UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2009/10

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/-

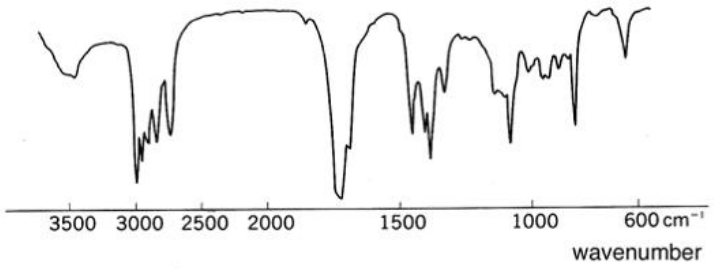
1. (a) Draw and name the six principal modes of vibration between carbon and hydrogen in methane.

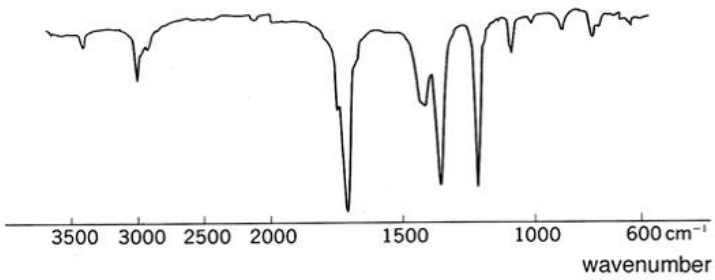
(6 marks)

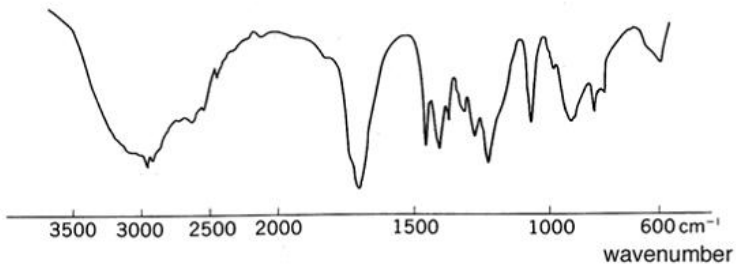
(b) In discussing quantitative analysis using the mid-IR region, it is suggested that either the O–H stretching band or the C–O stretching band could be used to measure hexanol in a mixture of hexanol and hexane. Which band would you choose to give more accurate results, and why?

(6 marks)

(c) The unidentified FTIR spectra of three different liquids, namely acetone, propanoic acid and propanal are shown below. Identify the FTIR spectrum of each of the compounds above and assign the major bands in the spectrum.







(8 marks)

…3/-

2. (a) Draw the schematic diagram of a double beam UV-vis spectrophotometer and describe the principles of its operation.

(6 marks)

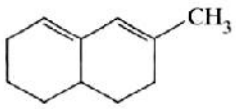
(b) Simple benzene compounds show medium intensity multiplets around 254 nm for non-conjugated derivatives, which shift to longer wavelengths when substituents are conjugated to the aromatic system. Predict the wavelengths for the following compounds, giving reasons for your answer:

(i) Benzoic acid

(ii) Naphthalene

(6 marks)

(c) A diene, $C_{11}H_{16}$ was thought to have the following structure:



Its UV-vis spectrum showed λ_{max} = 263 nm, with A_{max} = 0.85

(i) Indicate whether the above structure is correct by calculating λ_{max} using the Woodward Feiser rules.

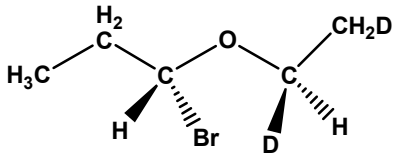
(ii) Using the same carbocyclic skeleton, draw a structure that satisfies the spectrum.

(iii) If the recorded spectrum was determined in a 1 cm cell with 3 mg of compound in 250 mL of ethanol, determine ε_{max}.

(iv) From your knowledge of electronic transition, is the value of ε_{max} reasonable? Explain.

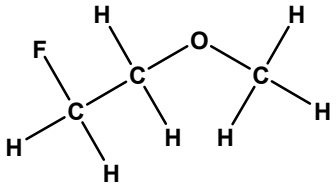
(8 marks)

3. (a) Predict the multiplicity and indicate the relative intensity of each ^{1}H signal for the following molecule:



(5 marks)

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



(5 marks)

(c) Why a ^{13}C NMR of $CDCl_3$ shows a triplet of equal intensity at about 77 ppm?

(5 marks)

(d) Calculate the maximum NOE, **η**, for proton-decoupled ^{13}C and ^{19}F NMR spectra using the following information: the magnetogyric ratio,**γ**, for ^{1}H, ^{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.

