UNIVERSITY OF SWAZILAND

JULY 2015 SUPPLEMENTARY EXAMINATION

TITLE OF PAPER	:	**Analytical Chemistry II: Fundamentals of Spectrophotometry**
COURSE NUMBER	:	**C304**
TIME	:	**3 HOURS**
Important Information	:	1. Each question is worth 25 marks. 2. Answer <u>**ALL**</u> questions in **SECTION A** and any other <u>**THREE**</u> **(3) in SECTION B** 3. Marks f or <u>**ALL**</u> procedural calculations will be awarded. 4. Start each question on a fresh page of the answer sheet. 5. Diagrams must be large and clearly labelled accordingly. 6. This paper contains an appendix of chemical constants 7. Additional material: graph paper and data sheet

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You are not supposed to open this paper until permission has been granted by the chief invigilator

SECTION A- MULTIPLE CHOICE [25Marks]

Instruction: Write the letter of choice next to the question number in this section. Show calculations and give explanations where stated.

1. Beer's Law (or the Beer Lambert Law) is .... **(2)**

(a) a linear relationship between the intensity of a UV absorbance and the concentration of the analyte.

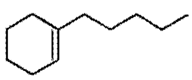
(b) an inverse relationship between the IR stretching frequency and the energy of light.

(c) used to calculate the chemical shift (δ) of an NMR resonance relative to that of the tetramethylsilane standard.

(d) used to derive a molecular formula from the mass-to-charge ratio of an analyte.

2. Which one of the following compounds is expected to have the longest wave length absorbance (λmax)? Explain choice **(2)**

a)



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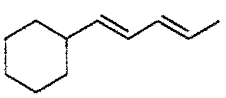

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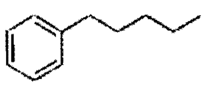

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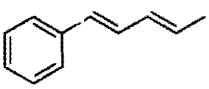
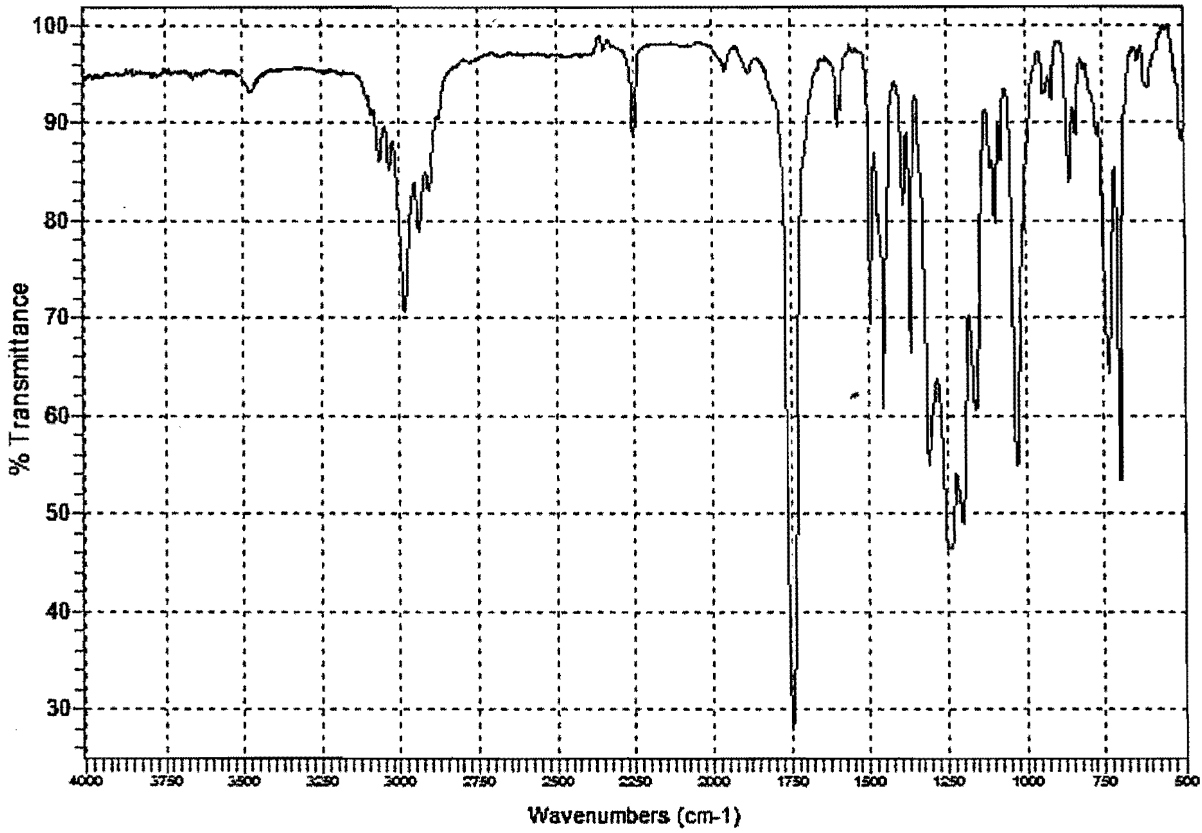
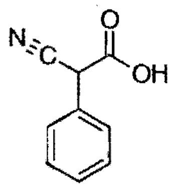


