DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C304 ANALYTICAL CHEMISTRY I I

DECEMBER 2011 FINAL EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. This examination has six (6) questions and one (1) data sheet. The total number of pages is five (5), including this page.
2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

Useful Physical Constants

$k = 1.381 \times 10^{-23}\ JK^{-1}$ C : atomic #12 H : atomic #1

O : atomic #16 $h = 6.626 \times 10^{-34}\ Js^{-1}$ $c = 2.998 \times 10^{8}\ cm\ sec^{-1}$

$1\ eV = 1.602 \times 10^{-19}\ J$

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

a) For a spectroscopic band occurring at 1685 cm^{-1},

(i) convert to energy in joules [1]
(ii) state in which region of the electromagnetic spectrum the band falls [1]
(iii) state the kind of transition expected in this region [1]

b) Explain using diagrams, why atomic spectra appear as lines, whereas molecular spectra appear as bands [4]

c) The cheapest (affordable) uv-visible instruments (typically the *Bosch and Laumb Spectronic 20* series) "Bunsen" arrangement of the optical components.

(i) By means of a diagram, explain what is meant by this arrangement. [3]
(ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

d) A typical GC instrument has several standard components and accessories, each of which is listed below. Give a brief, but informative description of its functions.

(i) Nitrogen Gas Cylinder [2]
(ii) Filter Cartridge [2]
(iii) Soap Bubble Flow Meter [3]
(iv) Syringe [2]
(v) Oven [3]

QUESTION 2 [25]

a) The stationary phase is a critical component in chromatography.

i) Explain the role of the stationary phase in gas chromatography. [1]

ii) List and discuss any two (2) desirable properties of a stationary phase in gas chromatography. [2]

iii) Explain how OV-17 as stationary phase is able to separate methanol from a mixture with its homolog ethanol in gas chromatography [3]

b) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [2]

c) i) What is meant by "stray light" in spectroscopy? [1]

ii) Use equations to explain why stray light leads to negative deviations from Beer's Law [3]

iii) How is stray light eliminated in spectroscopy? [1]

d) Draw a schematic diagram of a Ge(Li) detector, connect it to an electrical circuit, and show how the voltage measured is directly related to intensity of uv-visible radiation in a spectrometer. [4]

e) Draw and label a vacuum phototube and explain how it works. [3]

f) Draw and label the "PMT", explain how it works, and explain its advantage over other detectors used in uv-visible spectrometers. [5]

Question 3 [25]

a) Analytical chemists agree that the technique of atomic absorption came of age with the invention of the hollow cathode lamp by Sir Walsh in 1955.

(i) Draw and label the hollow cathode lamp [2]
(ii) Explain how the hollow cathode lamp works [2]

b) There are several unique techniques employed by the agronomy laboratory at the Simunye Sugar Estate when using the Varian Spectr-AA-10 spectrophotometer. Explain:

(i) Why in the analysis of Sr, 100 ppm La is added to all solutions[2]
(ii) Why in the analysis of Cu, the instrument is operated under "standard additions" mode [2]

c) A major breakthrough in atomic absorption spectrophotometry since the invention of the hollow cathode lamp was graphite furnace AA.

(i) What is the major structural difference between flame AA and graphite furnace AA? Use diagrams to support your answer [3]

(ii) Identify the physical stages involved in a furnace program and describe the processes that occur during each stage. At what stage is the signal sampled, and why? [5]

(iii) Outline three (3) advantages of graphite furnace AA over flame AA [3]

d) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called Liberty 110 ICP.

(i) What does ICP stand for? [1]
(ii) With the aid of a diagram briefly describe the ICP torch, how the ICP is initiated, and how it is maintained and stabilized. [3]
(iii) What are the normal operating values of the ICP in terms of:

Power in kW ---------- Temperature in K ---------- [2]

Question 4 [25]

a) The cheapest (affordable) infrared instrument rely on the use of a "Czerny-Turner" arrangement of the optical components.