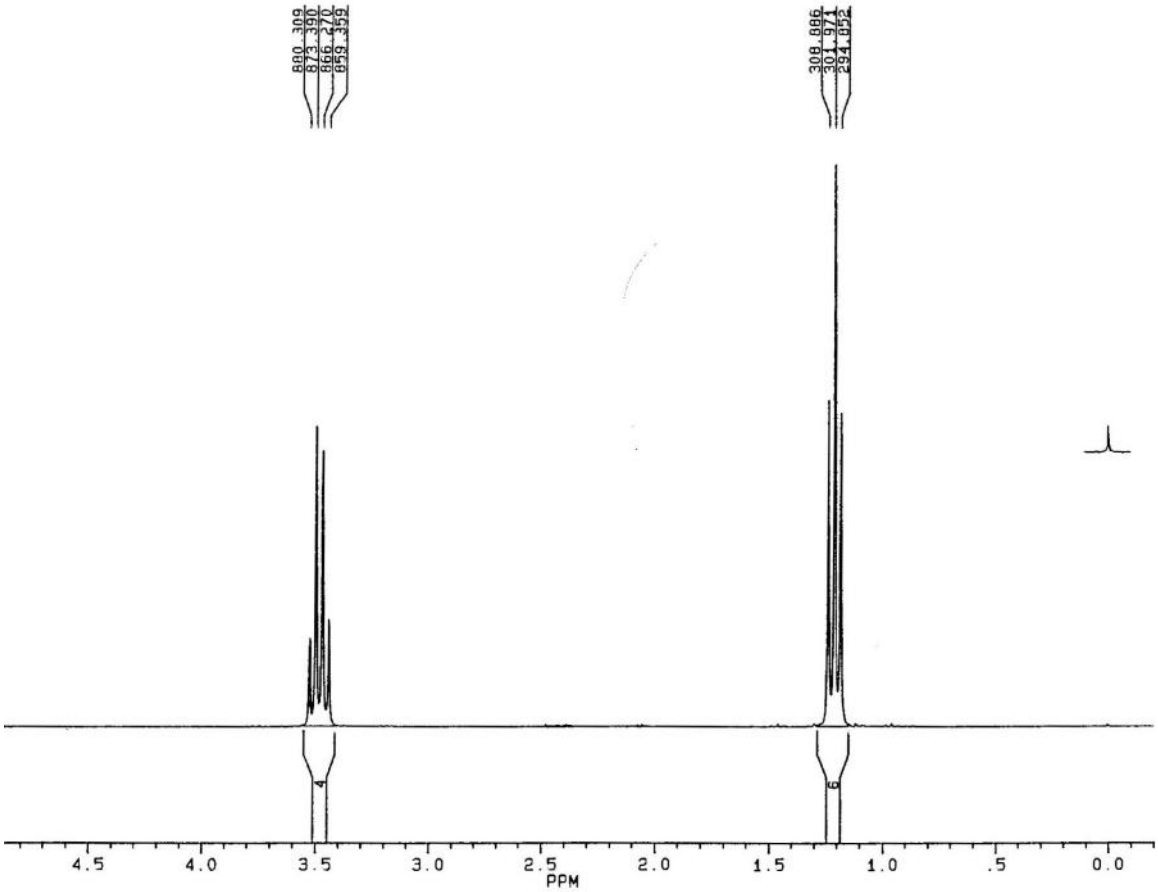
(5 marks)

…5/-

4. (a) One of the isomers of chloronitropropane, $C_3H_6ClNO_2$, has a proton NMR spectrum consisting of a triplet at δ 5.8, an approximate quintet at δ 2.3 and a triplet at δ 1.1. What isomer is this?

(6 marks)

(b) Describe the NMR spectrum of diethyl ether depicted below in the form of condensed format.



The 250-MHz ^1H spectrum of diethyl ether.

(6 marks)

