UNIVERSITI SAINS MALAYSIA

First Semester Examination
2010/2011 Academic Session

November 2010

IWK 307 – ADVANCED PAPER TECHNOLOGY – INSTRUMENTAL ANALYSIS FOR PULP AND PAPER
[TEKNOLOGI KERTAS TERMAJU – ANALISA INSTRUMENTAL BAGI PULP DAN KERTAS]

Duration: 2 hours
Masa: [2 jam]

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

[Sila pastikan bahawa kertas peperiksaan ini mengandungi SEBELAS muka surat yang bercetak sebelum anda memulakan peperiksaan ini.]

Instructions: Answer FOUR questions. You may answer the questions either in Bahasa Malaysia or in English.

[Arahan: *Jawab EMPAT soalan. Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.]*

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

[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.]

1. Instrumental analysis is known for its sophistication, efficiency and reliability.

   (a) Elaborate on the difference between classical and instrumental techniques of analysis based on ONE example of classical technique and ONE example of instrumental technique of analysis.

   [10 marks]

   (b) Reliability lies in the high precision and accuracy, typical of instrumental techniques of analysis. Define precision and accuracy with the guide of a dart chart.

   [10 marks]

2. At a crime scene, a Forensic Analyst collected evidences that could help explain the cause of death of a victim. One of the items the analyst brought to his laboratory was a paper cup containing blood. Help the Forensic Analyst diagnose the cause of the death if the blood in the paper cup could provide the strongest clue by considering these circumstances:

   (a) Poisoning of organic substances.

   [10 marks]

   (b) Poisoning of inorganic substances.

   [10 marks]

3. Researchers at B-Gates synthesized an organic compound, T, to speed up dewatering and dispersion the short and translucent fibres for the making of tracing papers. From instrumental analysis of T, an FTIR spectrum in Figure 1 was obtained.

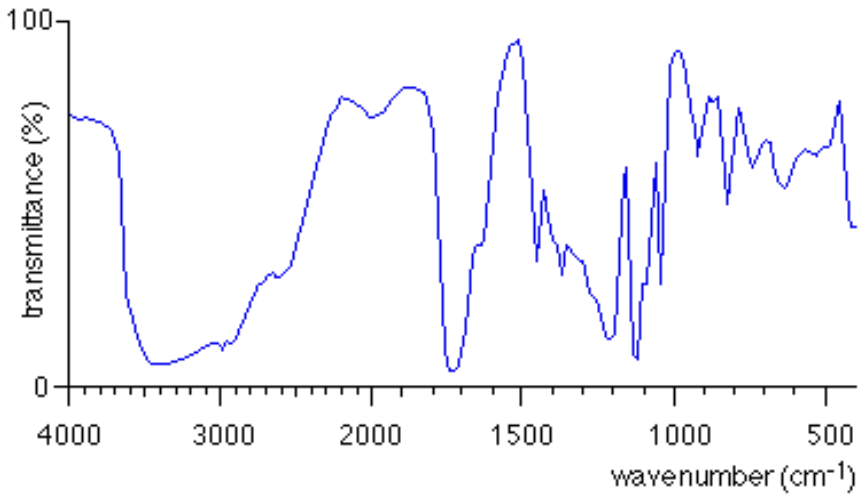

Figure 1: FTIR Spectrum of T.

(a) Assign the important functional groups to the corresponding troughs with the help of Appendix 1.

[5 marks]

(b) If T has a general chemical formula of CH_3-COH-COOH , sketch the likely ^{1}H-NMR of T with the help of Appendix 2.

[10 marks]

(c) Predict also 5 fragments likely to show up on the Mass Spectrum of T.

[5 marks]

4. The overlay of spectra in Fig. 2 show 2 sets of signals corresponding to complexing agent at about 350 nm and a complex at about 550-580 nm wavelength region, based on the reaction given by equation 1.

$$C+SI \rightarrow C\text{-}SI \ldots.(1)$$

Evidently, the complexing agent, C, is orange in colour while the complex, C-SI, is dark blue.

(a) Explain the shift and the decreasing intensity of signals in the **350 nm** wavelength region as SI concentrations decreased from 0.29% to 0.14% (Fig. 2).

[20 marks]

(b) A standard procedure recommended a fixed wavelength of 550 nm for reading of signal intensity. Put yourself as an expert and comment on the likely impact this would have on the accuracy of the results.

