compound weighing 0.3598 g was burned in a steam of oxygen. The CO_2 produced was passed into a solution of barium hydroxide, forming 1.1226 g of $BaCO_3$. Calculate the % of carbon in the organic compound. [5]

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

i) Standard additions
ii) External standards
iii) Back titration [3]

d) Using litmus as an example of an indicator, explain the **mechanism** responsible for the characteristic colour changes observed when;

i) Hydroxide ions are added [2]
ii) Hydrogen ions are added [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.