DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

NOVEMBER 2017 RE-SIT EXAMINATION

TITLE OF PAPER **:Analytical Chemistry II: Fundamentals of Spectrophotometry**

COURSE NUMBER **:C304/CHE 312**

TIMEHOURS **: 3 Hours**

Important Information

: Each question is worth 25 marks.

: Answer **questions one (1)** and any other three **(3)** questions in this paper.

: Marks for <u>ALL</u> procedural calculations will be awarded.

: Start each question on a fresh page of the answer sheet.

: Diagrams must be large and clearly labelled accordingly.

: This paper contains an appendix of chemical constants.

: Additional material: graph paper and data sheet.

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

Question 1 [25 Marks]

a) The absorbance of an iron thiocyanate solution containing 0.00500 mg Fe/mL was reported as 0.4900 at 540 nm.

   (i) Calculate the specific absorptivity, including units, of iron thyocyanate on the assumption that a 1.00 cm cuvette was used. [3]

   (ii) What will be the absorbance if (1) the solution is diluted to twice its original volume and (2) the solution is placed in a 5.00 cm cuvette? [3]

b) Direct nebulization is the most common method of sample introduction with continuous atomizers. Discuss two types of nebulizers, with the aid of diagrams [8]

c) In renewable energy, there is a growing interest into lignocellulosic biomass as feedstock. The aromaticity of the feedstock is used to predict the gasification reactivity. Outline a simplest / user-friendly analytical experiment you would carry out to determine aromatic functional groups of a solid biomass sample. [5]

d) Describe how the "injector" in a gas chromatograph (GC) is similar to, and different from, the "injector" in an HPLC. [6]

Question 2 [25 Marks]

a) Describe how a deuterium lamp can be used to provide background correction for an atomic absorption spectrum. [5]

b) Many instruments use monochromators to isolate the desired wavelength band for analysis. With the aid of a diagram, outline how wavelength selection is carried out by one of the two well-known monochromators. [5]

c) How does the Hollow Cathode Lamp work? [5]

d) The ICP is a useful component of an instrument used for the analysis of various metals.

   (i) What does ICP stand for? [1]

   (ii) Draw and label a schematic of an ICP. [6]

e) Describe the Beer – Lambert Law and illustrate how it may be related to the transmittance [3]

Question 3 [25 Marks]

a) The design of different spectrophotometers depends on the type of measurement (e.g. atomic emission, atomic absorption, UV-visible absorption, fluorescence) they are intended to take. Draw a block diagram of a single beam spectrophotometer that might be used for UV-visible molecular absorbance. [6]

b) IR absorbance spectra are primarily used to monitor molecular vibrations. Modern FTIRs dominate the market, why are they favoured over dispersive (monochromator based) instruments? [4]

c) Identify two effects of the absorption of infrared radiation on the bonds of carbon dioxide. Explain why an Oxygen molecule does not absorb radiation. [5]

d) For paper chromatography and column chromatography, identify;

   (i) The stationary and mobile phases [6]

   (ii) How the mobile phase moves [4]

Question 4 [25 Marks]

a) Define the following; (i) a standard, (ii) detection limit and (iii) electromagnetic radiation [3]

b) The draw and label the atomiser in Flame Atomic Absorption spectroscopy [6]

c) What is 'column efficiency', in high performance liquid chromatography? How is its value influenced by 'loading' of the column, N (number of theoretical plates), and H (the plate height)? What other factors influence it (list 2)? [8]

d) Derivatization is the process of chemically modifying a compound to produce a new compound which has properties that are suitable for analysis using a GC.

   (i) Explain three (3) scenarios which would require that a sample be first derivatized before being analysed using GC. [3]

   (ii) Explain how the derivatization is carried out. [2]

(iii)Give one example of a reagent used to achieve the form of derivatization. [1]

e) Which detector is used for the analysis of halogenated hydrocarbons using the GC method [2]

Question 5 [25 Marks]

a) Give definitions/descriptions of the following terms and phenomena used in spectroscopy;

(i) Analyte (2), Aliquot (2), the Beer-Lambert Law (3) and Spectroscopy (1). [9]

b) An absorption in an electronic spectrum is recorded at 17 000 cm^{-1}. What does this correspond to in nm? [2]

c) Explain the process of atomization and why it is important for analysis using the AAS. [3]

d) Using an illustrative diagram discuss how chromatographic methods (GC and HPLC) can be employed for both qualitative and quantitative analysis of a sample. [6]

e) A 7.25 X 10-5 M solution of potassium permanganate has a transmittance of 47.1% when measure in a 210 mm cell at wavelength 525 nm. Calculate the absorbance, A, of this solution and the molar absorptivity of potassium permanganate. [5]

Question 6 [25 Marks]

a) Compare and contrast between Soxhlet extraction and solid phase extraction [8]

b) Draw and label a Flame structure carefully characterizing each zone [9]

c) Explain in detail how the UV spectrophotometer can be used for both quantitative and qualitative analysis. [5]

d) How is atomic absorption different from molecular absorption [3]

The End

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	$F = N_A e$	9.6485×10^4 C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\ 51$ J K^{-1} mol^{-1}
		$8.205\ 78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		6.2364×10 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		
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 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}
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
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\ 79 \times 10^{-27}$ J T^{-1}
g value	g_e	$2.002\ 32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\ 77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\ 35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\ 37 \times 10^7$ m^{-1}
Standard acceleration of free fall	g	$9.806\ 65$ m s^{-2}
Gravitational constant	G	$6.672\ 59 \times 10^{-11}$ N m^2 Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\ 2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

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 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										Atomic mass → Symbol → Atomic No. →	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.