FACULTY OF SCIENCE

DEPARTMENT OF CHEMICAL SCIENCES

MODULE:	CEM2B20 / CEM02B2
	Principles of Analytical Chemistry
CAMPUS:	APK
EXAM:	NOVEMBER 2019

DATE:	18/11/2019	**SESSION:**	8:30
DURATION:	3 hours	**MARKS:**	100
ASSESSOR:	Dr E Smit	**MODERATOR:**	Dr A Ambushe

PLEASE READ THE FOLLOWING INSTRUCTIONS CAREFULLY:

- This paper consists of 10 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.

Question 1 (9 marks)

1.1   Name three aspects that need to be considered when selecting an analytical method.   (3)

1.2   For solutions of liquids or gasses, the gross sample can be relatively small compared to the gross sample taken from solids. Explain.   (3)

1.3   What is a refractory substance?   (1)

1.4   If a substance is insoluble in aqueous solutions, which techniques (list only two techniques) may be used to decompose or dissolve the sample?   (2)

Question 2 (9 marks)

2.1   Is it more important to perform an analysis more accurately or more precisely? Explain your answer.   (3)

2.2   A standard serum sample containing 102 meq/L chloride was analysed by coulometric titration with silver ion. Duplicate results of 101 and 98.0 meq/L were obtained. Calculate   (3)
        2.2.1. the mean.
        2.2.2. the absolute error of the mean.
        2.2.3. the relative error of the mean in percent.

2.3   In a titration the initial reading on the burette is 3.51 mL and the final reading is 15.67 mL, both with a standard deviation of 0.02 mL. What is the volume of titrant used and what is its standard deviation?   (3)

Question 3 (9 marks)

3.1   An area of land is being investigated to determine the concentration of lead present in the soil. Thirty samples of soil are submitted to the laboratory for analysis and the mean lead concentration is found to be 513.8 mg/kg with a standard deviation of 13.1 mg/kg. The concentration of lead in the soil must not exceed 500 mg/kg. Based on the results obtained, is there any evidence to suggest that the concentration of lead in the soil exceeds this limit? Assume a significance level of $\alpha = 0.05$. (6)

3.2   Describe the Type I error for Question 3.1. What is the probability of this error occurring? (3)

Question 4 (10 marks)

4.1   In order to minimize errors during calibrations, the internal standard method or the standard additions method may be used.

   4.1.1   Which of these two methods will require a standard that is identical to the analyte? (1)

   4.1.2   Which of these two methods will require a standard that is similar to (but not the same as) the analyte? (1)

   4.1.3   Name three other methods that can be used to minimize errors during analytical measurements. (3)

4.2   In the Bradford protein determination, the color of a dye changes from brown to blue when it binds to protein. This experiment was performed and the absorbance of light was measured for a range of standards:

Protein (µg)	0.00	9.36	18.72	28.08	37.44
Absorbance at 595 nm	0.466	0.676	0.883	1.086	1.280

Linear regression was performed and the equation for the least squares straight line through these points was found to be $y = 0.0218x + 0.4706$. A sample with unknown concentration of protein gave an absorbance of 0.973. Calculate the number of micrograms of protein in the sample. (2)

4.3   A spectrophotometric method for the quantitative analysis of Pb^{2+} in blood yields a response signal (S_{sample}) of 0.193 when a 1.00 mL sample of blood is diluted to 5.00 mL. A second 1.00 mL sample of blood is spiked with 1.00 µL of 1560 ppb Pb^{2+} standard and diluted to 5.00 mL, yielding a response signal (S_{spike}) of 0.419. What is the concentration of Pb^{2+} in the original sample of blood?   (3)

Question 5 (8 marks)

5.1   A solution contains three anions with the following concentrations: 0.20 M CrO_4^{2-}, 0.10 M CO_3^{2-} and 0.010 M Cl^-. If a dilute $AgNO_3$ solution is slowly added to the solution, what is the first compound to precipitate?   (4)

5.2   If the pH of the solution (in Question 5.1) is changed, which precipitation reaction will be influenced and how? Give the necessary chemical equations to support your answer.   (4)

Question 6 (9 marks)

6.1   Name two methods that can be used to convert colloids into filterable solids.(2)

6.2   Name two types of co-precipitation.   (2)

6.3   Marie Curie dissolved 0.09192 g of $RaCl_2$, and treated it with excess $AgNO_3$ to precipitate 0.08890 g of AgCl. In her time (1900), the atomic mass of Ag was known to be 107.8 g/mol and that of Cl was 35.4 g/mol. From these values, find the atomic mass of Ra that Marie Curie would have calculated.   (5)

Question 7 (9 marks)

7.1   Like all equilibrium constants, the value of K_w depends on temperature. At body temperature (37 °C), $K_w = 2.4 \times 10^{-14}$. Calculate the pH of pure water at body temperature.   (4)

7.2   Show the stepwise dissociation for the ethylene diammonium ion ($^+H_3NCH_2CH_2NH_3^+$).   (2)

7.3   Suppose that 0.5 *M* solutions of each of the following compounds are prepared. Predict whether each solution will be acidic, basic or neutral.   (3)
      a) KF
      b) (NH₄)Br
      c) KBr

Question 8 (9 marks)

