UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KAA 503 – Molecular Spectroscopy
[Spektroskopi Molekul]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **TWENTY ONE** printed pages before you begin the examination.

Instructions:

Answer **FIVE** (5) questions.

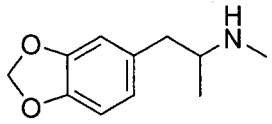
Begin the answer to each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

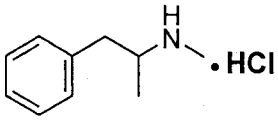
If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

...2/-

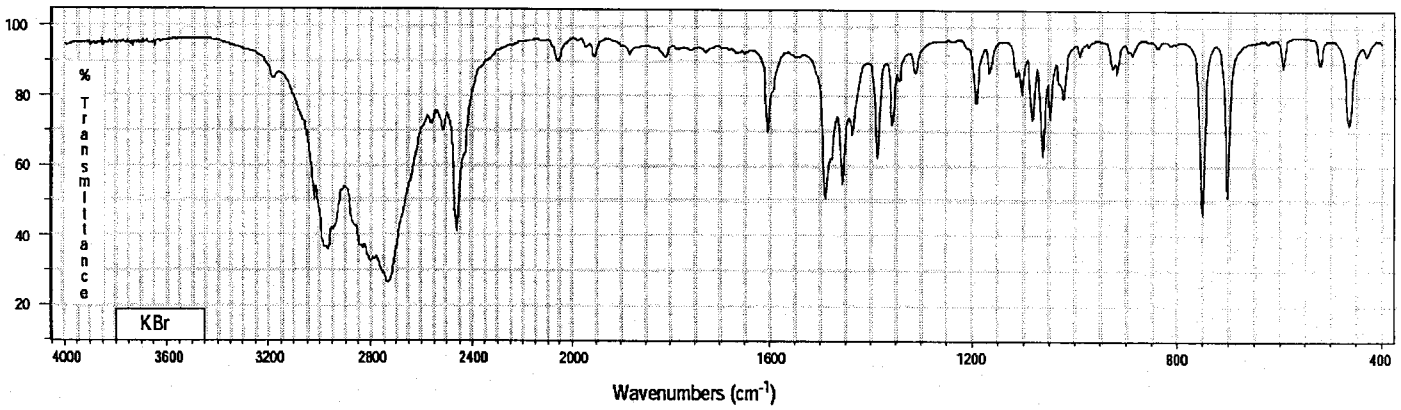
1. A chemical sample suspected to be either 3,4-methylenedioxy-*N*-methylamphetamine (**Ecstasy**) or methamphetamine hydrochloride (**Syabu**) is subjected to FTIR scan, the spectrum of which is shown below.



Ecstasy



Syabu



(a) Identify the chemical sample from the list given above on the basis of the FTIR spectrum and justify your answer by assigning the structurally informative bands.

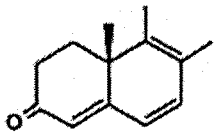
(10 marks)

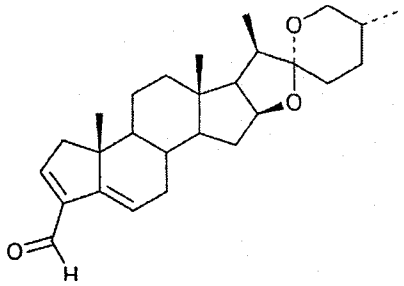
(b) The Jacquinot, or throughput advantage, arises because unlike dispersive spectrometers, FTIR spectrometers have no slits which attenuate the infrared light. Explain the advantage of FTIR spectrometer on the basis of the Michelson interferometer.

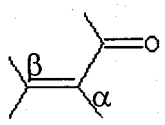
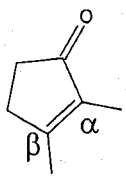
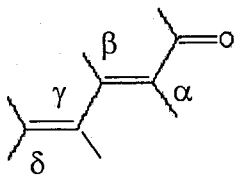
(10 marks)

...3/-

2. (a) Use the table below to calculate the λ_{max} of the following compounds.

(i) 

(ii) 

Core Chromophore	Substituent and Influence
 R = Alkyl **215 nm** R = H **210 nm** R = OR' **195 nm**	**α- Substituent** R- (Alkyl Group) **+10 nm** Cl- (Chloro Group) **+15** Br- (Bromo Group) **+25** HO- (Hydroxyl Group) **+35** RO- (Alkoxyl Group) **+35** RCO_2- (Acyl Group) **+6** **β- Substituent** R- (Alkyl Group) **+12 nm** Cl- (Chloro Group) **+12** Br- (Bromo Group) **+30** HO- (Hydroxyl Group) **+30** RO- (Alkoxyl Group) **+30** RCO_2- (Acyl Group) **+6** RS- (Sulfide Group) **+85** R_2N- (Amino Group) **+95** **γ & δ- Substituents** R- (Alkyl Group) **+18 nm** (both γ & δ) HO- (Hydroxyl Group) **+50 nm** (γ) RO- (Alkoxyl Group) **+30 nm** (γ) **Further π-Conjugation** C=C (Double Bond) **+30** C_6H_5 (Phenyl Group) **+60**
 Cyclopentenone **202 nm**	
	

(A) Each exocyclic double bond adds **5 nm.**

(B) Homoannular cyclohexadiene component adds **+35 nm** (ring atoms must be counted separately as substituents)

(10 marks)

...4/-

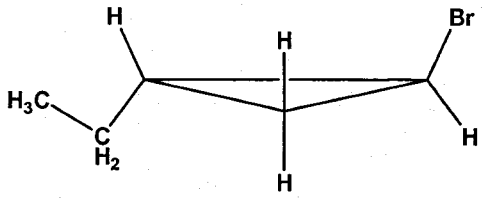
(b) Aromatic compounds display several absorption bands in the UV region. Usually the bands are commonly named E and B bands representing π to π^* excitations. E band is in the 180 - 210 nm range with the ε_{max} of 2 - 6 x 10^3. The B band appears in the 250 - 295 nm range with ε_{max} from 10^2 - 10^3. Describe what you will observe in the UV-Vis spectrum if

(i) the aromatic compounds contain an attached functional group with a nonbonded pair of electrons, such as alkoxy group, and

(ii) the aromatic compounds contain electron donating substituents.

