UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2007/2008

KAA 503 – Molecular Spectroscopy
[Spektroskopi Molekul]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

Answer **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

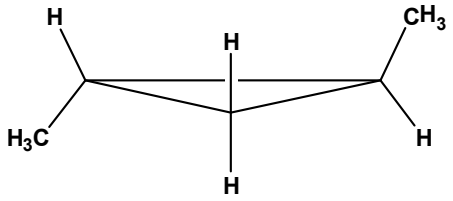
Answer each question on a new page.

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

In the event of any discrepancies, the English version shall be used.

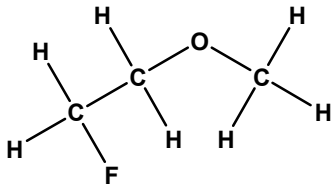
…2/-

1. (a) Predict the multiplicity of each ^{1}H signal for *trans*-1,2-dimethylcyclopropane



(5 marks)

(b) Draw ^{1}H multiplets for the following molecule, using the following typical values of coupling constants: $^{3}J_{HH}$ = 7 Hz; $^{2}J_{HF}$ = 60 Hz; $^{3}J_{HF}$ = 20 Hz. Indicate the sizes of the coupling constants in the multiplets and also give the relative intensities of individual spectral lines.



(5 marks)

(c) Explain why a ^{13}C NMR of $CDCl_3$ shows three resonances of equal intensity at about 77 ppm.

(5 marks)

(d) Given the following magnetogyric ratios (γ, 10^6 rad T^{-1} s^{-1}): ^{1}H, 267.512; ^{13}C, 67.264; ^{15}N, -27.107. Calculate the maximum possible NOE, η, in ^{13}C-{^{1}H}, and ^{15}N-{^{1}H} spectra.

(5 marks)

2. (a) What is the energy difference between the two spin states of ^{31}P ($\gamma_P = 108.29 \times 10^6$ rad T^{-1} s^{-1}) in magnetic field of

(i) 5.78 Tesla (400 MHz instrument) and

(ii) 17.4 Tesla (800 MHz instrument)?

(4 marks)

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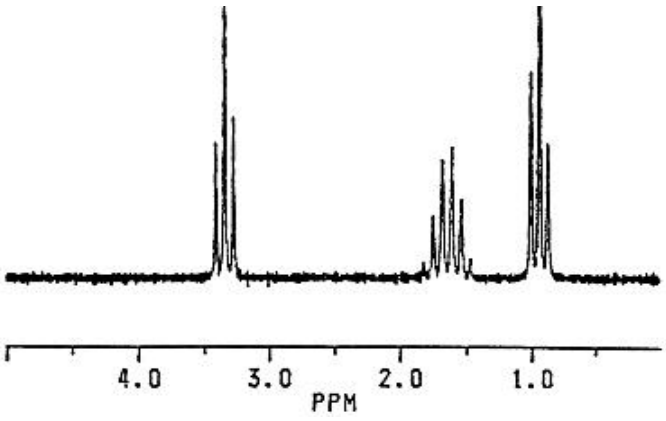
(b) Besides gain in spectral resolution, state and explain one more fundamental advantage that can be obtained by acquiring a ^{1}H NMR spectrum using an instrument working at 800 MHz as compared to that working at 400 MHz.

(4 marks)

(c) The ^{1}H NMR spectrum of dipropylether, $(CH_3CH_2CH_2)_2O$, is given below. The spectrum consists of 3 distinct resonances at δ 3.4 (triplet, 2H), δ 1.6 (multiplet, 2H) and δ 1.0 (triplet, 3H). Assign the spectrum and clearly describe the spectra that would be obtained while applying a *strong* Rf field at δ = 1.6 ppm.



(6 marks)

