Second Semester Examination
Academic Session 2020/2021

July 2021

KAT345 – Spectroscopic Methods
[Kaedah Spektroskopi]

Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of **NINE (9)** pages of printed material before you begin the examination.

Answer **FOUR (4)** questions only.

SECTION A : Answer all the questions.

SECTION B : Select and answer only **ONE (1)** question.

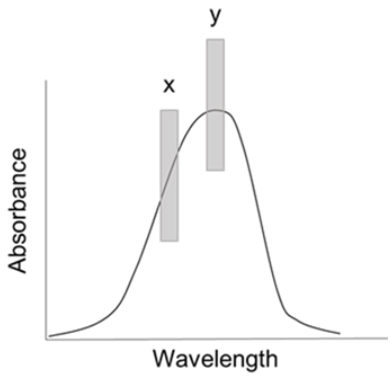
Answer each question on a new page. You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answered more than four questions, only the first four questions in order of the arrangement in the received answer script will be marked.

SECTION A

Answer **ALL** question.

1. (a) The following figure shows an absorption spectrum of a compound using UV/Vis spectrophotometer.



(i) Provide **THREE** reasons for an absorption measurement must be taken at wavelength of maximum absorbance (λ_{max}).

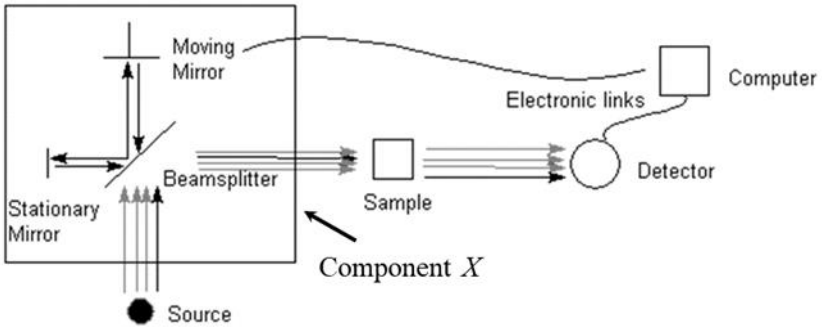
(ii) Explain the effect of selecting band-x and -y on Beer's Law.

(5 marks)

(b) Nicotinamide adenine dinucleotide hydride (NADH) is a reduced form of nicotinamide adenine dinucleotide (NAD), a cofactor found in all living cells. A 0.725 mL aqueous solution of NADH shows an absorbance of 0.257 at 340 nm in 1.0-cm cuvette. Calculate the concentration of NaDH (in nmol units) contained in the sample. Given, molar absorptivity of the sample is 6290 L mol^{-1} cm^{-1}.

(4 marks)

(c) The diagram below is the representation of Fourier transformed Infrared (FTIR) spectrometer.

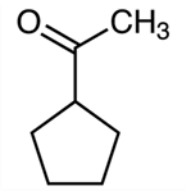


(i) Describe the function of component X in the IR spectroscopy.

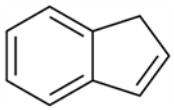
(ii) Explain the mechanism of component X to produce an absorption spectrum in the IR analysis.

(9 marks)

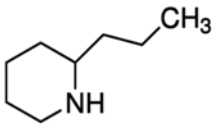
(d) The electronic transitions that take place in the UV and Vis regions of electromagnetic spectrum are due to the absorption of radiation by specific types of functional groups and chemical within the molecule. Based on the chemical structures below, analyse the mode of electronic transition in each compound.



Cyclopentylethanone



Indene



Coniine

(7 marks)

2. Inductively coupled plasma – optical emission spectrophotometry (ICP-OES) offers several advantages when compared with that of flame emission spectrometry.

(a) Define a plasma in the ICP-OES method.

(2 marks)

(b) Illustrate with proper description, the excitation process that takes place in an ICP torch.

(5 marks)

(c) List **FOUR** properties of ICP which make it highly suitable for atomic emission spectrophotometry.