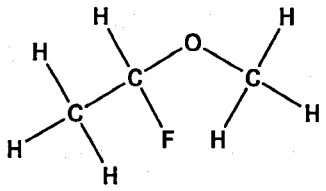
(10 marks)

3. (a) Predict the multiplicity and indicate the relative intensity of each ^1H signal for *trans*-1-bromo-2-ethylcyclopropane.



(7 marks)

(b) Using the coupling constants values of $^3J_{HH}$ = 7 Hz, $^2J_{HF}$ = 60 Hz and $^3J_{HF}$ = 20 Hz, draw the ^1H multiplets for the following molecule:



(7 marks)

(c) Calculate the maximum NOE, η, for proton-decoupled ^{13}C and ^{19}F NMR spectra using the following information: the magnetogyric ratio,γ, for ^1H, ^{13}C and ^{19}F is 267.512 x 10^6 rad T^{-1} s^{-1}, 67.264 x 10^6 rad T^{-1} s^{-1} and 251.667 x 10^6 rad T^{-1} s^{-1}, respectively.

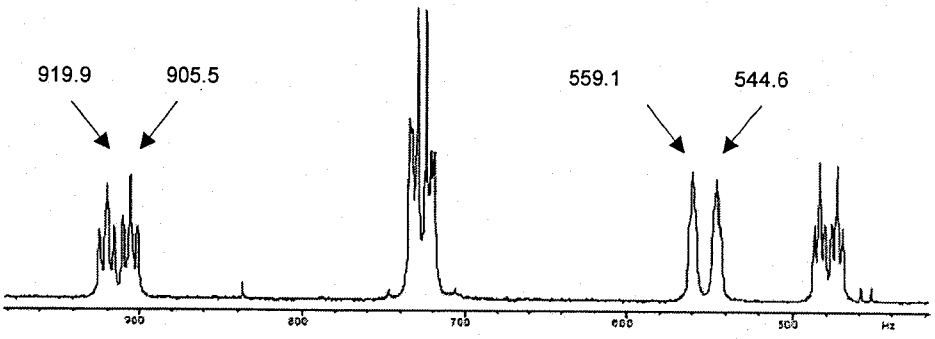
(6 marks)

...5/-

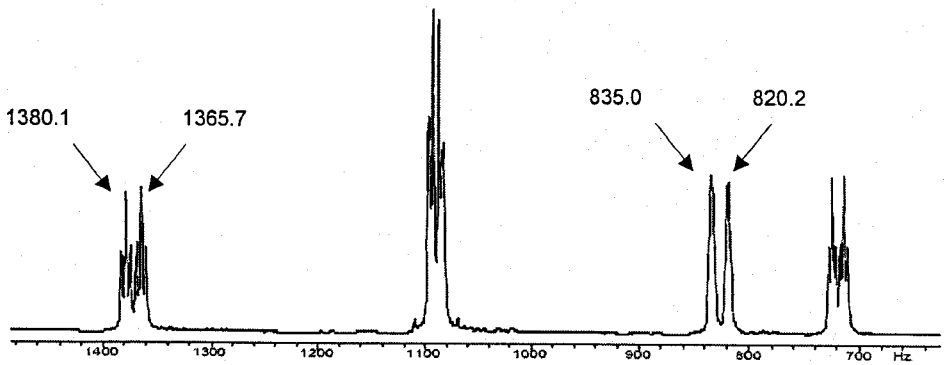
4. (a) Two ^{1}H spectra of strychnine acquired on INOVA400 and Omega600 are depicted below.

(i) Calculate the chemical shifts of the four labeled signals from both instruments.

(ii) Calculate the homonuclear J coupling of the two protons using the data on the spectra.



Part of the proton spectrum of strychnine. Acquired on INOVA400 (Proton frequency 399.95 MHz)

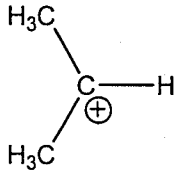


Part of the proton spectrum of strychnine. Acquired on OMEGA600 (Proton frequency 599.64 MHz)

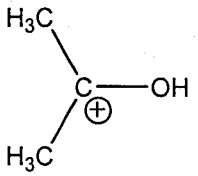
(6 marks)

...6/-

(b) One of the ions, **I** and **II**, shown below exhibits a ^{13}C signal at δ 320.6 for the charged carbon while that of the other occurs at δ 250.3. Which chemical shift belong to **I** and which belong to **II**? Clarify your answer.