(i) By means of a diagram, explain what is meant by this arrangement. [3]
(ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

b) In the *Jasco* instrument used by researchers at the University of Swaziland for functional group identification o molluscicidal compounds in traditional herbs, a bolometer is used for detection. With the aid of a diagram, explain how this component works. [4]

c) State two (2) reasons why in IR (e.g., the *Jasco*) instrument, the sample is placed before the monochromator, whereas it the UV-Visible (e.g., *Spectronic 20*), instrument the sample is placed after it. [2]

d) With the aid of a diagram, briefly but informatively explain the function of one of the following detectors

i) TCD [4]

ii) FID [4]

e) Use chemical equations to explain how benzoic acid, which is difficult to be detected by the electron capture method, can be detected after derivatization in gas chromatography. [5]

Question 5 [25]

a) For the molecule CH_2O, formaldehyde, its UV and UV-visible spectra are attributed to "outer electron" transitions its molecular orbitals. In regard to this,

i). Draw the molecular energy level diagram showing these orbitals [2]

ii). Show how a $\sigma \longrightarrow \sigma^*$ transition takes place when the molecule absorbs radiation. [1]

iii). Show how an $n \longrightarrow \pi^*$ transition takes place when the molecule absorbs radiation. [1]

iv). Of the transitions in ii and iii above, λ_{max} is observed at 350 nm and 780 nm. Assign these wavelengths to each of the two transitions. [2]

v). Use diagrams to explain how the $\sigma \longrightarrow \sigma^*$ transition would result in an absorption band rather than a single line. [3]

b) i). In liquid chromatography, two solvent reservoirs are usually used. Explain the reason for this. [2]

ii). In gas chromatography, dual columns are often used simultaneously. Explain the reason for this. [2]

c) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene. A typical chromatogram of this mixture in a 2-m long column shows the appearance of peaks as follows:

Air peak (retention time - 0.5 minutes ; peak width - 5 seconds)
Cyclohexane peak (retention time - 1 minute ; peak width - 9 seconds)
Benzene peak (retention time – 1.5 minute ; peak width - 11 seconds)
Toluene peak (retention time – 1.8 minutes ; peak width - 13 seconds)

(i) In the experiment, explain the role of toluene (explain how it serves this role) [3]
(ii) Calculate the capacity factor of cyclohexane [3]
(iii) Are the cyclohexane and benzene peaks properly resolved [3]
(iv) Use the benzene peak in the sample chromatogram to calculate N; show how this value was obtained [3]

Question 6 [25]

a) Of the many applications of UV-visible spectroscopy, the determination of stoichiometry has been of interest in complexation reactions.

i) Describe the "Molar Ratio Method", and explain how it is used to determine stoichiometry. [2]

ii) Describe the "Jobs Method", and how it is used to determine stoichiometry. [2]

b) The Globar is a useful source of radiation in infrared spectroscopy. However, there is a throughput disadvantage if a Globar used in dispersive instruments.

i) Describe the Globar as used in IR spectroscopy. [1]
ii) Draw a plot of a blackbody radiator as a source of infrared radiation for spectroscopy in terms of energy density vs wavelength at 6000 K. and at10000 K. [2]
iii) Explain, using the blackbody radiation plot in (ii) above, why dispersive IR instruments are throughput-limited. [2]

c) Nebulization is a very wasteful approach to atomization.

i) What does the term "nebulization" mean? [1]
ii) Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [3]
iii) Use your answer in (a) ii above to explain why nebulization is considered inefficient. [2]

d) Bandbroadening is important for peak resolution in HPLC.

i) Use a drawing to explain the importance of linear velocity on HETP [3]
ii) On this drawing, indicate the optimum linear velocity [2]
iii) Use diagrams to explain the phenomenon of "race track effect", how it affects bandbroadening, and how it is eliminated. [5]