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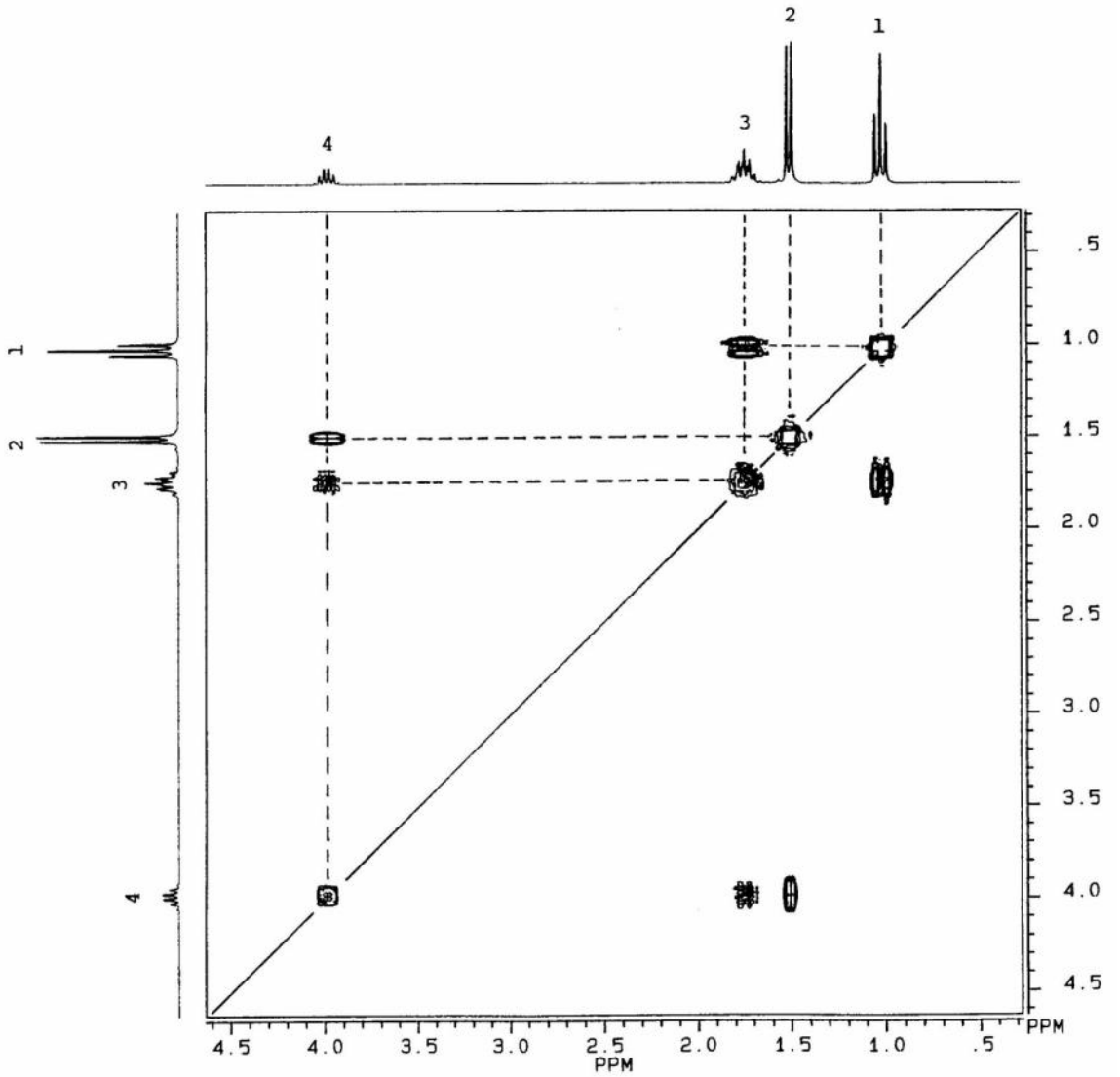
(c) Deduce the structure of C_4H_9Cl using its ^1H-^1H COSY spectrum shown below.



^1H-^1H COSY spectrum of C_4H_9Cl

(8 marks)

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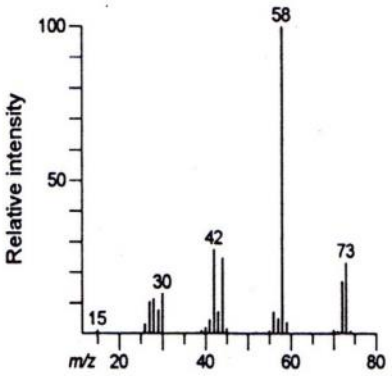
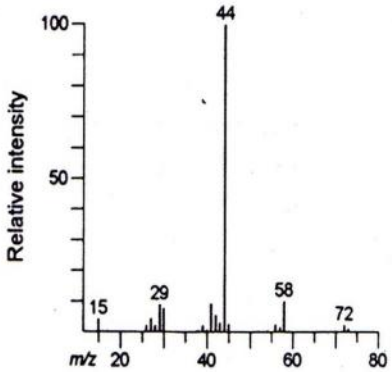
5. (a) The following are the spectra of four possible amine isomers. Assign the structure for each spectrum.

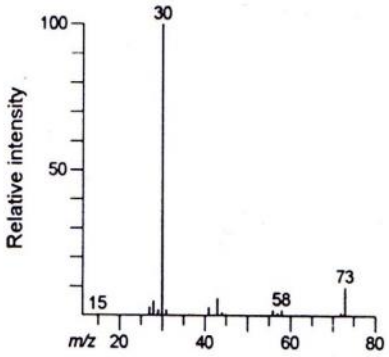
(i)



(ii)



(iii)



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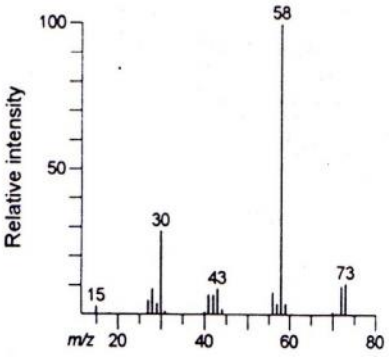
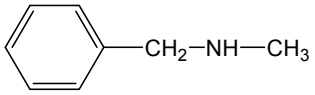


(8 marks)

(b) List and explain with the aid of a schematic diagram the main components of a mass spectrometer.

(4 marks)

(c) What are the products of the collision between a high-energy electron and the following molecules?