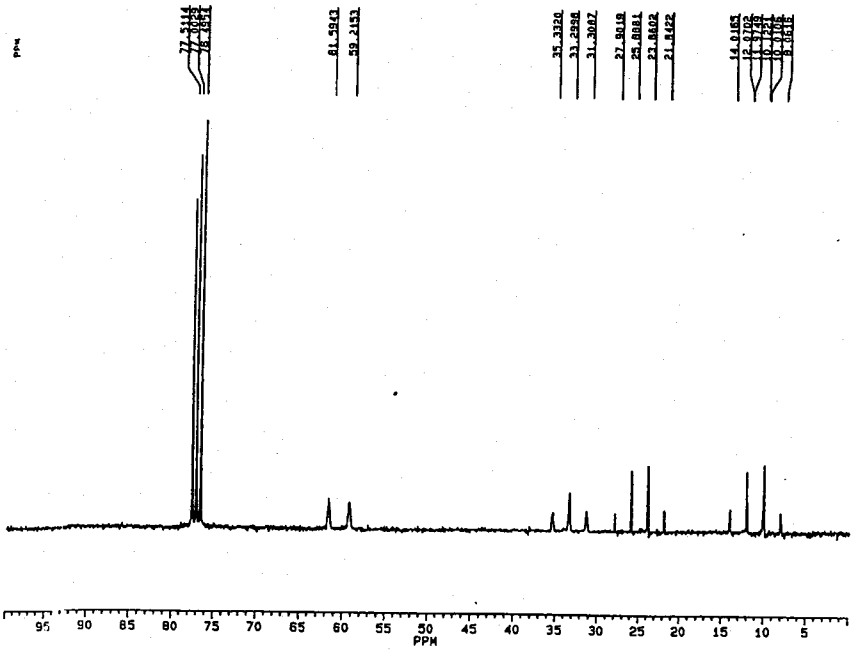
I



II

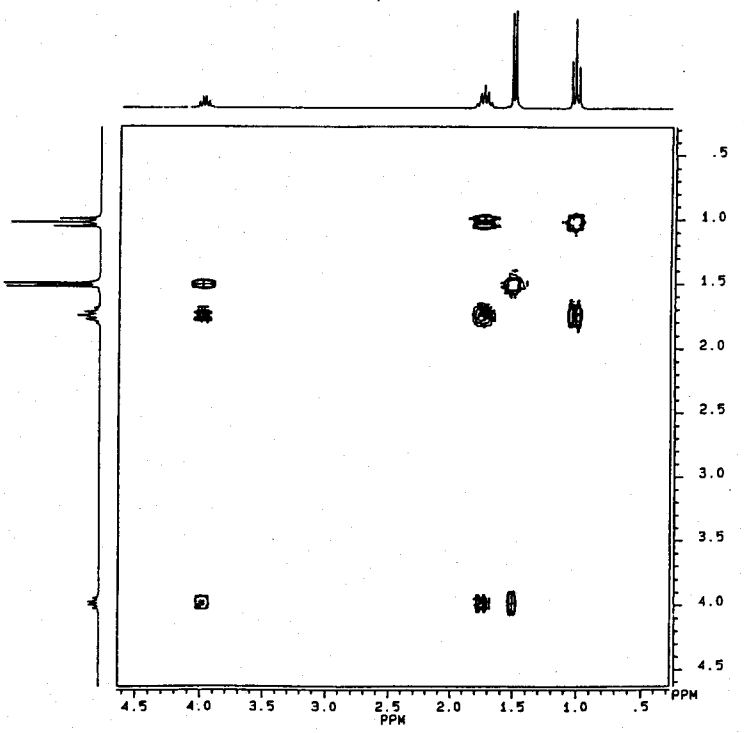
(6 marks)

(c) Explain how the structure of the compound, C_4H_9Cl, can be deduced using both its ^{13}C NMR and ^{1}H-^{1}H COSY spectra shown below.



^{13}C spectrum of C_4H_9Cl, acquired at 62.5 MHz without proton decoupling

...7/-



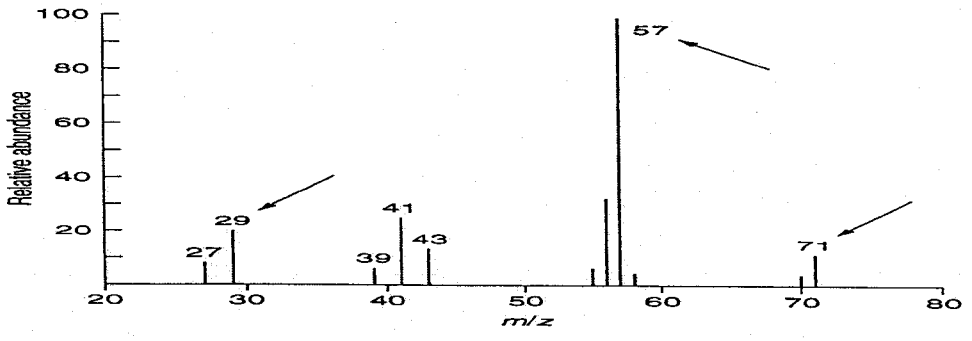
^{1}H-^{1}H COSY spectrum of C_4H_9Cl

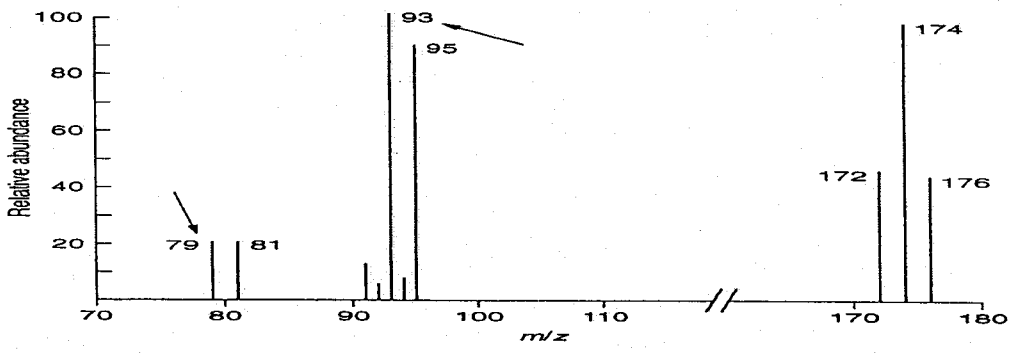
(8 marks)

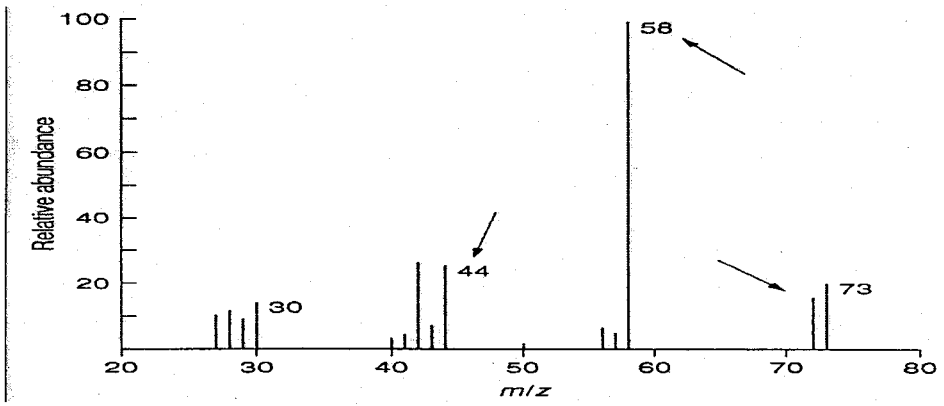
...8/-

5. (a) For each of the following mass spectra, assign the spectrum for each formula and write a reasonable path (using the appropriate curved arrows) to explain the origin of each of the fragment ions designated by an arrow.