[20 marks]

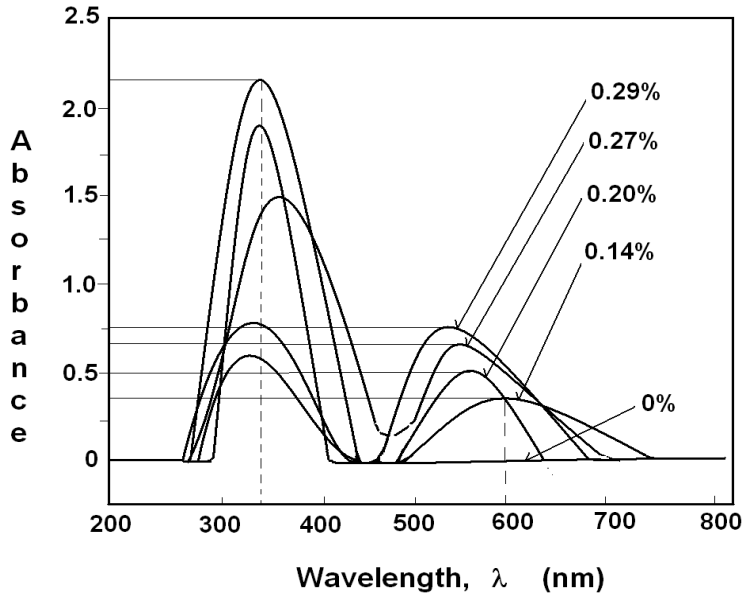

Fig. 2: UV-visible spectra overlay for SI calibration.

APPENDIX 1
Characteristic Frequency for FTIR

GROUP		FREQUENCY RANGE (cm^{-1})	INTENSITY[a]
A. Akly			
C-H (stretching)		2853 – 2962	(m-s)
Isopropyl, -$CH(CH_3)_3$		1380 – 1385	(s)
	and	1365 -1370	(s)
tert-Butyl,-$C(CH_3)_3$		1385 – 1395	(m)
	and	~1365	(s)
B. Alkenyl			
C-H (stretching)		3010 – 3095	(m)
C=C (stretching)		1620 – 1680	(v)
R-$CH=CH_2$		985 – 1000	(s)
	and	905 – 920	(s)
$R_2C=CH_2$	(out-of-plane C-H bendings)	880 – 900	(s)
c*is*-RCH=CHR		675 – 730	(s)
trans-RCH=CHR		960 – 975	(s)
C. Alkynyl			
≡C-H (stretching)		3300	(s)
C≡C (stretching)		2100 – 2260	
D. Aromatic			
Ar-H (stretching)		3030	(v)
Aromatic substitution type (C-H out-of-plane bendings)			
Monosubstituted		690 – 710	(very s)
	and	730 – 770	(very s)
o-Disubstituted		735 – 770	(s)
m-Disubstituted		680 – 725	(s)
	and	750 – 810	(very s)
p-Disubstituted		800 – 840	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
O-H (stretching)			
Alcohols, phenols (dilute solutions)		3590 – 3650	(shrap, v)
Alcohols, phenols (hydrogen bonded)		3200 – 3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500 – 3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O (stretching)		1630 – 1780	(s)
Aldehydes		1690 – 1740	(s)
Ketones		1680 – 1750	(s)
Esters		1735 – 1750	(s)
Carboxylic acids		1710 – 1780	(s)
Amides		1630 – 1690	(s)

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APPENDIX 2
Chemical Shift for Proton NMR

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8 – 1.0
2° Alkyl, RCH_2R	1.2 – 1.4
3° Alkyl, R_3CH	1.4 – 1.7
Allylic, $R_2C{=}C{-}CH_3$	1.6 – 1.9
Benzylic, $ArCH_3$	2.2 – 2.5
Alkyl chloride, RCH_2Cl	3.6 – 3.8
Alkyl bromide, RCH_2Br	3.4 – 3.6
Alkyl iodide, RCH_2I	3.1 – 3.3
Ether, $ROCH_2R$	3.3 – 3.9
Alcohol, $HOCH_2R$	3.3 – 4.0
Ketone, $RCCH_3$	2.1 – 2.6
Aldehyde, RCH	9.5 – 9.6
Vinylic, $R_2C{=}CH_2$	4.6 – 5.0
Vinylic, $R_2C{=}CH$	5.2 – 5.7
Aromatic, ArH	6.0 – 9.5
Acetylenic, RC≡CH	2.5 – 3.1
Alcohol hydroxyl, ROH	0.5 – 6.0[a]
Carboxylic, RCOH	10 – 5.0[a]
Phenolic, ArOH	4.5 – 7.7[a]
Amino, $R{-}NH_2$	1.0 – 5.0[a]

[a] The chemical shifts of these protons vary in different solvents and with temperature and concentration

1. *Analisis beralat dikenali dengan sifat-sifat sofistikated, cekap dan berkeutuhan.*

   (a) Perincikan perbezaan antara teknik klasikal dan teknik beralat dengan memberikan SATU contoh teknik klasikal dan SATU teknik analisis beralat.