(4 marks)

(d) Plasma emission is routinely used in agricultural science to study elements in soil, plant tissue and fertilizer. Suggest the reasons that this method is preferred over flame photometry.

(4 marks)

(e) Gold (Au) can be determined in solutions containing high concentrations of diverse ions by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Aliquots of 50.0 mL of the sample solution were transferred to each of four 100.0 mL volumetric flasks. A solution was prepared containing 10.0 mg L^{-1} Au in 20% H2SO4 and quantities of this solution were added to the sample solutions to give 0, 2.5, 5, and 10 mg L^{-1} added Au in each of the flasks. The solutions were made up to a total volume of 100.0 mL, mixed, and analysed by ICP-AES. The resulting data are presented in the following table. By performing a least-square analysis, determine

Added Au / mg L^{-1}	Emission intensity / counts
0.0	12,568
2.5	19,324
5.0	26,622
10.0	40,021

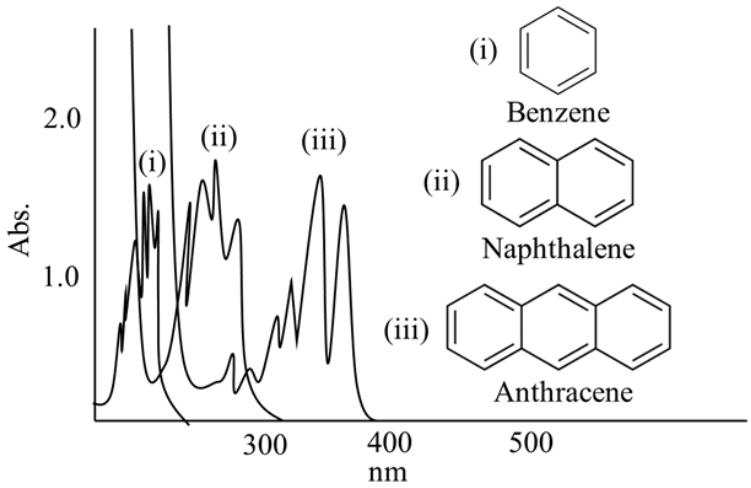
(i) the slope,

(ii) the intercept, and

(iii) calculate the concentration of Au in the sample solution in mg L^{-1}.

(10 marks)

3. (a) A scientist found that anthracene absorbs at longer wavelength of UV radiation compared to naphthalene and benzene as shown in the figure below. Explain this observation.



(3 marks)

(b) Quinine in a 1.664-g antimalarial tablet was dissolved in sufficient 0.1 M HCl to give 500 mL of solution. A 15.00-mL aliquot was then diluted to 100.0 mL with the acid. The fluorescence intensity for the diluted sample at 347.5 nm provided a reading of 288 on an arbitrary scale. A standard 100 ppm quinine solution registered 180 intensity when measured under conditions identical to those for the diluted sample. Calculate the mass of quinine (in mg) in the tablet.

(4 marks)

(c) With the aid of a simple Jablonski diagram, describe the relationship between electronic absorption and fluorescence emission.

(5 marks)

(d) Suggest **THREE** conditions which can be used for identification of a molecular ion peak in a mass spectroscopy spectrum.

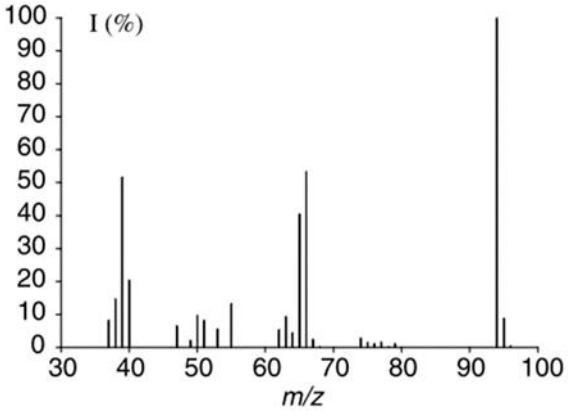
(3 marks)

(e) Electrospray ionisation (ESI) is preferred in pharmaceutical chemistry because this method ionises large biomolecule compounds into multiple charged ions with little fragmentation. Describe, by using a proper diagram, the corresponding ionisation process that takes place in the ESI instrument.