Dibromomethane, 2,2,4-trimethylhexane, and ethyldimethylamine







(6 marks)

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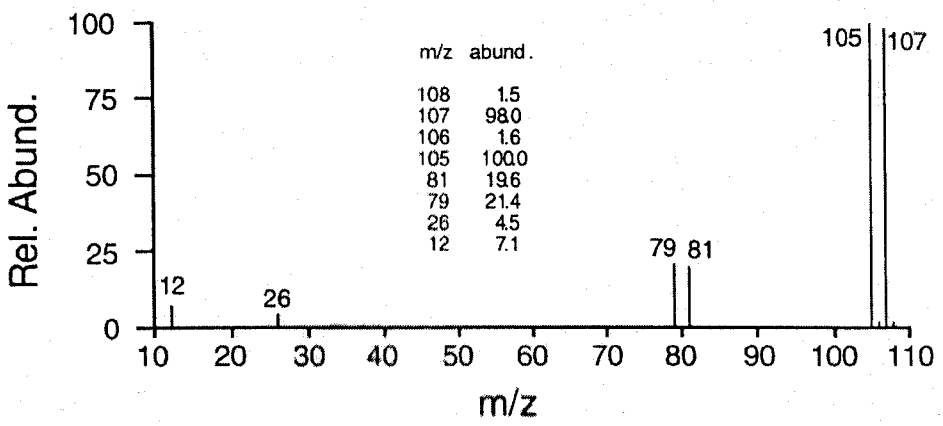
(b) Identify the halogen-containing compound the spectrum of which is shown below.



(4 marks)

(c) Give the structure of a compound, $C_{10}H_{12}O$, the mass spectrum of which shows *m/z* values of 15, 43, 57, 91, 105, and 148.

(2 marks)

(d) The following are three deuterated forms of ethyl methyl ketone. Show how mass spectroscopy can be used to distinguish the three isomers?

(i) $DCH_2CH_2COCH_3$

(ii) $CH_3CH_2COCH_2D$

(iii) $CH_3CHDCOCH_3$

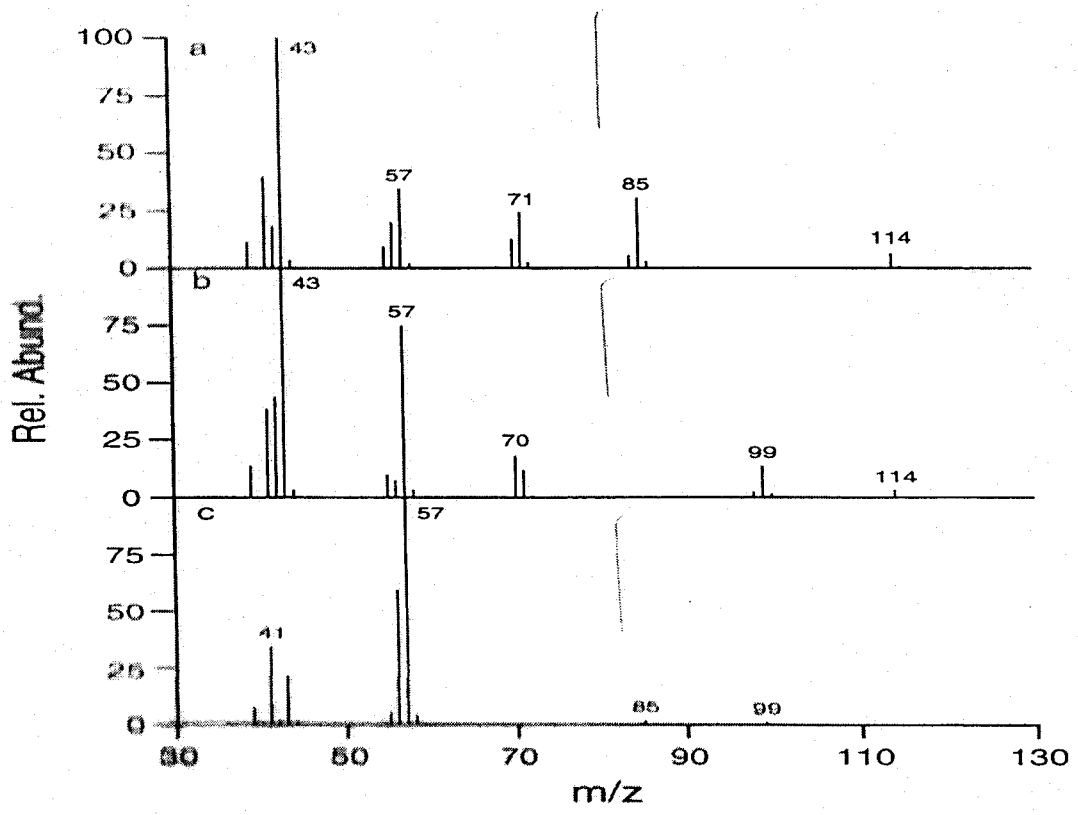
(3 marks)

(e) Describe with the aid of schematic diagram the ionization mechanism involved in the ionization of molecule in the electrospray ionization mass spectrometry.

(5 marks)

...10/-

6. (a) The following are the spectra of three C_7H_{16} isomers. Assign the structures for each spectrum.



(6 marks)

(b) The mass spectrum of a compound containing C, H, O, and N gives a maximum *m/z* of 121. Its IR spectrum shows peaks at 700, 750, 1520, 1685, and 3100 cm^{-1}, and a twin peak at 3440 cm^{-1}. Suggest a reasonable structure for the compound.

(4 marks)

(c) Calculate the abundance of the M^++1 and M^++2 peaks for ethene and carbon monoxide, respectively.

(4 marks)

(d) There are a several combinations of mass analyzers commercially available. The most common one is triple stage quadrupole analyzer. Describe the principles of the technique and explain its main capabilities.

(6 marks)

...11/-

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

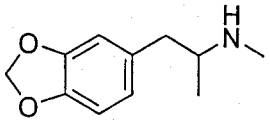
Anda perlu mulakan setiap soalan pada muka surat baru.

Anda boleh menjawab sama ada dalam Bahasa Melayu atau Bahasa Inggeris.