(i) $CH_3CH_2—O—CH_3$ (ii) 

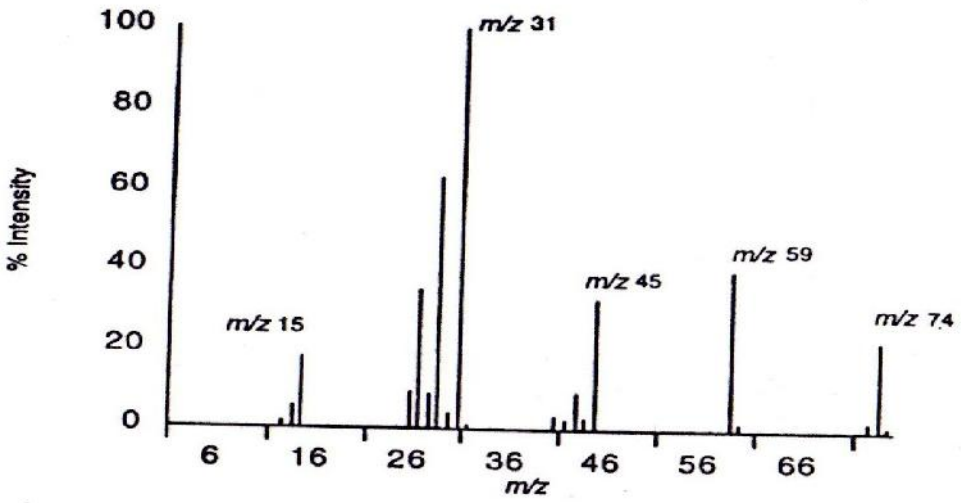
(4 marks)

…8/-

(d) Describe how you distinguish between 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane by mass spectrometry while observing the relative abundance of the peak at m/z = 86.18. Explain using fragmentations of each.

(4 marks)

6. (a) The exact mass of a compound determined by high-resolution mass spectrometry is 74.12160. With the help of the spectrum and table below, find the molecular formula of the compound.



m/z	% Intensity	m/z	% Intensity	m/z	% Intensity	m/z	% Intensity
2	0.6	27	34.6	41	3.2	58	0.3
12	0.5	28	8.5	42	2.1	59	39.6
13	1.4	29	62.8	43	9.0	60	1.4
14	5.5	30	3.6	44	2.6	72	0.3
15	17.4	31	100	45	32.6	73	2.1
16	0.8	32	1.2	46	0.8	74	22.5
25	0.7	39	0.3	47	0.2	75	1.1
26	8.8	40	0.2	57	0.4		

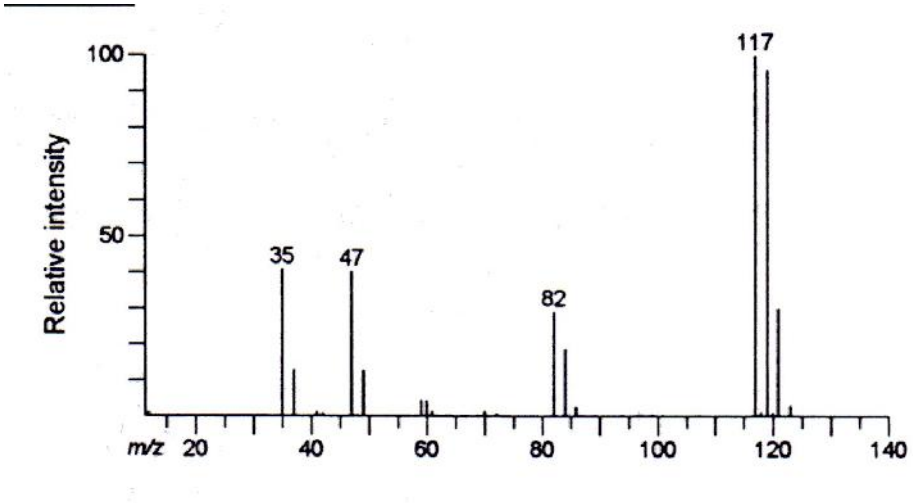
(6 marks)

(b) List five methods of ionization techniques used in mass spectrometry and explain why chemicals of interest have to be ionized for mass spectrometry.

(6 marks)

…9/-

(c) An unknown compound was subjected to ^{1}H NMR, ^{13}C NMR and mass spectrometry to determine its molecular structure. Both NMR results showed singlet peaks at 7.26 and 77.0 for ^{1}H NMR and ^{13}C NMR, respectively. Using the mass spectroscopy spectrum below, identify the unknown compound and label the fragmentations.



(4 marks)

(d) Calculate the m/z and relative abundance (intensity) for the M^{+} and $M^{+}+1$ peaks for the following molecules. Assume the molecular ion to be the base peak in each case.

(i) C_6H_7NO

(ii) $C_{11}H_7Cl$

(4 marks)

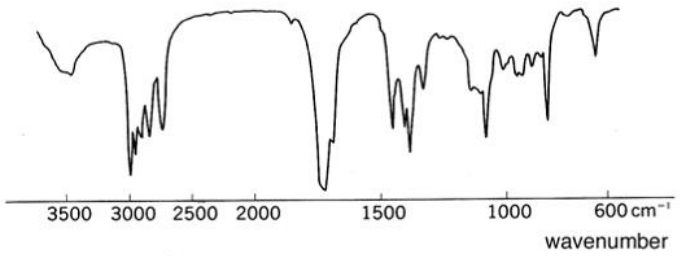
1. (a) Lukiskan dan namakan keenam mod prinsipal bagi getaran antara karbon dan hidrogen dalam metana.