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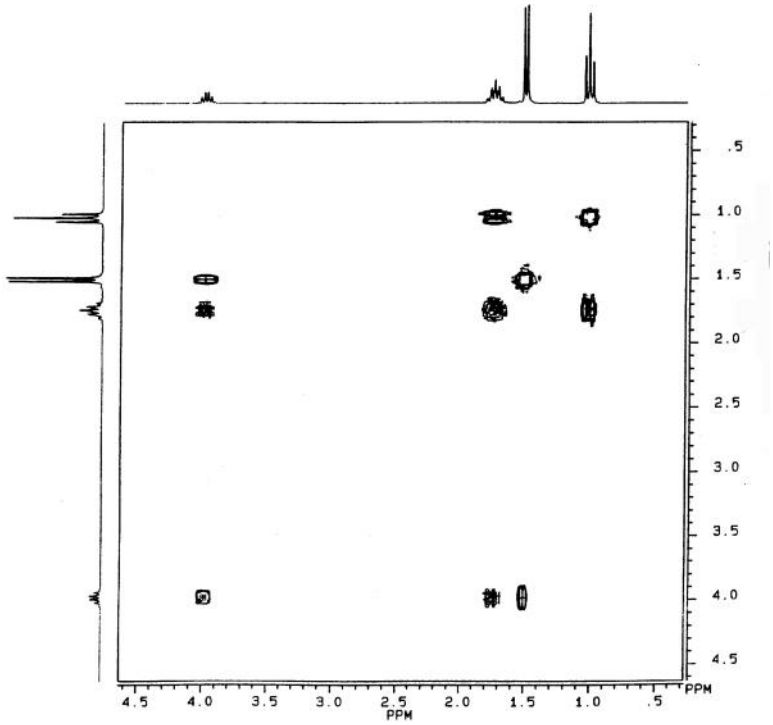
(d) Explain how the structure of the compound, C_4H_9Cl, can be deduced using the ^1H-^1H COSY spectrum shown below.



The 2D hydrogen COSY spectrum of C_4H_9Cl

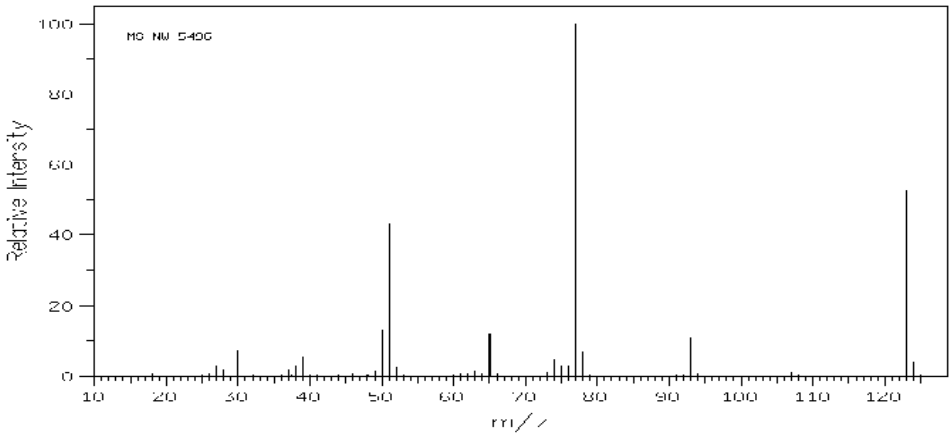
(6 marks)

3. (a) Fast atom bombardment (FAB) is one type of ionization techniques that is used in mass spectrometry. Describe the technique. List three other sample ionization techniques used for mass spectroscopy.

(6 marks)

…5/-

(b) The exact mass of a compound determined by high-resolution mass spectrometry is 123.10944. With the help of the spectrum below, find the molecular formula of the compound.



(4 marks)

(c) With the aid of a schematic diagram, describe the principles of a mass spectrometer. Explain how structural information could be obtained from a mass spectrum.

(6 marks)

(d) Show how mass spectrometry can be used to differentiate between the two isomers in each of the following sets.

(i) $(CH_3)_2CHCONH_2$ and $CH_3CH_2CONHCH_3$

(ii) CH_3CH_2OH and CH_3OCH_3

(iii) $CH_3CH_2CH_2CH_3$ and $(CH_3)_2CHCH_3$

(iv) $CH_2=CBrCH_2CH_3$ and $CH_3CBr=CHCH_3$

(4 marks)

4. (a) What are the advantages of linking;

(i) Gas chromatography-Mass spectroscopy (GCMA)