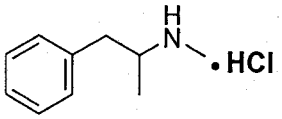
Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

...12/-

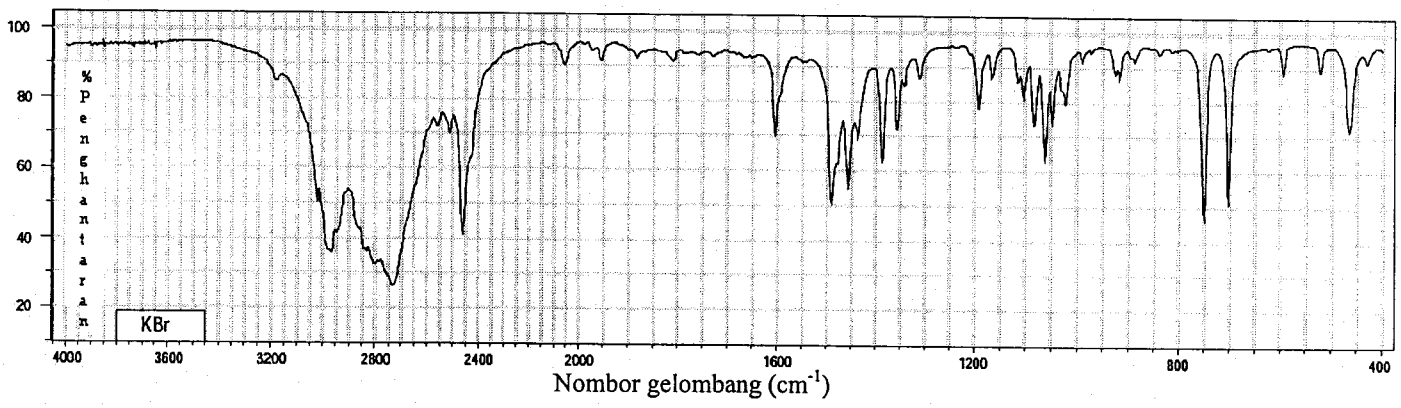
1. Suatu sampel bahan kimia yang disyaki sebagai 3,4-metilenadioksi-*N*-metilamfetamina (**Ecstasy**) atau metamfetamina hidroklorida (**Syabu**) dijalankan imbasan FTIR dan spektrum yang diperolehi ditunjukkan di bawah.



Ecstasy



Syabu



(a) Kenalpastikan sampel bahan kimia tersebut berdasarkan pada senarai bahan kimia dan spektrum FTIR diberi di atas dan justifikasikan jawapan anda dengan memperuntukkan jalur yang boleh memberi maklumat tentang struktur sebatian itu.

(10 markah)

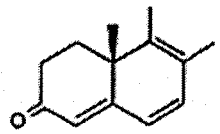
(b) Kelebihan Jacquinot, atau kelebihan keluaran hantaran, ditimbulkan kerana selain daripada spektrometer serakan, spektrometer FTIR tidak ada celah yang mengurangkan cahaya inframerah. Jelaskan kelebihan spektrometer FTIR berdasarkan pada interferometer Michelson.

(10 markah)

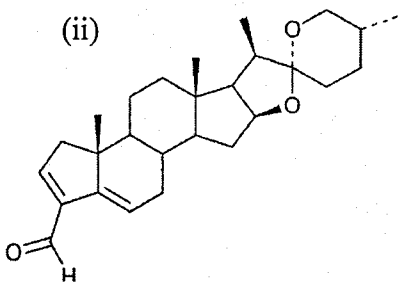
...13/-

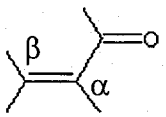
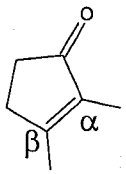
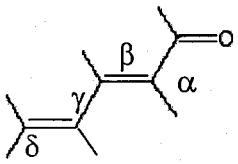
2. (a) Gunakan jadual di bawah untuk mengira nilai λ_{max} bagi sebatian berikut.

(i)



(ii)



Kromofor teras	Penukarganti dan kesannya
 R = Alkil **215 nm** R = H **210 nm** R = OR' **195 nm**	**Penukarganti-α** R- (Kumpulan Alkil) **+10 nm** Cl- (Kumpulan Kloro) **+15** Br- (Kumpulan Bromo) **+25** HO- (Kumpulan Hidroksil) **+35** RO- (Kumpulan Alkoksil) **+35** RCO_2- (Kumpulan Asil) **+6** **Penukarganti-β** R- (Kumpulan Alkil) **+12 nm** Cl- (Kumpulan Kloro) **+12** Br- (Kumpulan Bromo) **+30** HO- (Kumpulan Hidroksil) **+30** RO- (Kumpulan Alkoksil) **+30** RCO_2- (Kumpulan Asil) **+6** RS- (Kumpulan Sulfid) **+85** R_2N- (Kumpulan Amino) **+95** **Penukarganti-γ & δ** R- (Kumpulan Alkil) **+18 nm** (kedua-dua γ & δ) HO- (Kumpulan Hidroksil) **+50 nm** (γ) RO- (Kumpulan Alkoksil) **+30 nm** (γ) **Konjugatan-π lanjut** C=C (Ikatan Dubel) **+30** C_6H_5 (Kumpulan Fenil) **+60**
 Siklopentenon **202 nm**	
	

(A) Bagi setiap ikatan dubel eksosiklik, tambah **5 nm**.

(B) Bagi komponen sikloheksadiena homoanular, tambah **+35 nm** (atom gelang mesti dikira berasingan sebagai penukarganti).

(10 markah)

...14/-

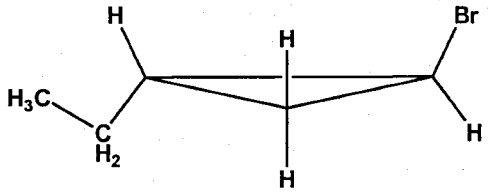
(b) Sebatian aromatik mempamerkan beberapa jalur penyerapan di dalam kawasan UV. Biasanya jalur tersebut digelar sebagai jalur E dan B yang mewakili pengujaan π ke π^*. Jalur E terdapat di dalam julat 180 - 210 nm dengan ε_{max} dari 2 - 6 x 10^3. Jalur B terdapat di dalam julat 250 - 295 nm dengan ε_{max} dari 10^2 - 10^3. Huraikan apa yang akan diperhatikan di dalam spektrum UV-Vis jika

(i) sebatian aromatik tersebut mengandungi suatu kumpulan berfungsi dengan suatu pasangan elektron tak berikatan, seperti kumpulan alkoksi, dan

(ii) sebatian aromatik tersebut mengandungi penukarganti penderma elektron.