3. Which structure is most consistent with the following infrared spectrum? **(1)**



a)



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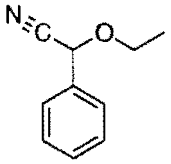
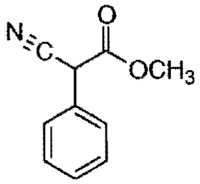
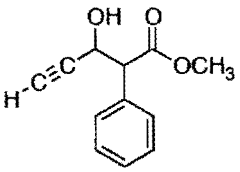


c)



d)



4. The wavenumber of a transition is 2000 cm^{-1}. In what part of the electromagnetic spectrum does this come? **(2)**

(a) Microwave (b)Ultraviolet-visible (c) Infrared (d) Radiowave

5. The frequency of a transition is 5.4 × 10^{15} Hz. What is the corresponding wavelength? (Show Calculation) **(2)**

(a) 180 000 cm^{-1} (b) 560 nm (d) 5.6 × 10^{-6} (e)5.6 × 10^{-8} m

6. Compound Z absorbs light of wavelength 320 nm. A 1.0×10^{-3} mol dm^{-3} solution of a compound Z gives an absorbance reading of 0.15 when placed in a solution cell of path length 1 cm. What is the value of the molar extinction (absorption) coefficient of Z? (Show calculation) **(2)**

(a) 150 dm3 mol^{-1} cm^{-1} (b)1.5×10^{-4} mol dm^{-3} cm^{-1} (c)1500 dm^3 mol^{-1} cm^{-1}

(d) 15 dm^3 mol^{-1} cm^{-1}

7. Which of the following statements is correct? **(2)**

(a) Microwave radiation possesses more energy than infrared radiation.
(b) Infrared radiation has a shorter wavelength than visible light.
(c) Infrared radiation has a lower wavenumber than visible light.
(d) Ultraviolet radiation has a longer wavelength than infrared radiation.

8. A copper(II) sulfate solution of unknown concentration is placed in a colorimeter and an absorbance reading of 0.46 is recorded. Using the same solution cell, a 0.055 M solution of copper(II) sulfate gives an absorbance reading of 0.34. What is the concentration of the first solution? (Show calculation) **(2)**

a) 0.041 mol dm^{-3} b) 0.35 mol dm^{-3} c) 8.60×10^{-3} mol dm^{-3} d) 0.074 mol dm^{-3}

9. In reverse phase chromatography, the stationary phase is made **(1)**

a) non-polar

b) polar

c) either non-polar or polar

d) none of these

10. Which of the following detectors give concentration-dependent signals ? **(1)**

a) Electron-capture detector b) Thermal conductivity

c) Infra-red detector d)All of these

11. A solid sample is being extracted into a solvent in a round bottom flask. Following extraction, the solids are filtered, put back into a round bottom flask and extracted a second time. The concentrations of the analytes from both extractions in this case can be used to test: **(1)**

a) extraction precision	b) extraction efficiency
c) extraction time needed	d) all of the above

12. Which of the following is not a step in atomic absorption spectroscopy (AAS)? **(1)**

a) Particles are adsorbed onto a stationary phase

b) A solution is vaporised.

c) A calibration curve is constructed.

d) Atoms absorb light.