(3 marks)

(f) Using appropriate methods, determine the chemical formula and the name of the organic compound characterised in the following mass spectrum.

m/z	Abund.(%)	*m/z*	Abund.(%)
37	8.3	64	4.4
38	14.6	65	40.5
39	51.6	66	53.3
40	20.3	67	2.35
47	6.5	74	2.8
49	2.1	75	1.5
50	9.7	76	1.2
51	8.3	77	1.6
53	5.5	79	1.2
55	13.2	94	100
62	5.4	95	6.6
63	9.4	96	0.4

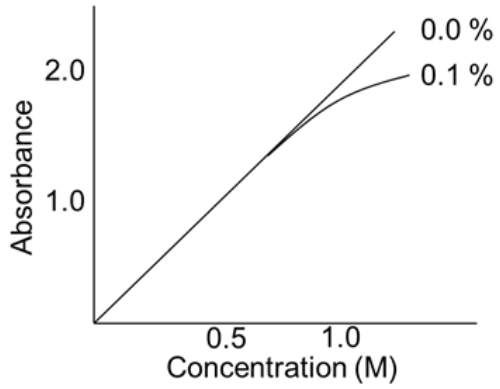


(7 marks)

SECTION B

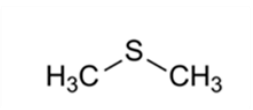
Answer at least **ONE (1)** question from this section.

4. (a) Based on the following figure, explain the effect of stray radiation on absorption measurement.

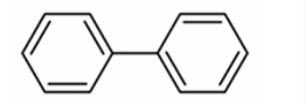


(6 marks)

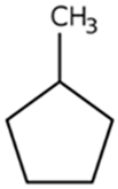
(b)



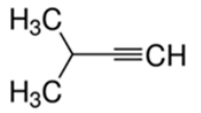
Dimethyl sulfide



Biphenyl



Methylcyclopentane



3-methyl-1-butyne

(i) Predict whether the above organic compounds are classified as a UV/Vis absorbing or non-absorbing compounds.

(ii) Give reason for each of your answer in (i).

(6 marks)

(c) Describe how X-rays are produced in a general X-ray spectrometer using an appropriate diagram.

(3 marks)

(d) Diffraction data from a crystal is very useful for the molecular structure determination. Using an appropriate equation, explain how atomic arrangements in a crystal lattice can provide information over its crystal structure.

(3 marks)

(e) Atomic X-ray spectroscopy (AXS) is highly useful and significant in archaeology. Discuss

(i) the reasons the AXS method is more preferred over other instrumental techniques in archaeological research, and

(ii) the AXS procedures used to determine composition and structures of arts and artifacts.

(7 marks)

5. (a) Dispersive IR instruments are similar in general design to the double-beam UV/Vis spectrophotometers. However, there are a few things that make them differ. List the differences for both instruments.

(6 marks)

(b) Concentration and dissolved oxygen are two variables that influence the fluorescence measurements. For each variable, discuss its relationship to the intensity of fluorescence emission.

(7 marks)

(c) List **THREE** pre-requirements for an ideal flame in obtaining optimum conversion of the sample into gaseous atoms.

(3 marks)

(d) A 5.00-mL sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation, the resulting solution was brought to pH 3 and extracted with two 5-mL portions of methyl isobutyl ketone containing the lead-complexing agent, ammonium pyrrolidine-*N*-carbodithioate (APCD). The extract was aspirated directly into an air/acetylene flame and yielded an absorbance of 0.502 at 283.3 nm. Five millilitre aliquots of standard solutions containing 0.400 and 0.600 ppm of lead were treated in the same way and yielded absorbances of 0.396 and 0.599. Determine the concentration of lead in the sample (in ppm) assuming that Beer's law is followed.

(9 marks)

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