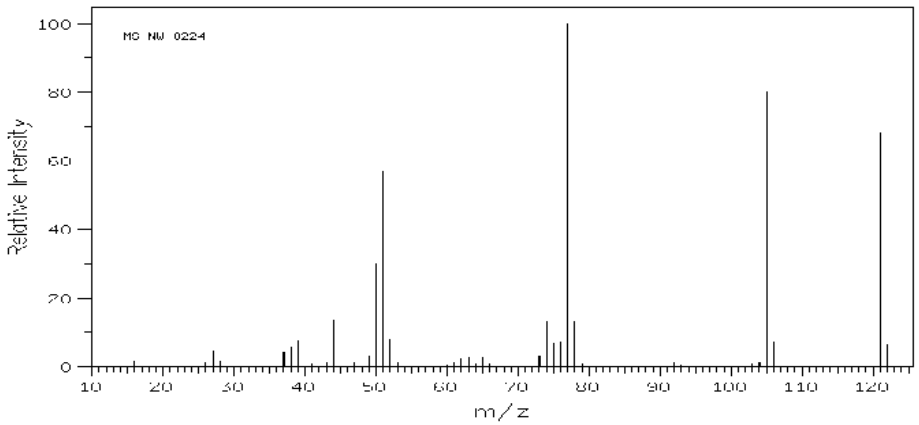
(ii) Liquid chromatography-Mass spectroscopy (LCMS)

(ii) Inductively coupled plasma-Mass spectroscopy (ICPMS)

(6 marks)

…6/-

(b) An unknown compound obtained by the reaction of NH_3 with chloride of benzene gives the element ratio of C (69.4 %) and H (50.8 %). With the help of the mass spectrum below, suggest the structure of the major fragments at m/z 51, 77 and 105, and find the structural formula of this compound.



(8 marks)

(c) Two isomeric compounds, A and B, have the molecular formula C_3H_9N. The important peaks in their mass spectra are tabulated below. Provide the structural formula for A and B.

Compound A		Compound B	
Mass Peak	**Relative Abundance**	**Mass Peak**	**Relative Abundance**
59	100	59	100
58	10	58	5
44	23	44	40
43	30	30	30
16	38	29	30
15	20	15	30

(6 marks)

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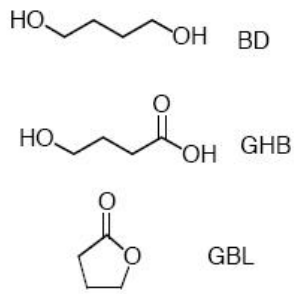
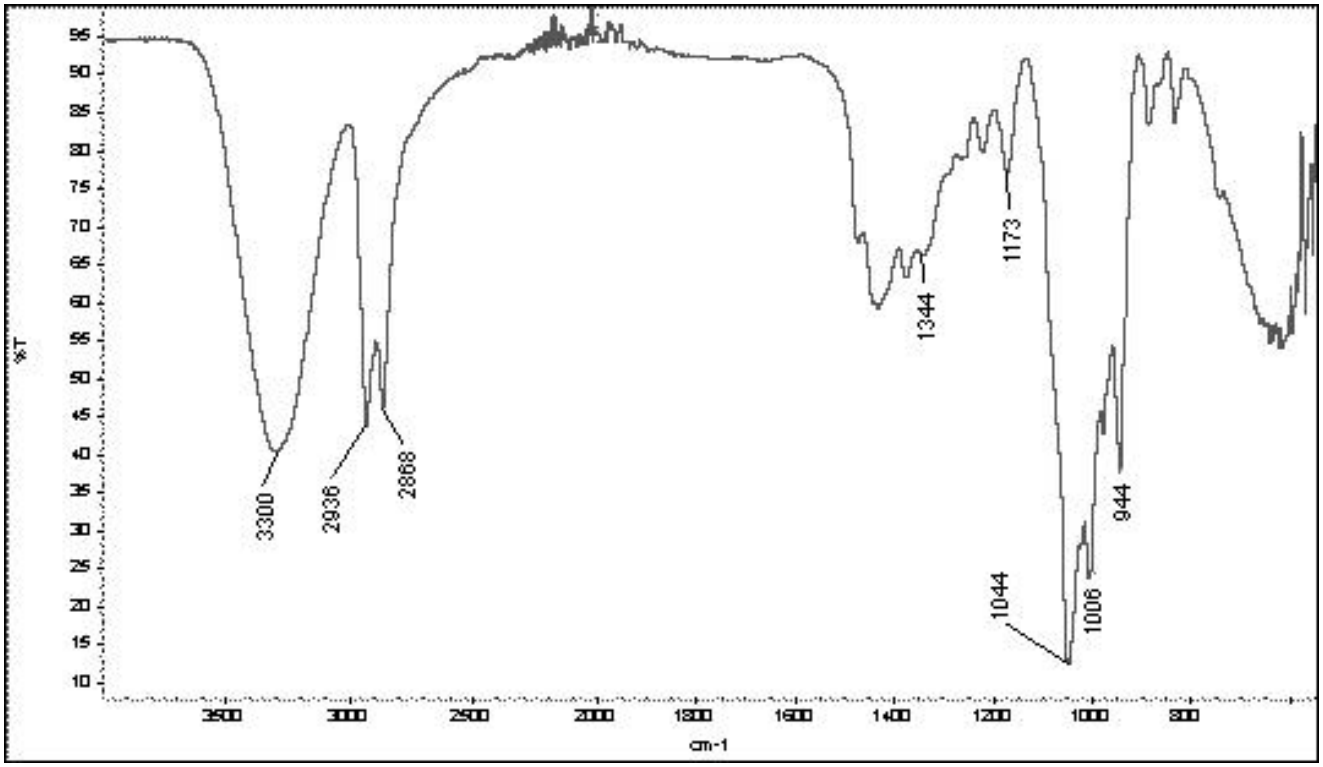
6. A chemical sample suspected to be either 1,4-butanediol (BD), γ-hydroxybutyric acid (GBH) or lactone (GBL) is subjected to ATR FTIR scan, the spectrum of which is shown below