13. In HPLC column efficiency is measured in terms of number of plates which is; **(1)**

a) inversely related to the square of the peak width

b) directly related to the square of the peak width

c) inversely related to the cube root of the peak width

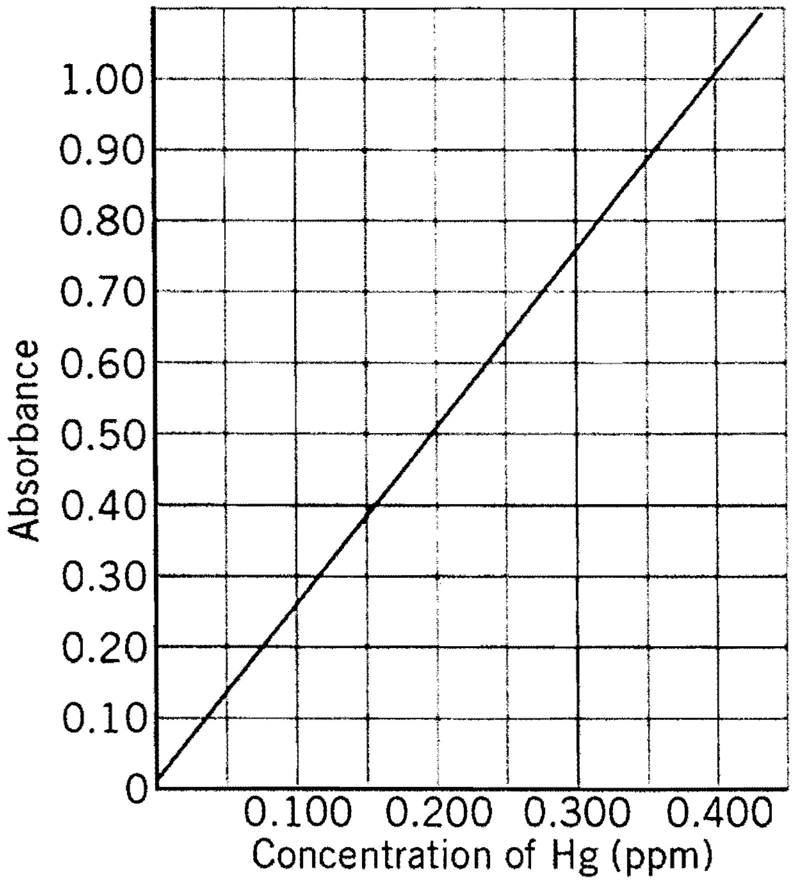
d) directly related to the square of the peak width

14. A sample was placed into a spectrophotometer, and it was found that the light reaching the detector at 450nm was exactly 75% the intensity of the light reaching the detector when a blank was placed in the spectrophotometer. What is the absorbance of the sample? Show working.

a) 1.845 b) -0.125 c) 0.347 d) 0.125

e) My answer is not listed

15. **In many countries, fish with more than 0.500ppm mercury is considered unsafe. In one experiment, a 0.750g piece of tuna was appropriately treated and made up to 10.0mL solution. This solution returned an absorbance of 0.70. Using the calibration graph below, what can be concluded from this analysis? (Show working)** **(3)**



a) The tuna does not contain mercury.
b) The concentration of mercury is exactly equal to 0.500ppm and may or may not be safe to eat
c) The concentration of mercury in the tuna is greater than 0.500ppm and it should not be eaten.
d) The concentration of mercury in the tuna is less than 0.500ppm and it can be eaten safely.

SECTION B

Instruction: Answer any **three (3)** questions from this section

QUESTION 1[25 Marks]

a) State the light source for AAS. Explain how it works, including why a different lamp must be used for each element [7]

b) A major breakthrough in atomic absorption spectrophotometry was the invention of graphite furnace AA.

   i) What is the major difference between flame AA and graphite furnace AA? Use diagrams to support your answer. [3]

   ii) Identify the physical stages involved in the furnace program and describe the processes that occur during each stage. [3]

   iii) Outline three (3) advantages of graphite furnace AA over flame AA [3]

c) An **internal standard** in analytical chemistry is a chemical substance that is added in a constant amount to samples, the blank and calibration standards in a chemical analysis. The method of internal standards is used to improve the precision of quantitative analysis.

   i) Give three characteristics of a "good" internal standard. [3]

   ii) In ICP-MS analysis, choose one internal standards; Bi, Sc or In for each of the following analytes; Cd, Pb and Cr and explain why you chose as you did? [3]