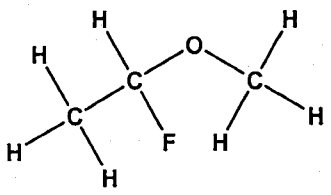
(10 markah)

3. (a) Ramalkan kemultipelan dan tunjukkan intensiti relatif bagi setiap isyarat ^{1}H pada *trans*-1-bromo-2-etilsiklopropana



(7 markah)

(b) Dengan menggunakan nilai pemalar pengkupelan bagi $^3J_{HH}$ = 7 Hz, $^2J_{HF}$ = 60 Hz dan $^3J_{HF}$ = 20 Hz, lukiskan multiplet ^{1}H bagi molekul berikut:



(7 markah)

(c) Kirakan nilai NOE, η, yang maksima bagi spektrum teryahganding proton ^{13}C dan ^{19}F dengan menggunakan maklumat berikut: γ bagi ^{1}H, ^{13}C dan ^{19}F adalah masing-masing, 267.512 x 10^6 rad T^{-1} s^{-1}, 67.264 x 10^6 rad T^{-1} s^{-1} dan 251.667 x 10^6 rad T^{-1} s^{-1}.

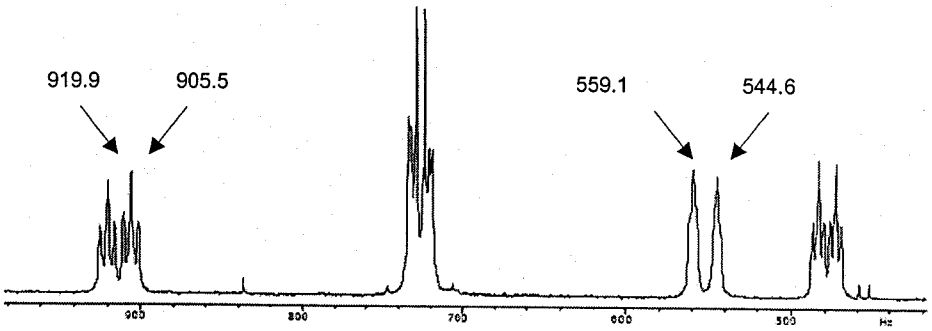
(6 markah)

...15/-

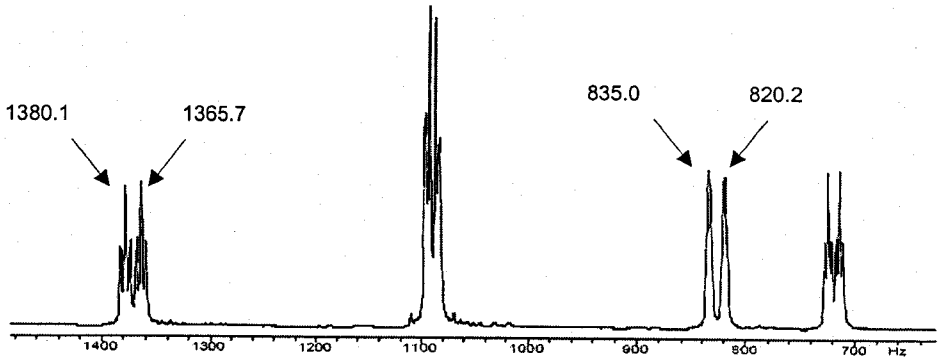
4. (a) Dua spekrum ^{1}H stricinin yang dirakamkan dengan INOVA400 dan Omega600 dikemukakan di bawah.

(i) Kirakan anjakan kimia bagi keempat-empat isyarat yang ditunjukkan dalam setiap spektrum tersebut.

(ii) Kirakan nilai pengkupelan homonuklues J bagi kedua-dua proton yang ditunjukkan itu.



daripada spektrum ^{1}H stricinin yang dirakamkan dengan INOVA400 (Frekuensi proton 399.95 MHz)

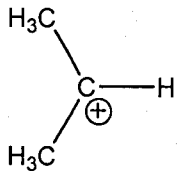


Sebahagian daripada spektrum ^{1}H stricinin yang dirakamkan dengan OMEGA600 (Frekuensi proton 599.64 MHz)

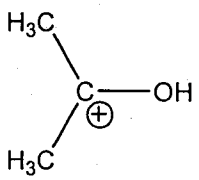
(6 markah)

...16/-

(b) Satu daripada ion-ion, **I** dan **II**, yang ditunjukkan di bawah mempunyai isyarat ^{13}C pada δ 320.6 bagi karbonnya yang bercaj, manakala karbon bercaj bagi ion yang lagi satu mempunyai isyarat ^{13}C pada δ 250.3. Anjakan kimia yang manakah dipunyai oleh **I** dan yang manakah dipunyai oleh **II**? Jelaskan jawapan anda.



