FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

MODULE:	CEM 2B20 Principles of Analytical Chemistry
CAMPUS:	APK
EXAM:	NOVEMBER 2018

DATE: 26/11/2018 **SESSION:** 8:30

ASSESSOR: Dr E Smit

MODERATOR: Dr A Ambushe

DURATION: 3 hours **MARKS:** 100

Name and Surname: ....

Student Number:

PLEASE READ THE FOLLOWING INSTRUCTIONS CAREFULLY:

- This paper consists of 15 pages including a Periodic Table and data sheet.
- Calculators are allowed but mobile phones may NOT be used.
- All results of calculations should be reported to the correct number of significant figures. Marks will be deducted for incorrect significant figures.
- Provide the answer in the space provided below each question. If more space is required, use the back of the page and clearly indicate that it should be marked.
- Student number should be provided on every page.

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Total

Question 1 (7 marks)

1.1 Name the three steps involved in acquiring a sample. (3)

1.2 Identify two sources of error that can occur when preparing solutions. (2)

1.3 Distinguish between quantitative and qualitative analysis. (2)

Question 2 (17 marks)

2.1 Suppose that in a gravimetric analysis, you forget to dry the filter crucibles before collecting precipitate. After filtering the product, you dry the product and crucible thoroughly before weighing them. Is the apparent mass of the product always high or always low? Is the error in mass systematic or random? (2)

2.2 Before agreeing to the purchase of a large order of solvent, a company wants to see conclusive evidence that the mean value of a particular impurity is less than 1.0 ppb. What hypotheses should be tested? What are the type I and type II errors in this situation? (4)

2.3 The phosphorous content was measured for three different soil locations. Five replicate determinations were made on each soil sample.

2.3.1 Complete the ANOVA table below (show all calculations): (5)

Variation Source	SS	df	MS	F
Between soils	0.2768	*(a)*	*(d)*	*(e)*
Within soils	0.0972	*(b)*	0.0081	
Total	0.374	*(c)*		

a)

b)

c)

d)

e)

2.3.2 State the null and alternative hypotheses. (2)

2.3.3 Do the three soils differ in phosphorous content at the 95 % confidence level? (4)

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Question 3 (11 marks)

3.1 List three figures of merit used in quality assurance. (3)

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3.2 Water can be determined in solid samples by infrared spectroscopy. The water content of calcium sulfate hydrates is to be measured using calcium carbonate as an internal standard. A series of standard solutions containing calcium sulfate dihydrate and a constant known amount of the internal standard is prepared. The solution containing unknown water content is also prepared with the same amount of internal standard. The absorbance of the dihydrate is measured at one wavelength (A_{sample}) along with that of the internal standard at another wavelength (A_{std}). The following results were obtained: (8)

% water	A_{sample}	A_{std}
4.0	0.15	0.75
8.0	0.23	0.60
12.0	0.19	0.31
16.0	0.57	0.70
20.0	0.43	0.45
Unknown	0.37	0.47

3.2.1 What mathematical method can you use to find the linear relationship between the % water and the absorbance of the sample?

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3.2.2 Identify the dependent variable (y). ______________________________

3.2.3 Identify the independent variable (x). ______________________________

Question 3.2 continues on the next page

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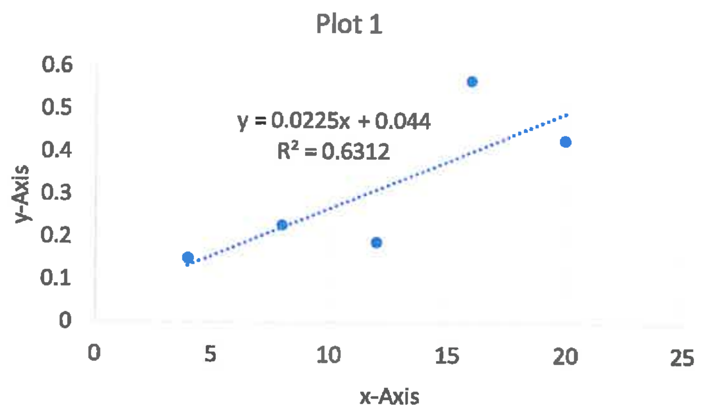
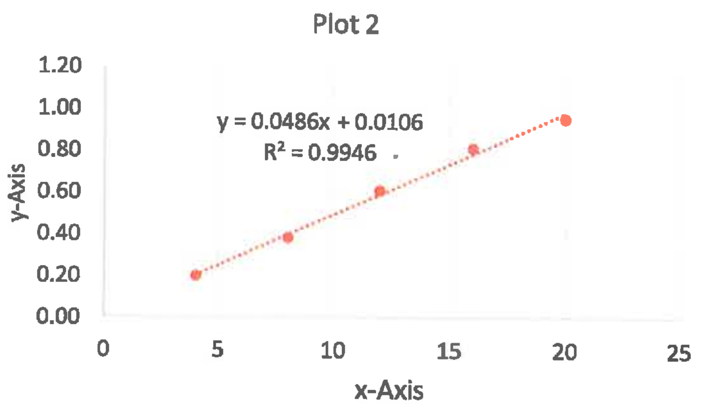
3.2.4 The following two plots were obtained in Excel:





Which one of these plots incorporates the information obtained from the internal standard? ______________________________

3.2.5 Give a suitable title for the y-axis of Plot 1. ______________________

3.2.6 Give a suitable title for the y-axis of Plot 2. ______________________

3.2.7 Calculate the % water in the unknown (include the internal standard data).

Question 4 (11 marks)

4.1 What pH is required to just precipitate iron(III)hydroxide from a 0.10 M $FeCl_3$ solution? K_{sp} for $Fe(OH)_3$ is 4×10^{-38} (7)

4.2 Precipitates used in the gravimetric determination of uranium include $Na_2U_2O_7$ (634 g/mol), $(UO_2)_2P_2O_7$ (714 g/mol) and $V_2O_5 \cdot 2UO_3$ (753.9 g/mol). Which of these weighing forms provides the greatest mass of precipitate from a given quantity of uranium? (4)

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Question 5 (5 marks)

Match each of the following terms to its correct definition given below (only write A, B, C, D or E): (5)

5.1 Adsorption _____

5.2 Coagulation _____

5.3 Mother Liquor _____

5.4 Occlusion _____

5.5 Nucleation _____

A. a process in which a minimum number of atoms, ions or molecules associate to give a stable solid
B. the solution from which a precipitate is formed
C. the process by which ions are retained on the surface of a solid
D. the process by which colloidal particles coalesce to form larger aggregates
E. a type of coprecipitation in which a compound is trapped within a pocket formed during rapid crystal formation

Question 6 (9 marks)

6.1 Arsenic acid, H_3AsO_4 is a triprotic acid. Write chemical equations for the three-step ionization. (3)

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6.2 Codeine, a cough suppressant extracted from crude opium, is a weak base with a pK_b of 5.80. What will be the pH of a 0.020 *M* solution of codeine? In your work and equations, use *Cod* as the symbol for codeine rather than a molecular formula. (6)

$$Cod + H_2O \rightleftarrows HCod^+ + OH^-$$

Question 7 (13 marks)

For the titration of 25.00 mL of 0.1000 *M* HCl with 0.1000 *M* NaOH, calculate the pH of the reaction mixture after each of the following total volumes of base have been added to the original solution. (Remember to take into account the change in total volume.)

7.1 10.00 mL (4)

Question 7 continues on the next page

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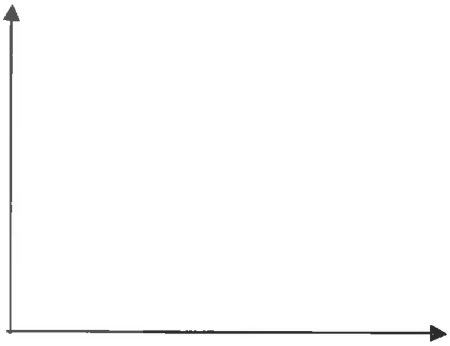
7.2 At the equivalence point (2)

7.3 26.00 mL (5)

7.4 Draw a rough titration curve for this experiment using the template provided.(2)



Question 8 (9 marks)

8.1 A solution of a weak monoprotic acid, HA (0.50 M), and its potassium salt, KA (0.75 M), has a measured pH = 4.88. What is the value of K_a for this acid? Will the pH of the solution increase, decrease or remain constant upon the addition of a strong base? Explain your answer by referring to the relevant chemical equation. (4)

8.2 Carbonic acid, H_2CO_3, is a diprotic acid with ionization constants: $K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$. What is the value of the ratio, $[H_2CO_3]/[HCO_3^-]$, in a solution containing both species which is maintained at pH = 7.00 by means of a buffer? (5)

Question 9 (9 marks)

9.1 Give 3 advantages of EDTA in complexometric titrations. (3)

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9.2 Calcium in powdered milk is determined by dry ashing a 1.50 g sample and then titrating the calcium with 12.1 mL EDTA solution. The EDTA was standardized by titrating 10.0 mL of a zinc solution prepared by dissolving 0.632 g zinc metal in acid and diluting to 1L. 10.8 mL of EDTA was required for the titration with the zinc solution. What is the concentration of calcium in the powdered milk in parts per million? (6)

Question 10 (9 marks)

10.1 Distinguish between activity and activity coefficient. (2)

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10.2 Use the Debye-Hückel equation to calculate the activity coefficient of Pb^{2+} at $\mu = 0.042$. (3)