   [10 markah]

   (b) Keutuhan data bergantung pada ketepatan dan kejituan, tipikal bagi teknik analisis beralat. Dengan bantuan carta "dart".

   [10 markah]

2. *Pada satu tempat kejadian jenayah, seorang Juru Analisis Forensik mengumpul bahan bukti yang dapat menjelaskan punca kematian seorang mangsa. Salah satu daripada bahan yang dikutip lalu dibawa ke makmal ialah cawan kertas yang mengandungi darah. Berikan bantuan kepada Juru Analisis Forensik tersebut jika cawan kertas tersebut merupakan bukti paling kuat bagi kematian mangsa. Pertimbangkan kedua-dua keadaan berikut:*

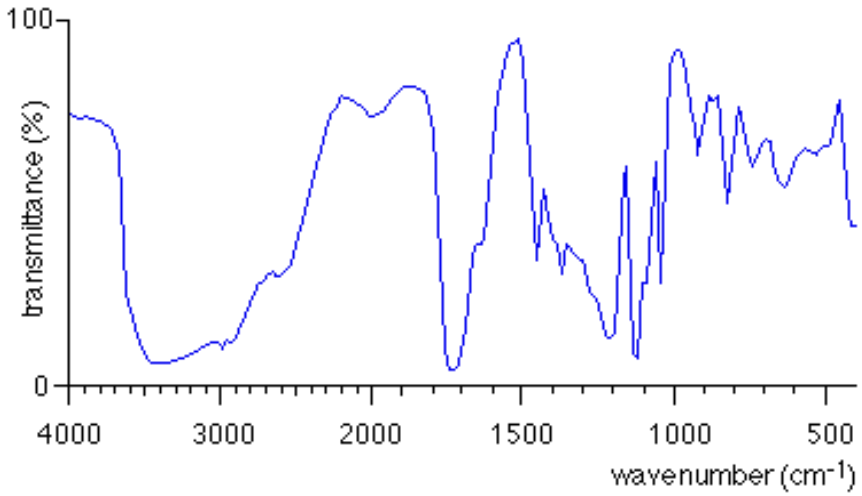
   (a) Keracunan bahan organik.

   [10 markah]

   (b) Keracunan bahan bukan organik.

   [10 markah]

3. *Para Penyelidik di B-Gates telah mensistesis bahan organic, T, bagi mempercepatkan proses pembuangan air dan penyerakan gentian pendek dan lut cahaya bagi pembuatan kertas menerap. Daripada analisis bahan T menggunakan FTIR, spektrum pada Rajah 1 telah diperolehi.*



Rajah 1: Spektrum FTIR bagi T.

(a) *Tanda dan padankan kumpulan berfungsi pada lurah yang berkenaan dengan bantuan Appendix 1.*

[5 markah]

(b) *Jika T memiliki formula kimia CH_3-COH-COOH , lakarkan ^{1}H-NMR bagi T dengan bantuan Appendix 2.*

[10 marks]

(c) *Ramalkan 5 fragmentasi yang mungkin dipaparkan pada spectrum jisim T.*

[5 markah]

4. *Penindihan spectrum pada Rajah 2 menunjukkan 2 set jalur yang merujuk pada agen pengkomplex pada jarak gelombang 350 nm dan komplex pada jarak gelombang 550-580 nm berasaskan tindakbalas 1.*

$$C+SI \rightarrow C\text{-}SI \ldots.(1)$$

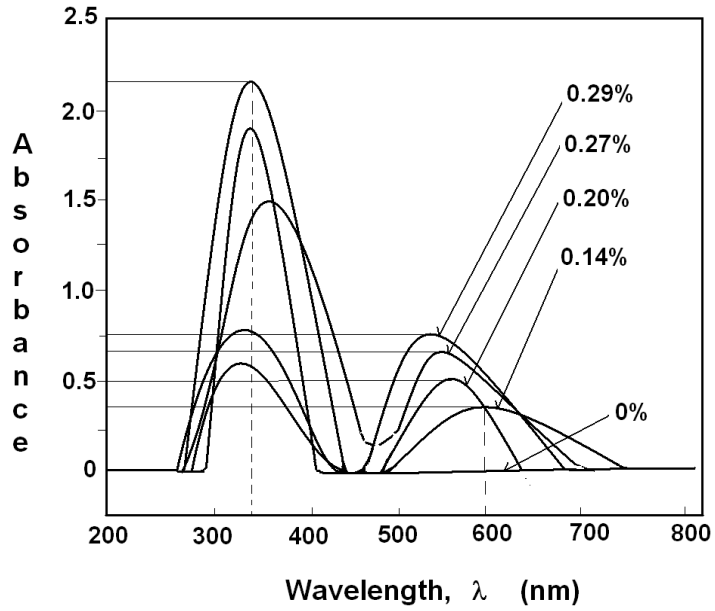
Jelasnya, agen pengkompleks , C, berwarna oren sementara komplx, C-SI, berwarna biru tua.