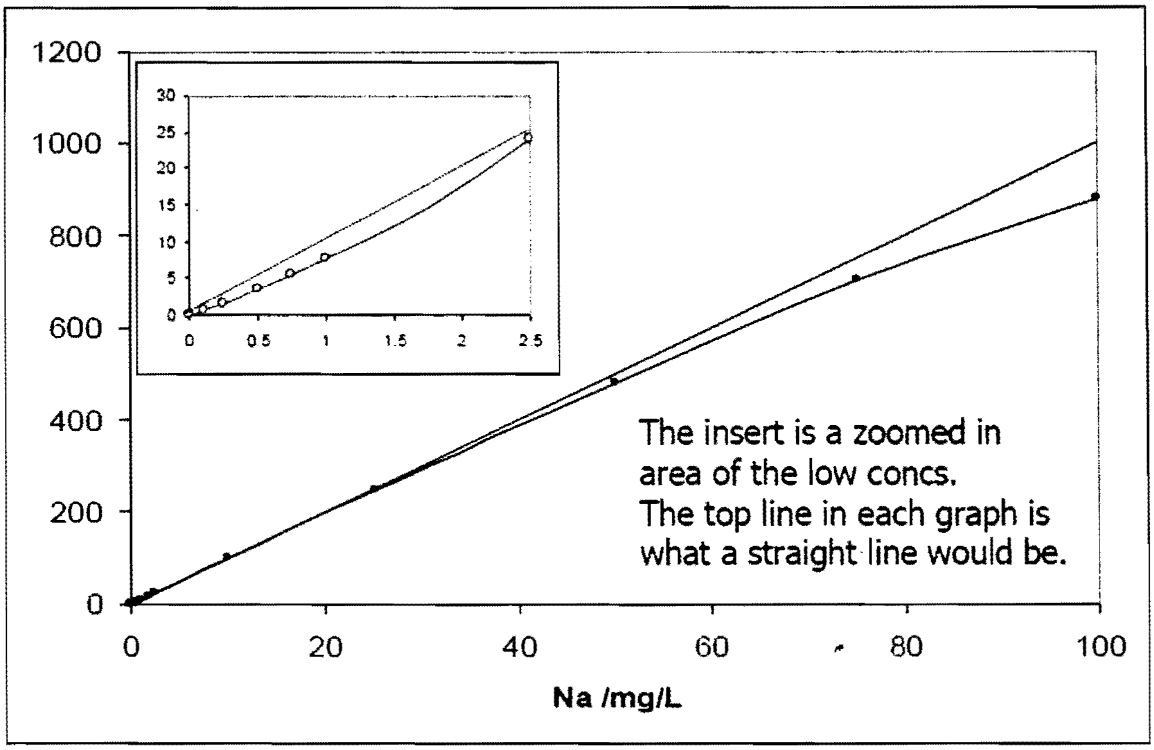
   iii) Explain why an internal standard can be used for ICP-AES but is not used for AAS [3]

QUESTION 2 [25 Marks]

a) What are the desirable characteristics of a GC detector? [4]

b) The retention of a compound in GC is determined by how much time a substance spends in the mobile phase versus the stationary phase. Explain three (3) factors which affect the retention of a substance in GC. [3]

c) Sodium in tap water was analysed by flame emission spectroscopy using a simple flame photometer utilising a butane/air flame. The following calibration graph was produced.



The insert is a zoomed in area of the low concs.
The top line in each graph is what a straight line would be.

i) Why does the graph slope down at high concentrations? [2]

ii) What can be done, if anything, to get a straight line for the calibration? [2]

iii) The inset shows a zoom of the low concentrations. Why does this show a negative deviation from a straight line calibration? [2]

iv) What can be done to remedy, if anything, this part of the calibration graph? [2]

v) Spectral interference can be a real problem in emission techniques, however in this scenario we don't have to worry about spectra interference; why? [3]

d) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [3]

i) What is meant by "stray light" in spectroscopy? [1]

ii) Use equations to explain why stray light leads to negative deviations from Beer's Law [3]

QUESTION 3 [25 Marks]

a) Differentiate between "Spectroscopy" and "Spectrometry" [3]

b) For a spectroscopic band occurring at 1685 cm^{-1},

i) Convert to energy in joules [1]

ii) State in which region of the electromagnetic spectrum the band falls [1]

(iii) State the kind of transition expected in this region [1]

c) Explain using diagrams, why atomic spectra appear as lines, whereas molecular spectra appear as bands [5]

d) With respect to Ca explain chemical interference in flame atomic absorption spectrometry and explain how it is eliminated. [4]

e) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called Liberty 110 ICP.

