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UNIVERSITY OF SWAZILAND

FINAL EXAMINATION, 2005

TITLE OF PAPER: INTRODUCTORY ANALYTICAL CHEMISTRY

COURSE NUMBER: C204

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS: ANSWER ANY FOUR(4) QUESTIONS. EACH QUESTION CARRIES 25 MARKS.

A periodic table and other useful data have been provided together with this paper.

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Question 1 (25 marks)

a) Explain the term 'replicate measurements'. Why is it a necessary step during the laboratory analysis of a sample? (3)

b) The results (in mg) obtained for the determination of acetaminophen tablets of an Excedrin Extra Strength pain reliever are given below:

261.7, 229.4, 255.5, 235.5, 249.7, 253.1, 239.4, 246.3, 224.3 and 240.4

i) Calculate the mean, median, standard deviation, standard deviation of the mean and the variance. (12)

ii) If the true value of the active ingredient in the tablet is 246.4 mg, calculate the absolute (mean) error, the % error and the $\%_0$ error. (6)

iii) Estimate the 95% confidence interval about the mean. What does this interval mean? (4)

Question 2(25 marks)

The standardized Gas Chromatographic (GC) method and a newly developed Enzymatic Method (EM) were employed separately to determine the alcohol content of a locally brewed wine. The results obtained (in % Ethanol) are as follows:

GC (% Ethanol): 13.0, 13.5, 13.3, 12.9
EM (% Ethanol): 15.1, 13.3, 12.7, 12.6, 13.1

i) Determine the pooled mean and the pooled standard deviation for the two data sets. (6)

ii) Employing both the t and the F-tests, determine if there is a significant difference between the two methods at the 95% C.L. (13)

iii) Identify any outlier in either of the two sets of data and use the Q-test to determine whether or not the datum concerned should be retained. (6)

Question 3(25 marks)

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

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

P(mg/L)	1.00	2.00	3.00	4.00	Urine Sample
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 of phosphorous in the urine sample. (12)

ii) Plot the 'best straight line' (i.e. the linear least squares line). (5)

iii) Estimate the confidence intervals for the slope, **m**, and the intercept, **b**, at the 95% confidence level. (6)

Question 4(25 marks)

a) What is 'co-precipitation'? Briefly describe the three types of co-precipitation that can occur during gravimetric analysis. In each case, give one step that can be taken to minimize it. (10)

b) Using an illustrative example, describe how you would confirm that a precipitate has been sufficiently washed. (5)

c) A given sample of $Zr(HPO_4)_2$ weighing 628 mg was ignited to $Zr\ P_2O_7$. Calculate the weight of the new product. (4)

d) A sample containing 8.00% Fe_3O_4 was treated and precipitated as $Fe(OH)_3$. The $Fe(OH)_3$ was ignited to Fe_2O_3, which weighed 150mg. Determine the weight of the sample used. (6)

Question 5(25 marks)

a) What is the essence of carrying out solvent extraction of a solute from an aqueous phase into an organic phase? (2)

b) Starting from the basic expression for the fraction of the solute extracted during solvent extraction, obtain an expression each for:

i) The percent of solute extracted, %E

ii) F_r, the fraction of the solute remaining after a single extraction, in terms of the distribution ratio, D, the volume of the aqueous phase and the volume of the organic phase. (8)

c) The distribution ratio, D, for the distribution of a metal chelate between water and chloroform is 6.4. Calculate the fraction of the chelate extracted when 25.0 mL of a 4.3 x 10^{-5}M sample is shaken with:
   i) One 10.0mL portion of chloroform
   ii) Two successive 10.0mL portions of chloroform. (6)

d) What volume of toluene is needed to extract 99% of a solute from 50.0mL of water in a single extraction for the following D values?
   i) 50 ii) 25 (6)

e) What deductions can you make from the results obtained in questions 5(c) and 5(d) above? (3)

<u>Question 6(25 marks)</u>

a) Differentiate between a primary standard and a secondary standard for titrimetric analysis. (4)

b) Give four essential requirements for a primary standard used for titration purposes. (4)

c) What are the requisite properties for a standard solution meant for titrimetric analysis? (4)

d) In an experiment for the standardization of sodium thiosulphate solution, 0.2500g of primary grade copper metal was dissolved and treated with excess KI. 44.90mL of the sodium thiosulphate was used to titrate the liberated I_2 to the end point. Given that the reactions involved are as follows:

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI_{(s)} + I_2 \text{ ....(i)}$$
(excess)
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \text{ ....(ii)}$$

Calculate the molarity of the sodium thiosulphate. (8)

e) Describe how you would prepare 250.00mL of 0.5000M $Na_2C_2O_4$ from a primary standard solid. (5)

Values of Student's t

Degrees of freedom	Confidence level (%) 50	80	90	95	99
1	1.000	3.078	6.314	12.706	63.657
2	0.816	1.886	2.920	4.303	9.925
3	0.765	1.638	2.353	3.182	5.841
4	0.741	1.533	2.132	2.776	4.604
5	0.727	1.476	2.015	2.571	4.032
6	0.718	1.440	1.943	2.447	3.707
7	0.711	1.415	1.895	2.365	3.500
8	0.706	1.397	1.860	2.306	3.355
9	0.703	1.383	1.833	2.262	3.250
10	0.700	1.372	1.812	2.228	3.169
15	0.691	1.341	1.753	2.131	2.947
20	0.687	1.325	1.725	2.086	2.845
∞	0.674	1.282	1.645	1.960	2.576

Values of t for ν Degrees of Freedom for Various Confidence Levels[a]

ν	*Confidence Level, 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.

Values of F at the 95% Confidence Level

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
$\nu_2 = 2$	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

Rejection Quotient, Q, at Different Confidence Limits[a]

No. of Observations	Confidence level		
	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
8	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

[a]Adapted from D. B. Rorabacher, *Anal. Chem.*, 63 (1991) 139.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3 c \varepsilon_0^2$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} kg^{-2}
Standard acceleration of free fall†	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

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

Key: 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.