For questions 8.1 to 8.3, choose the correct answer (only write A, B, C or D).   (3)

8.1   Which pair of compounds below <u>cannot</u> be used to prepare a buffer solution?
      A. NH_4NO_3 and NH_3
      B. KH_2PO_4 and K_2HPO_4
      C.   HCN and NaCN
      D. HNO_3 and $NaNO_3$

8.2   A buffer was prepared by mixing solutions of H_2CO_3 and $NaHCO_3$. A small amount of NaOH was added to the buffer. Choose the statement that correctly explains what happens upon NaOH addition.
      A. OH^- reacted with $NaHCO_3$ and the pH increased.
      B. OH^- reacted with H_2CO_3 and the pH decreased.
      C. OH^- did not react. The buffer components blocked the OH^- from changing the pH.
      D. OH^- reacted with H_2CO_3 and the pH increased.

8.3   Which statement below concerning [H⁺] or pH of a buffer solution is correct?

    A.   When the [HA] / [A⁻] ratio is greater than 1, the [H⁺] is less than the K_a.

    B.   When [HA] = [A⁻], the pH equals the pK_a.

    C.   When the [HA] / [A⁻] ratio is less than 1, the [H⁺] is greater than the K_a.

    D.   The larger the K_a of the weak acid component of the buffer, the higher the pH

8.4   A buffer was prepared to contain 0.20 M HNO_2 and 0.30 M $NaNO_2$. Calculate the pH of this solution. Show the relevant chemical equation(s). (3)

8.5   Which has the greater buffer capacity: (a) a mixture containing 0.100 mol of NH_3 and 0.200 mol of NH_4Cl or (b) a mixture containing 0.0500 mol of NH_3 and 0.100 mol of NH_4Cl? Explain your answer. (3)

Question 9 (9 marks)

9.1   What is the difference between the equivalence point and end point in an acid-base titration and how are they measured / determined? (4)

9.2   25 mL of a 0.0256 M solution of the weak base aniline, $C_6H_5NH_2$, is titrated with 0.0195 M HCl solution. What is the pH at the equivalence point of the titration? Draw a rough titration curve for this experiment. (5)
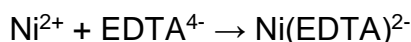
Question 10 (9 marks)

10.1 Name two indicators that can be used during titrations with EDTA.   (2)

10.2 A cyanide solution with a volume of 12.73 mL was treated with 25.00 mL of Ni^{2+} solution to convert the cyanide into tetracyanonickelate(II):

$$4CN^- + Ni^{2+} \rightarrow Ni(CN)_4^{2-}$$
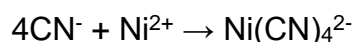
The excess Ni^{2+} was then titrated with 10.15 mL of 0.01307 M ethylene-diaminetetraacetic acid (EDTA):

$$Ni^{2+} + EDTA^{4-} \rightarrow Ni(EDTA)^{2-}$$

$Ni(CN)_4^{2-}$ does not react with EDTA. If 39.95 mL of EDTA were required to react with 30.10 mL of the original Ni^{2+} solution, calculate the molarity of CN^- in the 12.73 mL cyanide sample.   (7)

Question 11 (10 marks)

11.1 Distinguish between thermodynamic equilibrium constant and concentration-based equilibrium constant.   (2)

11.2 Calculate the % relative error in solubility by using concentrations instead of activities for $Fe(OH)_2$ in 0.0500 M KNO_3. The thermodynamic solubility product constant for $Fe(OH)_2$ is 4.1×10^{-15}.   (8)

Formula sheet:

The Periodic Table

	1	2												13/III	14/IV	15/V	16/VI	17/VII	18/VIII
	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	3	4	5	6	7	8	9	10	11	12		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

$$E = x_i - x_t$$

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

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

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

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

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

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

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

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

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

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

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

$$y = mx + b$$

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

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

$K_{sp}\ (Ag_2CrO_4) = 1.2 \times 10^{-12}$

$K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$

$K_{sp}\ (AgCl) = 1.8 \times 10^{-10}$

$K_a\ (HF) = 6.8 \times 10^{-4}$

$K_b\ (NH_3) = 1.76 \times 10^{-5}$

$K_a\ (HNO_2) = 7.1 \times 10^{-4}$

$K_a(C_6H_5NH_3^+) = 2.51 \times 10^{-5}$

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

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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

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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

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

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	$y = a \times b/c$	$\dfrac{s_y}{y} = \sqrt{\left(\dfrac{s_a}{a}\right)^2 + \left(\dfrac{s_b}{b}\right)^2 + \left(\dfrac{s_c}{c}\right)^2}$	(2)
Exponentiation	$y = a^x$	$\dfrac{s_y}{y} = x\left(\dfrac{s_a}{a}\right)$	(3)
Logarithm	$y = \log_{10} a$	$s_y = 0.434\dfrac{s_a}{a}$	(4)
Antilogarithm	$y = \text{antilog}_{10} a$	$\dfrac{s_y}{y} = 2.303\, s_a$	(5)

*a, b, and c are experimental variables with standard deviations of s_a, s_b, and s_c, respectively
$\dagger$These relationships are derived in Appendix 9. The values for s_y/y are absolute values if y is a negative number.