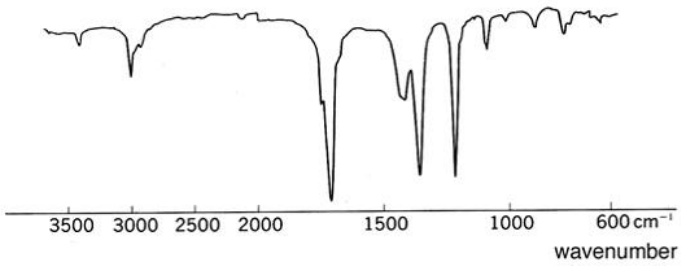
(6 markah)

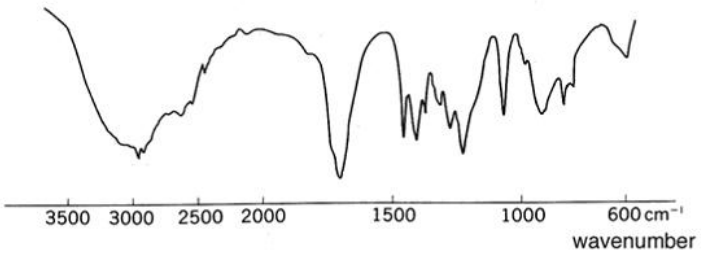
(b) Dalam perbincangan analisis kuantitatif dengan menggunakan kawasan tengah-inframerah, adalah dicadangkan bahawa jalur regangan O–H atau jalur regangan C–O boleh digunakan untuk menyukat heksanol di dalam campuran heksanol dan heksana. Jalur yang mana menjadi pilihan anda untuk memberi keputusan yang lebih jitu, dan mengapa?

(6 markah)

(c) Spektrum FTIR yang tidak dikenalpasti bagi tiga cecair berbeza, iaitu aseton, asid propanoik dan propanal ditunjukkan di bawah. Kenalpastikan spektrum FTIR bagi setiap dari sebatian tersebut dan peruntukkan jalur utama di dalam setiap spektrumnya







(8 markah)

…12/-

2. (a) Lukiskan gambarajah skema bagi spektrofotometer bim dubel UV-vis dan huraikan prinsip operasinya.

(6 markah)

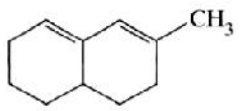
(b) Sebatian benzena ringkas menunjukkan multiplet keamatan sederhana pada 254 nm bagi terbitan tak-berkonjugat, yang menganjak ke panjang gelombang lebih panjang bila penukargantinya terkonjugat kepada sistem aromatik. Ramalkan panjang gelombang bagi sebatian berikut, dengan memberi alasan bagi jawapan anda:

(i) Asid benzoik

(ii) Naftalena

(6 markah)

(c) Suatu diena, $C_{11}H_{16}$ dianggap mempunyai struktur berikut:



Spektrum UV-visnya menunjukkan λ_{max} = 263 nm, dengan A_{max} = 0.85

(i) Nyatakan sama ada struktur di atas adalah betul dengan mengira λ_{max} menggunakan peraturan Woodward-Feiser.

(ii) Dengan menggunakan rangka karbosiklik yang sama, lukiskan suatu struktur yang memenuhi spektrum tersebut.

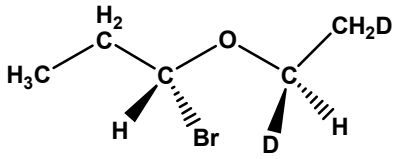
(iii) Jika spektrum yang dirakam itu diperolehi dalam sel 1 cm dengan 3 mg sebatian di dalam 250 mL etanol, tentukan ε_{max}.

(iv) Daripada pengetahuan anda mengenai peralihan elektron, adakah nilai ε_{max} berpatutan? Jelaskan.

(8 markah)

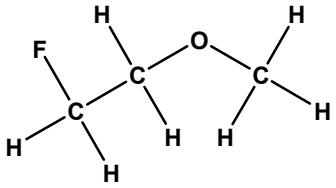
…13/-

3. (a) Ramalkan kemultipelan dan tunjukkan intensiti relatif bagi setiap isyarat ^{1}H pada molekul berikut:



(5 markah)

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



(5 markah)

(c) Kenapakah ^{13}C NMR dalam $CDCl_3$ menunjukkan triplet dengan intensiti yang sama pada 77 ppm?

(5 markah)

(d) Kirakan nilai NOE, **η**, yang maksima bagi spektrum ternyahganding 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}.