(a) *Terangkan anjakan dan pengurangan intensity jalur pada jarak gelombang* ***350 nm*** *apabila kepekatan SI concentrations berkurangan daripada 0.29% to 0.14% (Rajah 2).*

[20 markah]

(b) *Suatu prosidur piawai mencadangkan satu jarak gelombang tetap pada 550 bagi membaca signal. Letakkan diri anda sebagai seorang pakar dan berikan komen bagi kesan jarak gelombang tetap terhadap kejituan keputusan yang bakal diperolehi.*

[20 markah]



Rajah 2: Penindihan spektrum ultralembayung/nampak bagi kalibrasi SI.

LAMPIRAN 1
Ciri-ciri Frekuensi untuk FTIR

GROUP		FREQUENCY RANGE (cm^{-1})	INTENSITY[a]
G. Akly			
C-H (stretching)		2853 – 2962	(m-s)
Isopropyl, $-CH(CH_3)_3$		1380 – 1385	(s)
	and	1365 -1370	(s)
tert-Butyl,$-C(CH_3)_3$		1385 – 1395	(m)
	and	~1365	(s)
H. Alkenyl			
C-H (stretching)		3010 – 3095	(m)
C=C (stretching)		1620 – 1680	(v)
$R-CH=CH_2$		985 – 1000	(s)
	and	905 – 920	(s)
$R_2C=CH_2$		880 – 900	(s)
cis-RCH=CHR		675 – 730	(s)
trans-RCH=CHR		960 – 975	(s)
I. Alkynyl			
≡C-H (stretching)		3300	(s)
C≡C (stretching)		2100 – 2260	
J. Aromatic			
Ar-H (stretching)		3030	(v)
Aromatic substitution type (C-H out-of-plane bendings)			
Monosubstituted		690 – 710	(very s)
	and	730 – 770	(very s)
o-Disubstituted		735 – 770	(s)
m-Disubstituted		680 – 725	(s)
	and	750 – 810	(very s)
p-Disubstituted		800 – 840	(very s)
K. Alcohols, Phenols, and Carboxylic Acids			
O-H (stretching)			
Alcohols, phenols (dilute solutions)		3590 – 3650	(shrap, v)
Alcohols, phenols (hydrogen bonded)		3200 – 3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500 – 3000	(broad, v)
L. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O (stretching)		1630 – 1780	(s)
Aldehydes		1690 – 1740	(s)
Ketones		1680 – 1750	(s)
Esters		1735 – 1750	(s)
Carboxylic acids		1710 – 1780	(s)
Amides		1630 – 1690	(s)

(out-of-plane C-H bendings)

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LAMPIRAN 2
Pergeseran Kimia untuk NMR proton

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8 – 1.0
2° Alkyl, RCH_2R	1.2 – 1.4
3° Alkyl, R_3CH	1.4 – 1.7
Allylic, $R_2C{=}C{-}CH_3$ ‖ C	1.6 – 1.9
Benzylic, $ArCH_3$	2.2 – 2.5
Alkyl chloride, RCH_2Cl	3.6 – 3.8
Alkyl bromide, RCH_2Br	3.4 – 3.6
Alkyl iodide, RCH_2I	3.1 – 3.3
Ether, $ROCH_2R$	3.3 – 3.9
Alcohol, $HOCH_2R$	3.3 – 4.0
Ketone, $RCCH_3$ ‖ O	2.1 – 2.6
Aldehyde, RCH ‖ O	9.5 – 9.6
Vinylic, $R_2C{=}CH_2$	4.6 – 5.0
Vinylic, $R_2C{=}CH$ ‖ R	5.2 – 5.7
Aromatic, ArH	6.0 – 9.5
Acetylenic, RC≡CH	2.5 – 3.1
Alcohol hydroxyl, ROH	0.5 – 6.0[a]
Carboxylic, RCOH ‖ O	10 – 5.0[a]
Phenolic, ArOH	4.5 – 7.7[a]
Amino, $R\text{-}NH_2$	1.0 – 5.0[a]

[a] pergeseran kimia proton ini berbeza dalam pelarut yang berbeza dan dengan suhu dan kepekatan

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