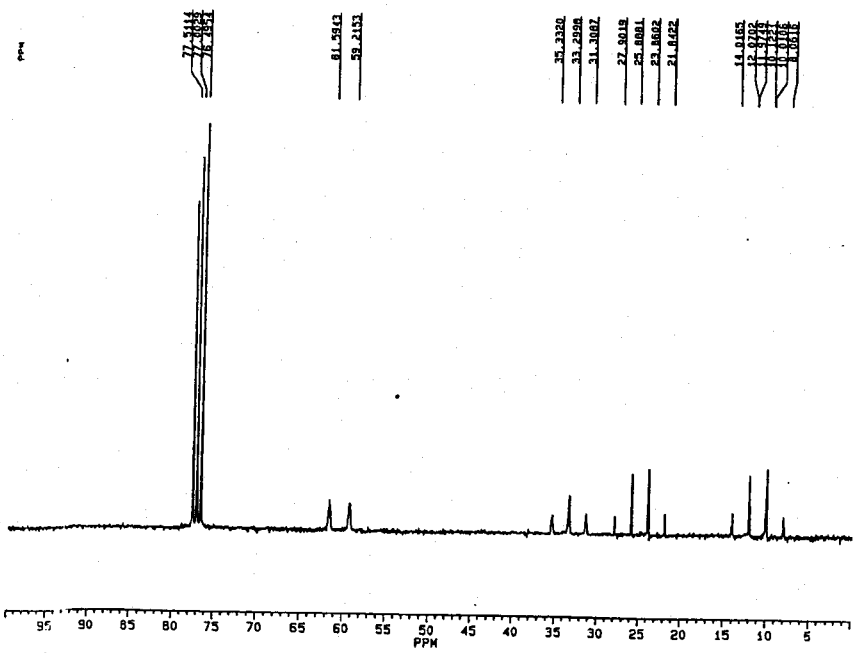
I



II

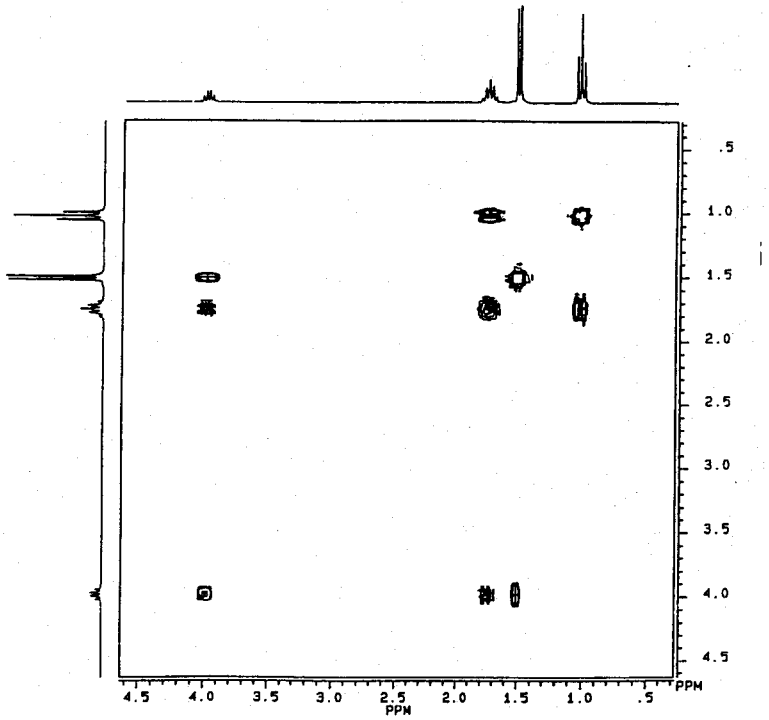
(6 markah)

(c) Jelaskan bagaimana struktur sebatian, C_4H_9Cl, dapat tentukan dengan menggunakan kedua-dua spektrum ^{13}C NMR dan ^{1}H-^{1}H COSY seperti yang diberikan di bawah.



Spektrum ^{13}C NMR C_4H_9Cl, dirakam pada 62.5 MHz tanpa penyahgadingan proton

...17/-



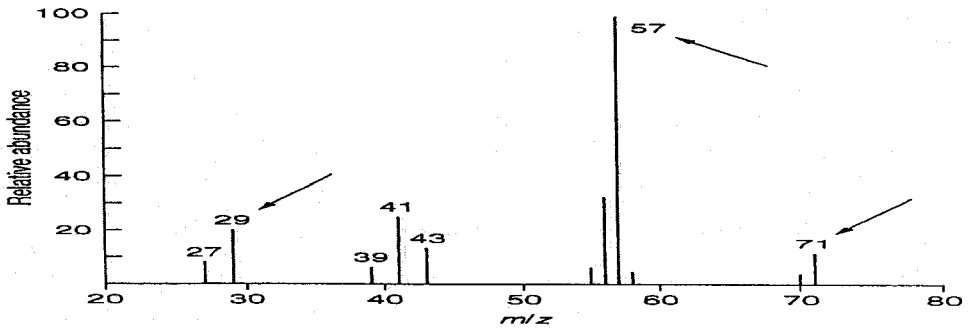
Spektrum ^{1}H-^{1}H COSY C_4H_9Cl

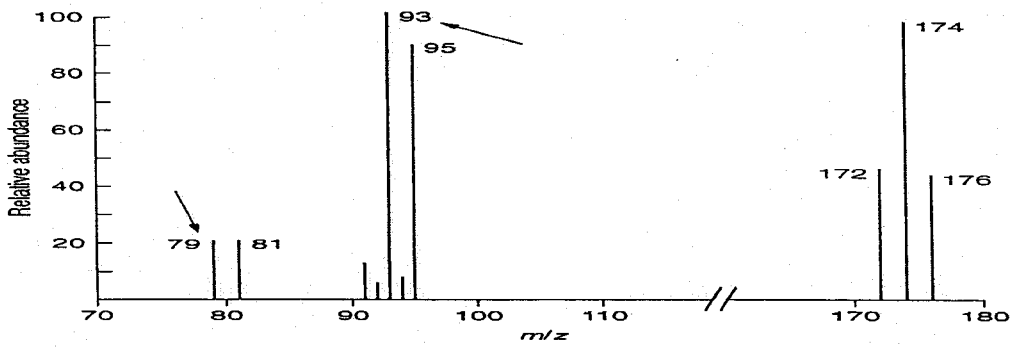
(8 markah)

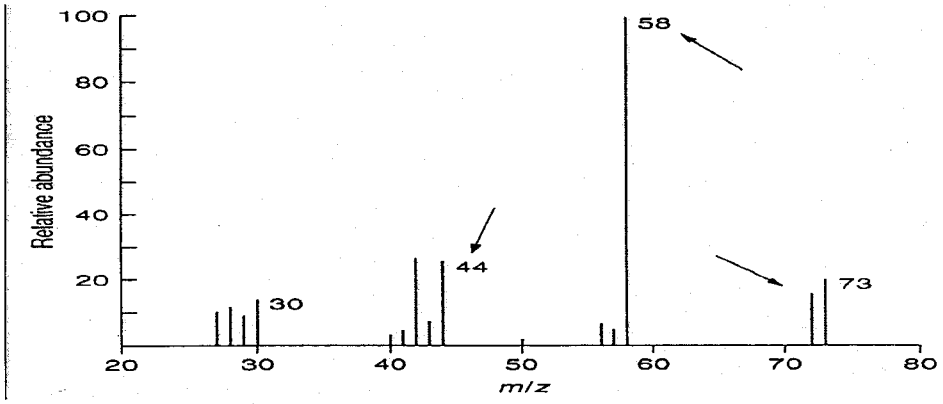
...18/-

5. (a) Bagi setiap dari spectrum jisim berikut, peruntukkan spektrum bagi setiap formula dan tulis suatu perjalanan (guna anak panah lengkung bersesuaian) untuk menjelaskan punca setiap ion serpihan ditunjukkan oleh anak panah.