(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)

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(b) The FTIR region from about 1000 to 400 cm^{-1} is called the fingerprint region. Explain why it is usually ignored in routine IR analysis.

(5 marks)

(c) What is the effect of conjugation on the energy of an infrared absorption band? Illustrate your answer with reference to α,β-unsaturated ketones.

(5 marks)

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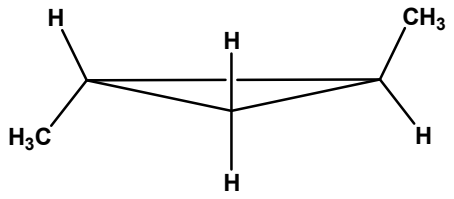
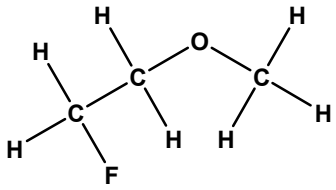
1. (a) Ramalkan kemultipelan bagi setiap isyarat ^{1}H pada *trans*-1,2-dimetilsiklopropana



(5 markah)

(b) Lukiskan multiplet ^{1}H bagi molekul berikut dengan menggunakan nilai-nilai pemalar pengkupelan tertentu: $^{3}J_{HH}$ = 7 Hz; $^{2}J_{HF}$ = 60 Hz; $^{3}J_{HF}$ = 20 Hz. Tunjukkan saiz pemalar pengkupelan pada kesemua multiplet dan berikan juga intensiti relatif bagi setiap isyarat spektrum.



(5markah)

(c) Jelaskan kenapa NMR ^{13}C $CDCl_3$ menunjukkan tiga resonans dengan keamatan yang sama pada linkungan 77 ppm.

(5 markah)

(d) Diberikan nisbah magnektogirik (γ, 10^6 rad T^{-1} s^{-1}) berikut: ^{1}H, 267.52; ^{13}C, 67.28; ^{15}N, -27.107. Kirakan nilai maksimum NOE , η, yang mungkin bagi spektrum ^{13}C-{^{1}H} dan spektrum ^{15}N-{^{1}H}.

(5 markah)

2. (a) Apakah nilai perbezaan tenaga di antara dua paras putaran ^{31}P (γ_P = 108.29 $\times$ 10^6 rad T^{-1} s^{-1}) dalam medan magnet

(iii) 5.78 Tesla (instrumen 400MHz) dan

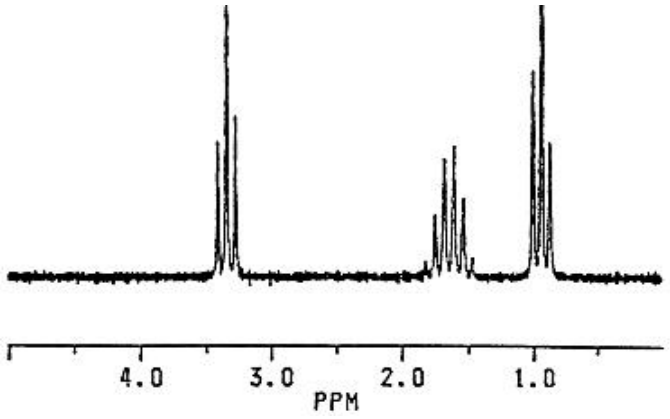
(iv) 17.4 Tesla (instrumen 800MHz)?