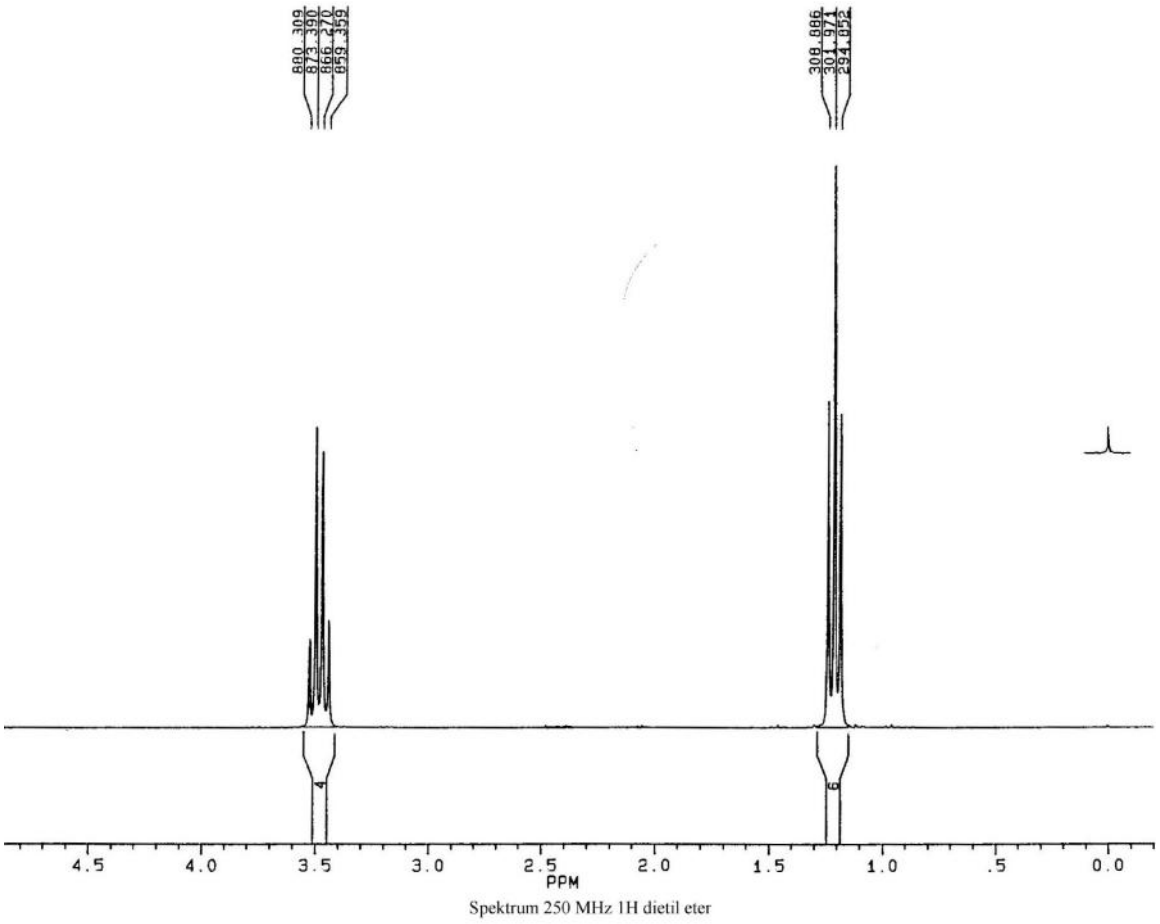
(5 markah)

…14/-

4. (a) Satu daripada isomer kloronitropropana, $C_3H_6ClNO_2$, mempunyai spektrum ^1H NMR yang mengandungi satu triplet pada δ 5.8, satu quintet pada lingkungan δ 2.3 dan satu lagi triplet pada δ 1.1. Apakah isomer ini?

(6 markah)

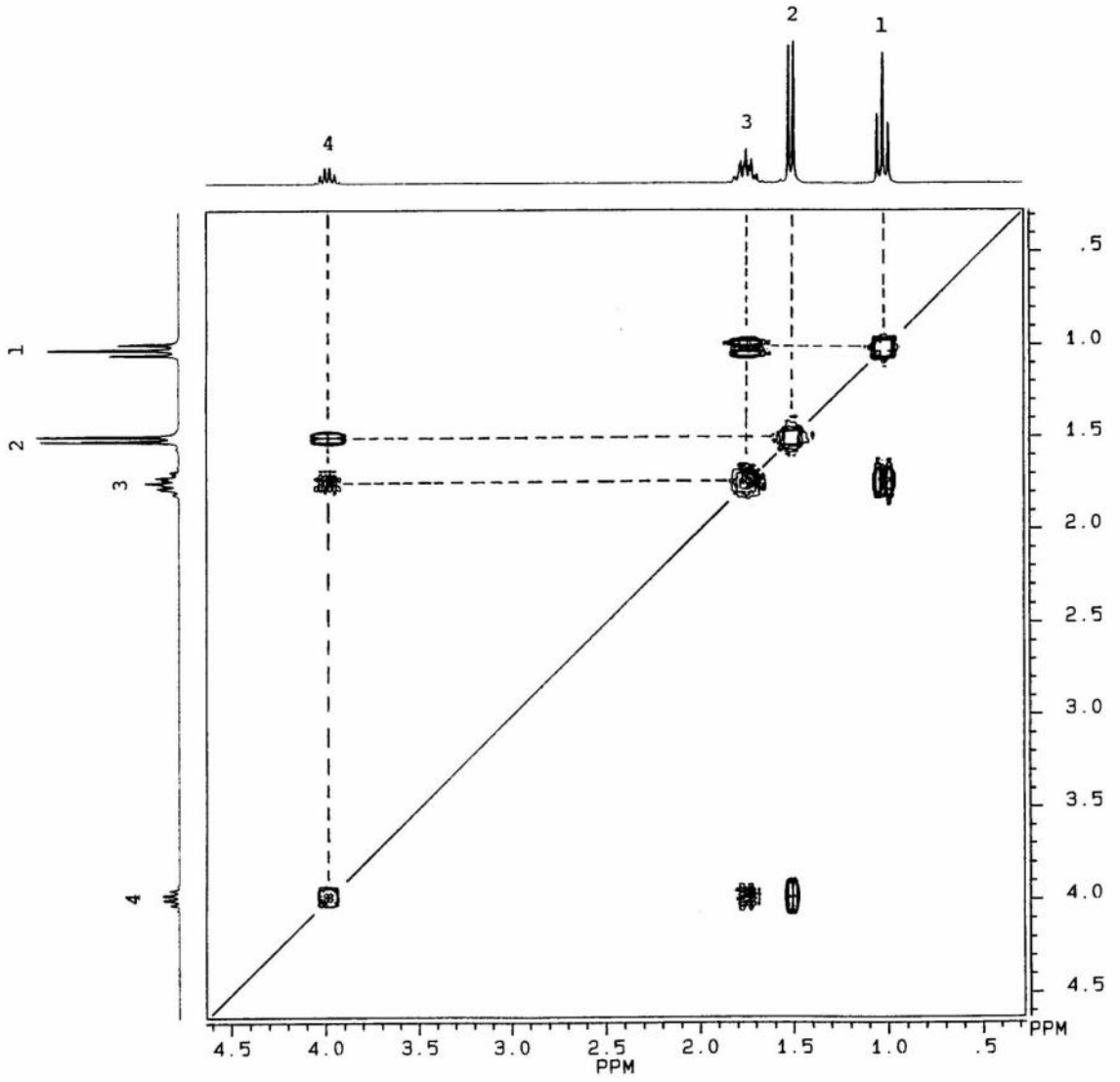
(b) Perikan spektrum NMR dietil eter yang dikemukakan di bawah dalam bentuk format jitu.