Dibromometana, 2,2,4-trimetilheksana, dan etildimetilamina



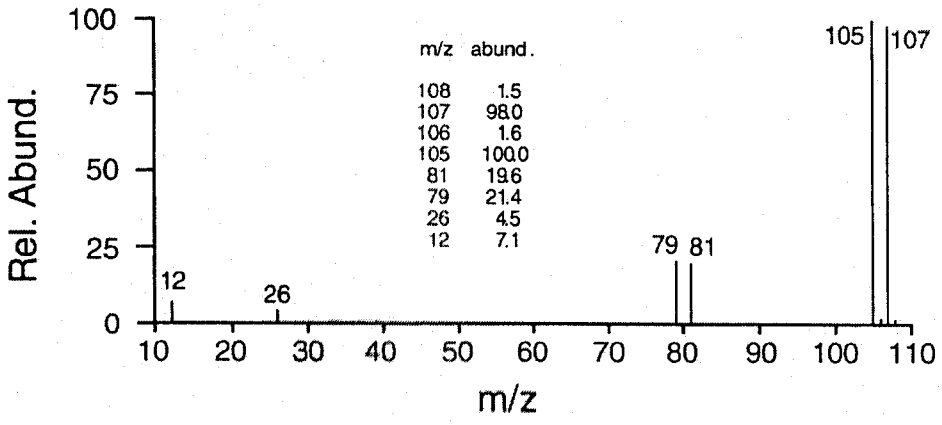




(6 markah)

...19/-

(b) Kenalpastikan sebatian yang mengandungi halogen di mana spektrumnya ditunjukkan di bawah.



(4 markah)

(c) Beri struktur bagi suatu sebatian, $C_{10}H_{12}O$, di mana spektrum jisimnya menunjukkan nilai *m/z* 15, 43, 57, 91, 105, dan 148.

(2 markah)

(d) Berikut adalah tiga bentuk etil metil keton terdeuterat. Tunjukkan bagaimana spektroskopi boleh digunakan untuk memperbezakan tiga isomer tersebut

(i) $DCH_2CH_2COCH_3$

(ii) $CH_3CH_2COCH_2D$

(iii) $CH_3CHDCOCH_3$

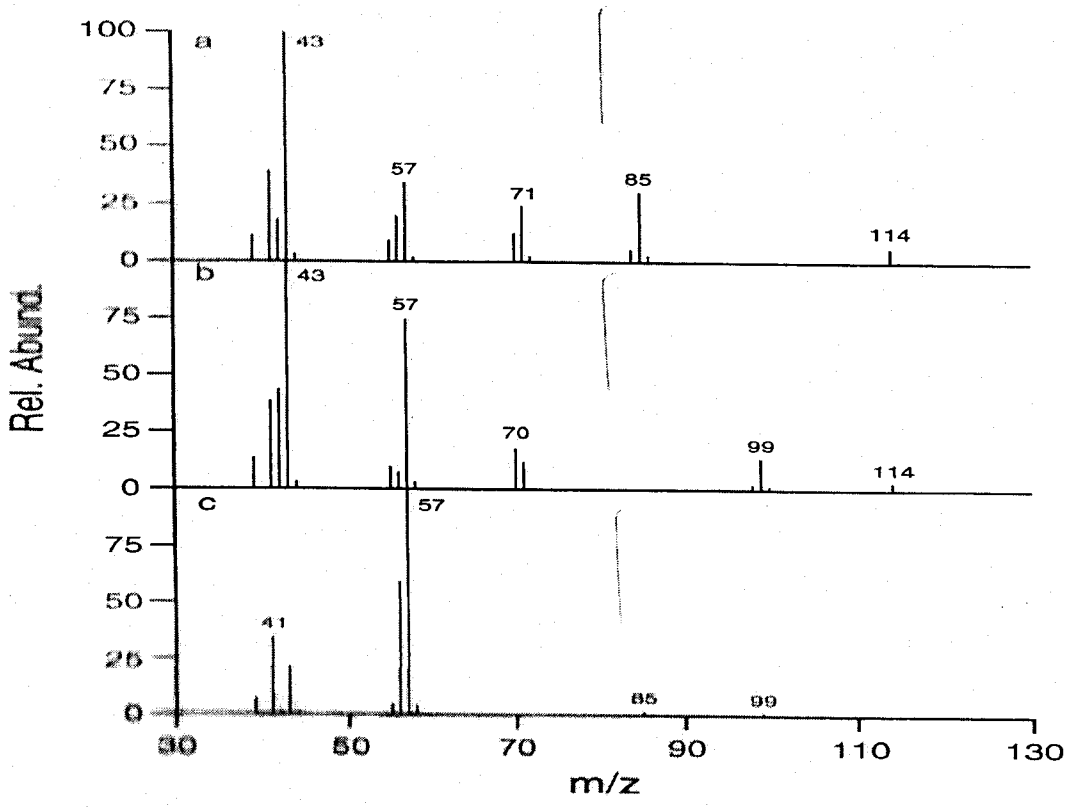
(3 markah)

(e) Huraikan dengan bantuan gambarajah skema mekanisme pengionan terlibat dengan pengionan molekul di dalam spektrometri jisim pengionan elektrosemburan.

(5 markah)

...20/-

6. (a) Berikut adalah spektrum bagi tiga isomer C_7H_{16}. Peruntukkan struktur bagi setiap spektrum



(6 markah)

(b) Spektrum jisim bagi suatu sebatian yang mengandungi C, H, O, dan N memberi nilai maksimum *m/z* 121. Spektrum IRnya menunjukkan puncak pada 700, 750, 1520, 1685, dan 3100 cm^{-1}, dan suatu puncak kembar pada 3440 cm^{-1}. Cadangkan suatu struktur munasabah untuk sebatian tersebut.

(4 markah)

(c) Kiralah kelimpahan puncak M^++1 and M^++2 bagi etena dan karbon monoksida masing-masing.

(4 markah)

...21/-

(d) Terdapat beberapa kombinasi penganalis jisim secara komersial. Penganalisis yang paling lazim ialah penganalisis kuadrupol peringkat tripel. Huraikan prinsip teknik tersebut dan jelaskan keupayaan utamanya.

(6 markah)

oooOOooo