UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION

JULY 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 <u>**ALL**</u> 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. Additional material; 4 graph papers.

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

Question 1 [25]

a) Explain the difference between the following;

i) Accuracy and Precision

ii) Mean and median

iii) Variance and Standard Deviation (9)

b) The acceptable value for chlorine content in a standard water sample is 54.2 %, with a standard deviation of 0.15 %. Five analyses were carried out on the same sample by a new instrumental procedure. The values obtained are tabulated below;

Replicate	Result
1	54.01
2	54.24
3	54.05
4	54.27
5	54.11

i) Is the new method giving results that are consistent with the acceptable value at the 95% confidence level? (12)

ii) A sixth value of 55.58 was obtained for the same analysis that the analyst rejected without performing any statistical justifications. Was the analyst right in rejecting the datum at the 95% confidence level? (4)

Question 2 [25]

a) What is meant by 'digestion of a precipitate'? Briefly describe what happens in the process of digesting a precipitate and give two (2) advantages of this step during gravimetric analysis. (4)

b) i) What is peptization? How can this phenomenon be avoided during gravimetric analysis? (2)

ii) What are the qualifying conditions that a perfect crystal should posses in gravimetric analysis? (3

d) 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? (3)

e) A 0.100 M solution of HCl is used to titrate 25 mL of 0.0100M $Ba(OH)_2$.

i) Calculate the pH at the following volumes of HCl added during the titration;

0.00 mL 2.00 mL 4.90 mL 5.00 mL 5.01 mL

10.00 mL [10]

ii) Plot the titration curve [3]

Question 3 [25]

a) What are the assumptions that are made in the establishment and application of the least squares method? (2)

b) The phosphorus content in a urine sample was analysed by employing a spectrophotometric method. The data for the standards and samples are given below:

Standard	1	2	3	4	Urine sample
P (mg/L)	1.00	2.00	3.00	4.00	x
Absorbance	0.205	0.410	0.615	0.820	0.625

Employ the least squares regression method to:

i) Calculate the slope, intercept and concentration, x, of phosphorus in the urine sample. (12)

ii) Plot the best straight line, i.e. the best least square line. (5)

c) An analysis is carried out in soil to determine the concentration of Zn at the RSSC. The data is shown in the table below. Using this information, advice the analyst on the quality of the data obtained.

Replicates	Concentration (ppm)
1.	329
2.	333
3.	345
4.	326
5.	322
Mean	**331**
Std Deviation	**9**

Your advice should include:

i) An Analytical Quality Control (AQC) chart showing all the necessary analytical control limits and data points. (5)

ii) An interpretation of the implications of the resulting chart. (1)

Question 4 [25]

a) Briefly define the following terms and acronyms as applied in analytical chemistry;

i) EDTA

ii) Chelate effect

iii) Electric Double layer (3)

b) Draw the titration curve for the titration of 50 mL of 0.05 M Mg^{2+} with 0.05 M EDTA at the following volumes of titrant added; (3)

5 ml, 50 mL, 51mL, (9)

The Mg^{2+} is buffered to pH 10 and the titration reaction is;

$$Mg^{2+} + EDTA \longrightarrow MgY^{2-}$$

And $Kf' = \alpha_{Y4-}.Kf$ where $Kf = 6.2 \times 10^{8}$ and $\alpha_{Y4-} = 0.36$ (at pH 10) (3)

c) i) What is coprecipitation? (2)

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

Question 5 [25]

a) 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)

b) What are the desirable properties of a standard solution meant for titrimetric method of analysis? (4)

c) A 0.6000 g pure sodium oxalate $Na_2C_2O_4$ was weighed, dissolved in an acid and titrated with a Potassium Permanganate solution, $KMnO_4$. The volume of the permanganate added to reach end-point was 34.00 mL. Calculate the molarity of the $KMnO_4$. The equation for the reaction is;

$$2MnO_4^- + 5C_2O_4^- \longrightarrow 2Mn^{2+} + 10CO_{2(g)} + 8H_2O$$

(6)

d) During the standardization of sodium thiosulphate solution, 0.2500 g of pure copper metal was dissolved and treated with excess KI. The liberated iodine required 44.90 mL of the solution of sodium thiosulphate to reach the end-point. Calculate the molarity of the sodium thiosulphate. The pertinent reactions are:

$$2Cu^{2+} + \underset{\text{(excess)}}{4I^-} \longrightarrow 2CuI\,(s) + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

(7)

Question 6 [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) 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 (4)

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

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	5.19	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.

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	$V_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
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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
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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

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PERIODIC TABLE OF ELEMENTS

Atomic mass → / Symbol → / Atomic No. →

	GROUPS																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	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				TRANSITION ELEMENTS							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								

*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.