(4 markah)

(b) Selain dari peningkatan resolusi spektrum, nyata dan terangkan satu lagi kelebihan asas yang dapat diperolehi dengan merakamkan spektrum ^{1}H NMR dengan menggunakan instrumen yang beroperasi pada 800 MHz berbanding dengan instrumen yang beroperasi pada 400 MHz.

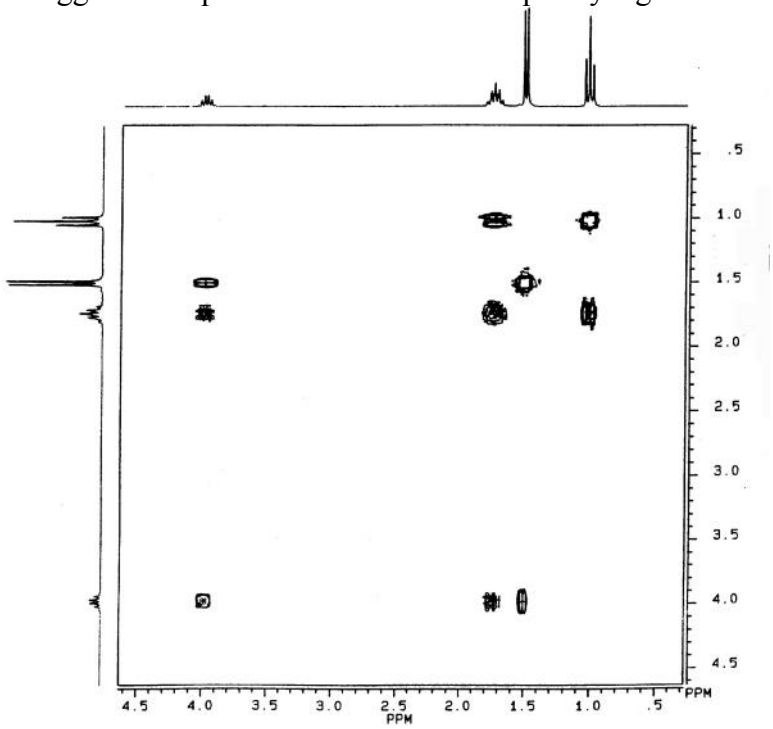
(4 markah)

(c) Spektrum ^{1}H NMR bagi dipropileter, $(CH_3CH_2CH_2)_2O$, diberikan di bawah. Spektrum tersebut mengandungi 3 kumpulan resonans yang berbeza: δ 3.4 (triplet, 2H), δ 1.6 (multiplet, 2H) dan δ 1.0 (triplet, 3H). Peruntukan spektrum tersebut dan jelaskan apa yang akan diperolehi bila menggenakan medan Rf yang kuat pada δ = 1.6 ppm.



(6 markah)

(d) Jelaskan bagaimana struktur sebatian, C_4H_9Cl, dapat ditentukan dengan menggunakan spektrum ^1H-^1H COSY seperti yang diberikan di bawah.



Spektrum 2D COSY hidrogen C_4H_9Cl

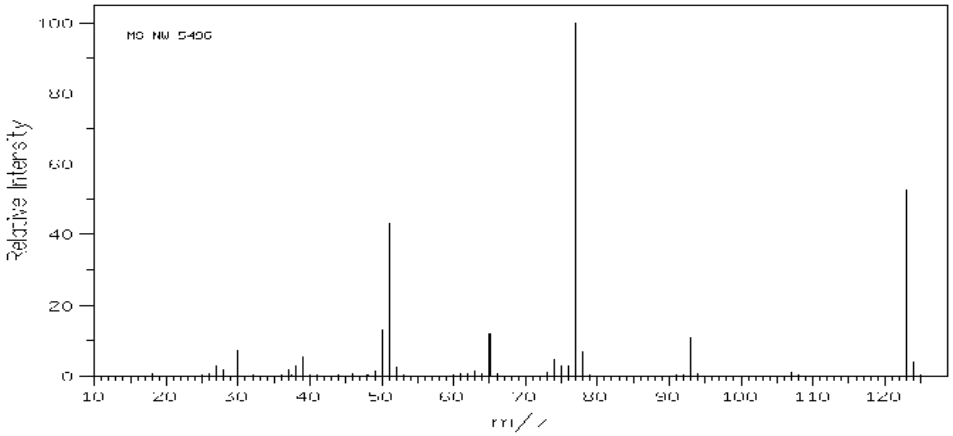
(6 markah)

3. (a) "Fast atom bombardment" (FAB) adalah satu jenis teknik pengionan yang digunakan di dalam spekrometri jisim. Berikan teknik ini. Senaraikan tiga teknik pengionan sampel lain yang digunakan untuk spektrometri jisim.