10.3 Use linear interpolation to calculate the activity coefficient of Pb^{2+} at $\mu = 0.042$. (4)

Formula sheet:

The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	......								
	s block		d block										p block					

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.1
	f block														

$$E = x_i - x_t$$

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

$$s_m = \frac{s}{\sqrt{N}}$$

$$RSD = \frac{s}{\bar{x}}$$

$$CV = \frac{s}{\bar{x}} \times 100\ \%$$

$$CI\ for\ \mu = \bar{x} \pm \frac{z\sigma}{\sqrt{N}}$$

$$CI\ for\ \mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

$$CL = (1 - \alpha) \times 100\ \%$$

$$z = \frac{\bar{x} - \mu_0}{\sigma/\sqrt{N}}$$

$$t = \frac{\bar{x} - \mu_0}{s/\sqrt{N}}$$

$$F = s_1^2/s_2^2$$

$$Q = \frac{|x_q - x_n|}{w}$$

$$y = mx + b$$

$$\frac{S_{sample}}{C_A \times \frac{V_0}{V_f}} = \frac{S_{spike}}{C_A \times \frac{V_0}{V_f} + C_{std} \times \frac{V_{std}}{V_f}}$$

$$-\log \gamma_X = \frac{0.51 Z_X^2 \sqrt{\mu}}{1 + 3.3\alpha_X \sqrt{\mu}}$$

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Source of variation	*SS*	*df*	*MS*	*F*
Between groups	SSF	$I-1$	$MSF = \frac{SSF}{I-1}$	$\frac{MSF}{MSE}$
Within groups	SSE	$N-I$	$MSE = \frac{SSE}{N-I}$	
Total	SST	$N-1$		

TABLE 7-1

Confidence Levels for Various Values of z

Confidence Level, %	z
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

TABLE 7-3

Values of t for Various Levels of Probability

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	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
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
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

TABLE 7-4

Critical Values of F at the 5% Probability Level (95 % confidence level)

Degrees of Freedom (Denominator)	Degrees of Freedom (Numerator)								
	2	3	4	5	6	10	12	20	∞
2	19.00	19.16	19.25	19.30	19.33	19.40	19.41	19.45	19.50
3	9.55	9.28	9.12	9.01	8.94	8.79	8.74	8.66	8.53
4	6.94	6.59	6.39	6.26	6.16	5.96	5.91	5.80	5.63
5	5.79	5.41	5.19	5.05	4.95	4.74	4.68	4.56	4.36
6	5.14	4.76	4.53	4.39	4.28	4.06	4.00	3.87	3.67
10	4.10	3.71	3.48	3.33	3.22	2.98	2.91	2.77	2.54
12	3.89	3.49	3.26	3.11	3.00	2.75	2.69	2.54	2.30
20	3.49	3.10	2.87	2.71	2.60	2.35	2.28	2.12	1.84
∞	3.00	2.60	2.37	2.21	2.10	1.83	1.75	1.57	1.00

TABLE 7-5

Critical Values for the Rejection Quotient, Q*

Number of Observations	Q_{crit} (Reject if $Q > Q_{crit}$)		
	90% Confidence	95% Confidence	99% Confidence
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
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

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TABLE 10-2

Activity Coefficients for Ions at 25°C

Ion	α_X, nm	Activity Coefficient at Indicated Ionic Strength				
		0.001	0.005	0.01	0.05	0.1
H_3O^+	0.9	0.967	0.934	0.913	0.85	0.83
Li^+, $C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, MnO_4^-	0.35	0.965	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.965	0.925	0.899	0.81	0.75
Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+	0.25	0.965	0.925	0.897	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.756	0.690	0.52	0.44
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $Phthalate^{2-}$	0.6	0.870	0.748	0.676	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.869	0.743	0.668	0.46	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, $C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, Cr_4^{2-}, HPO_4^{2-}	0.40	0.867	0.738	0.661	0.44	0.35
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.737	0.540	0.443	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.587	0.348	0.252	0.10	0.063
$Fe(CN)_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020

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TABLE 6-4

Error Propagation in Arithmetic Calculations

Type of Calculation	Example*	Standard Deviation of $y^\dagger$	
Addition or subtraction	$y = a + b - c$	$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$	(1)
Multiplication or division	$y = a \times b/c$	$\frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2}$	(2)
Exponentiation	$y = a^x$	$\frac{s_y}{y} = x\left(\frac{s_a}{a}\right)$	(3)
Logarithm	$y = \log_{10} a$	$s_y = 0.434\frac{s_a}{a}$	(4)
Antilogarithm	$y = \text{antilog}_{10} a$	$\frac{s_y}{y} = 2.303\, s_a$	(5)

*a, b, and c are experimental variables with standard deviations of s_a, s_b, and s_c, respectively

†These relationships are derived in Appendix 9. The values for s_y/y are absolute values if y is a negative number.

Student Number: ____________________