Spektrum 250 MHz 1H dietil eter

(6 markah)

(c) Jelaskan struktur C_4H_9Cl dengan menggunakan spektrum ^1H-^1H COSYnya seperti yang diberikan di bawah.



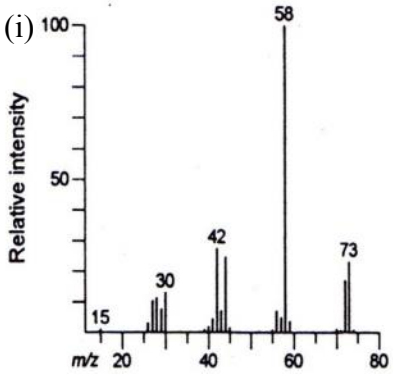
Spektrum ^1H-^1H COSY C_4H_9Cl

(8 markah)

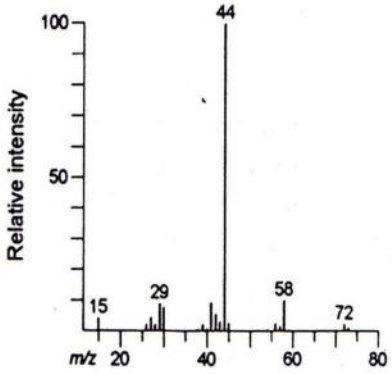
…16/-

5. (a) Berikut adalah spektrum bagi empat isomer amina yang mungkin. Tentukan struktur bagi setiap spektrum tersebut.

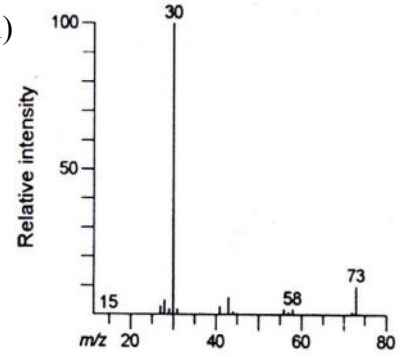
(i)



(ii)



(iii)



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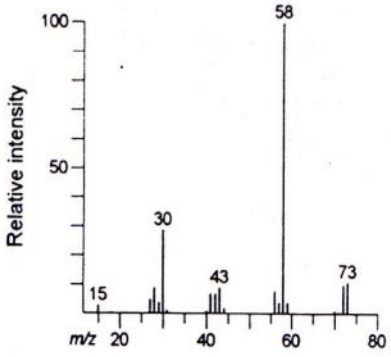


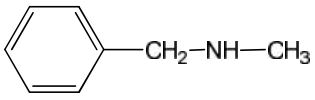
(8 markah)

(b) Senaraikan dan jelaskan dengan bantuan suatu gambarajah skema komponen utama suatu spektrometer jisim.

(4 markah)

(c) Apakah hasil bagi pelanggaran di antara suatu elektron tenaga tinggi dan molekul berikut?