(6 markah)

...14/-

(b) Jisim tetap suatu sebatian yang ditentukan melalui spektrometri jisim beresolusi tinggi adalh 123.10944. Dengan bantuan spektrum di bawah, tentukan formula melekul sebatian ini.



(4 markah)

(c) Dengan menggunakan suatu gambarajah skema, berikan prinsip suatu spektrometer jisim. Terangkan bagaimana maklumat tentang struktur boleh didapati dari suatu spektrum jisim.

(6 markah)

(d) Tunjukkan bagaimana spektrometri jisim boleh digunakan untuk membeza jelaskan di antara dua isomer di dalam setiap set berikut.

(i) $(CH_3)_2CHCONH_2$ dan $CH_3CH_2CONHCH_3$

(ii) CH_3CH_2OH dan CH_3OCH_3

(iii) $CH_3CH_2CH_2CH_3$ dan $(CH_3)_2CHCH_3$

(iv) $CH_2=CBrCH_2CH_3$ dan $CH_3CBr=CHCH_3$

(4 markah)

4. (a) Apakah kelebihan rangkaian di dalam;

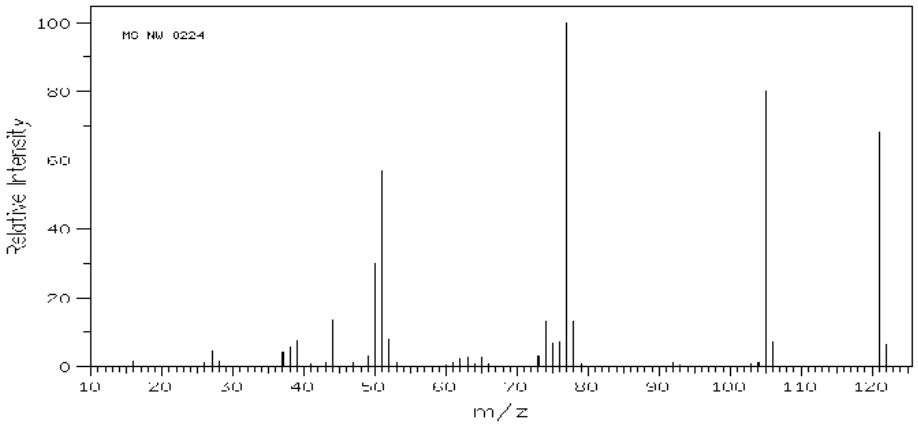
(i) Kromatografi gas-spektrometri jisim (GCMS)

(ii) Kromatografi cecair-spektrometri jisim (LCMS)

(iii) Plasma gandingan teraruh-spektrometri jisim (ICPMS)

(6 markah)

(b) Suatu sebatian anu yang diperolehi melalui NH_3 terhadap klorida benzene memberikan nisbah unsur bagi C (69.4 %) dan H (5.8 %). Dengan bantuan spektrum jisim di bawah, cadangkan struktur pecahan utama pada m/z 51, 77 dan 105, dan tentukan formula struktur sebatian ini.



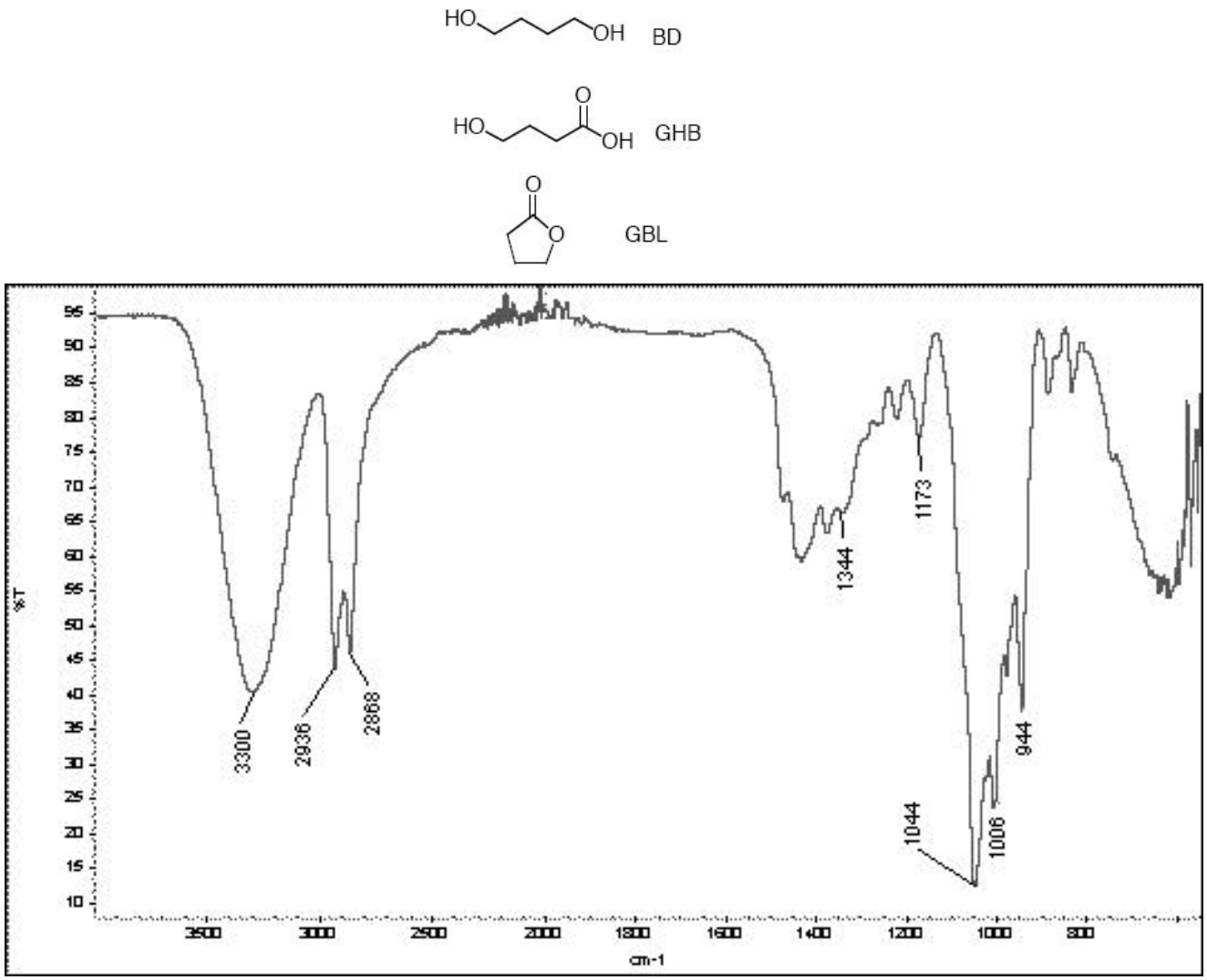
(8 markah)

(c) Dua sebatian isomer A dan B mempunyai formula melekul C_3H_9N. Puncak-puncak yang penting di dalam spektrum jisim mereka adalah seperti di dalam jadual di bawah. Dapatkan formula struktur bagi A dan B.

Sebatian A		**Sepatian B**	
Puncak Jisim	**Kelimpahan Relatif**	**Puncak Jisim**	**Kelimpahan Relatif**
59	100	59	100
58	10	58	5
44	23	44	40
43	30	30	30
16	38	29	30
15	20	15	30

(6 Markah)

6. Suatu sampel bahan kimia yang disyaki sebagai 1,4-butanadiol (BD), asid γ-hidroksibutirik (GBH) atau lakton (GBL) telah dijalankan imbasan ATR FTIR, dan spektrum yang diperolehi ditunjukkan di bawah.



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

(10 markah)

(b) Kawasan FTIR dari 1000 to 400 cm^{-1} digelar kawasan kesan jari . Jelaskan mengapa kawasan ini biasanya diabaikan dalam analisis IR secara lazim.

(5 markah)

(d) Apakah kesan konjugatan terhadap tenaga bagi sesuatu jalur penyerapan inframerah? Gambarkan jawapan anda dengan merujuk pada sebatian keton tak tepu-α,β.

(5 markah)

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