(i) $CH_3CH_2—O—CH_3$ (ii)



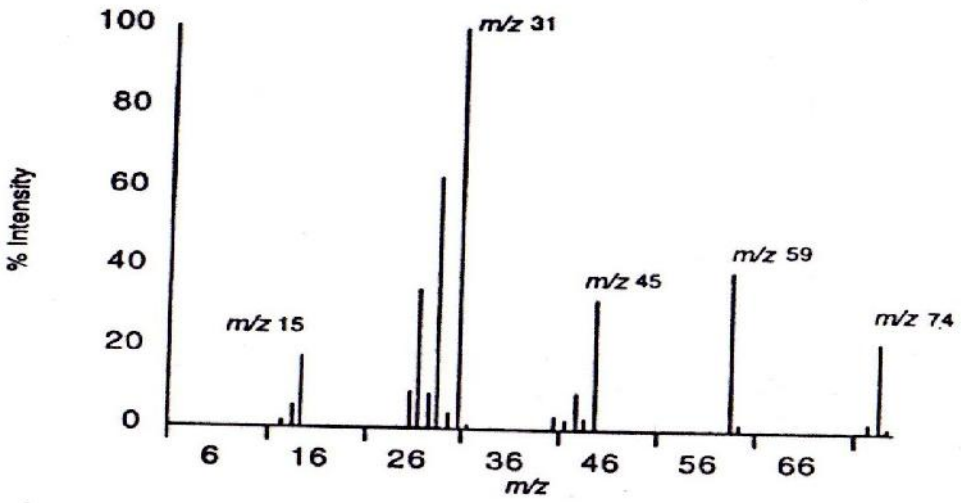
(4 markah)

…17/-

(d) Huraikan bagaimana anda membezakan di antara 2-metilpentana, 3-metilpentana dan 2,3-dimetilbutana melalui spectrometri jisim apabila memerhatikan kelimpahan relatif puncak pada m/z = 86.18. Jelaskan dengan menggunakan penyerpihan setiap satu.

(4 markah)

6. (a) Jisim tepat bagi suatu sebatian ditentukan oleh spektrometri jisim leraian tinggi adalah 74.12160. Dengan bantuan spektrum dan jadual di bawah, tentukan formula molekul bagi sebatian tersebut.



m/z	% Keamatan	m/z	% Keamatan	m/z	% Keamatan	m/z	% Keamatan
2	0.6	27	34.6	41	3.2	58	0.3
12	0.5	28	8.5	42	2.1	59	39.6
13	1.4	29	62.8	43	9.0	60	1.4
14	5.5	30	3.6	44	2.6	72	0.3
15	17.4	31	100	45	32.6	73	2.1
16	0.8	32	1.2	46	0.8	74	22.5
25	0.7	39	0.3	47	0.2	75	1.1
26	8.8	40	0.2	57	0.4		

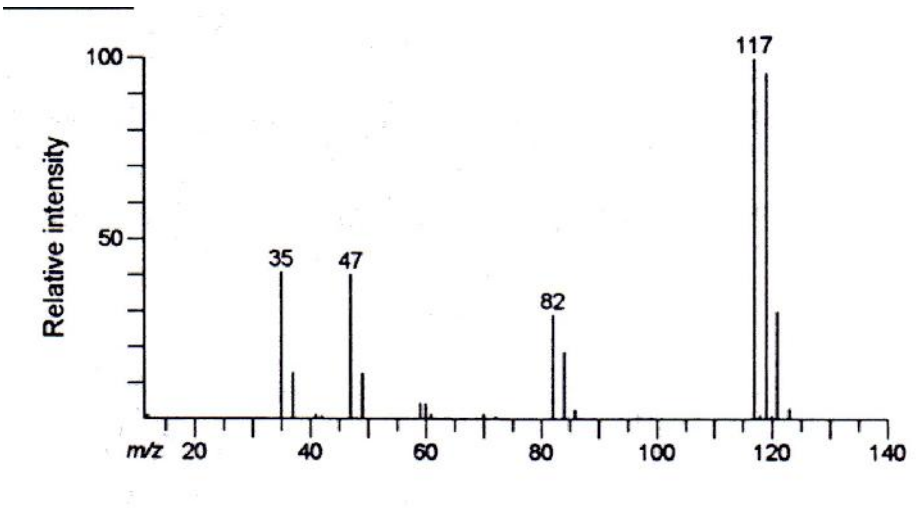
(6 markah)

(b) Senaraikan lima kaedah teknik pengionan yang digunakan dalam spektrometri jisim dan jelaskan mengapa bahan kimia kepentingan perlu diionkan untuk spektrometri jisim.

(6 markah)

…18/-

(c) Suatu sebatian yang tidak diketahui dijalankan spektrometri ^{1}H NMR, ^{13}C NMR dan jisim untuk menentukan struktur molekulnya. Kedu-dua keputusan NMR menunjukkan puncak singlet pada 7.26 dan 77.0 untuk ^{1}H NMR dan ^{13}C NMR, masing-masing. Dengan menggunakan spektrum spektrometri jisim di bawah, kenalpastikan sebatian yang tidak diketahui itu dan labelkan penyerpihannya.



(4 markah)

(d) Kiralah m/z dan kelimpahan relatif (keamatan) bagi puncak M^+ dan $M^+ +1$ bagi molekul berikut. Andaikan ion molekul sebagai puncak dasar dalam setiap kes.

(i) C_6H_7NO

(ii) $C_{11}H_7Cl$

(4 markah)

oooOOooo