(i) What does ICP stand for? [1]

(ii) Draw the ICP torch and label its components [4]

(iii) Concisely explain why chemical interferences are less common in ICP-AES than they are in flame AAS. [2]

(iv) List and describe each of the three (3) advantages that ICP has over flame atomic absorption spectroscopy [3]

QUESTION 4 [25 MARKS]

a) UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions and biological macromolecules. For a particular assay, your plot of absorbance versus concentration is not linear. Explain the possible reasons for this. [4]

b) What criteria should be used to choose an appropriate wavelength at which to make absorbance measurements in UV-visible spectroscopy? Why is that choice important? [4]

c) Explain the difference between electromagnetic radiation in the UV and visible ranges. How does quantitative spectroscopy using the UV range differ from that using the visible range? [5]

d) Considering a typical spectrophotometer, what is the effect of decreasing the exit slit width of the monochromator on the light incident to the sample? [3]

e) Consider the reactions of two unknown compounds X and Y.

$$X + 2H_2 \rightarrow C_5H_{12}$$
$$Y + 2H_2 \rightarrow C_5H_{12}$$

i) Deduce the molecular formula of the two unknown compounds [2]

The UV spectra of the compounds are compared to pent-1-ene in the table below.

Compound	**λ_{max}**
X	176

Y	211
Pent-1-ene	178

ii) Draw the structures of compounds X and Y and explain the choice of structure for each. [5]

f) Which of the molecules oxygen and hydrogen chloride is IR active and why? [2]

QUESTION 5 [25Marks]

a) Why is the injection port of a GC at a higher temperature than the oven temperature? [2]

b) Why must sugars and fatty acids be derivatized before GC analysis while pesticides and aroma compounds need not be derivatized. [3]

c) What is solid-phase extraction and why is it advantageous over traditional liquid-liquid extraction? Give three (3) advantages. [5]

d) What is a guard column and why is it used? [3]

e) What is the separation principle in Size Exclusion Chromatography? [2]

f) In HPLC what do you understand by Isocratic and Gradient elution? [3]

g) Which is the most commonly used detector in High Performance Liquid Chromatography and why? [3]

h) What are the main differences between High Performance Liquid Chromatography and Gas Chromatography? Give four (4) [4]

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.88	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 105.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (?)	111 **Rg** (?)							

Lanthanides	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinides	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

PHYSICAL CONSTANTS AND UNITS

Table 1 : General Physical Constants			
Constant	**Symbol**	**SI Units**	**Non-SI Units**
Velocity of Light	c	2.9979×10^{8} m s^{-1}	
Electronic charge	e	-1.6022×10^{-19} C	
Avogadro's constant	N_A	6.0220×10^{23} mol^{-1}	
Atomic mass unit	u	1.6606×10^{-27} kg	
Electron rest mass	m_e	9.1095×10^{-31} kg	
Proton rest mass	m_p	1.6726×10^{-27} kg	
Neutron rest mass	m_n	1.6750×10^{-27} kg	
Planck's constant	h	6.6262×10^{-34} J s	
Rydberg constant	R_H	1.0974×10^{7} m^{-1}	
Ideal gas constant	R	8.314 J mol^{-1} K^{-1}	0.08206 l atm mol^{-1} K^{-1}
Gas molar volume (STP)	V_o	2.21414×10^{-2} m^{3} mol^{-1}	22.4 l mol^{-1}
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	
Faraday constant	F	96485 C mol^{-1}	
Gravitational acceleration	g	9.80 m s^{-2}	
Permittivity of a vacuum	ε_o	8.8542×10^{-12} F m^{-1}	
Mechanical equivalent of heat		1 calorie ≡ 4.18 J	

Table 2: IR Correlation table for common functional groups

Functional group	**band (cm^{-1})**
$-CH_3$	2950–75 (s), 2870–90 (m), 1440–65 (m), 1370–90 (s)
$-CH_2$ (acyclic)	2910–40 (s), 2840–80 (m), 1440–80 (m), ~720 (w)
–CH	2880–90 (w), ~1340 (w)
$-C{=}CH_2$	2970–3070 (m), 1290-1420 (w), 860-900 (w)
–CH=CH– (*cis*)	675–730 (m)
–CH=CH– (*trans*)	960–70 (m)
–C=C–	1620–80 (m)
Aryl–H	3010–80 (m), 1000–1250 (w), 700–900 (m)
Aryl C=C	1590–1620 (v), 1575–90 (v), 1470–1525 (v), 1430–65 (v), 400–625 (m)
–C≡C–H	~3300–40 (s), 700–900 (m)
–C≡C–	2100–2250 (v)
water	~3700
water of crystallisation	3100–3700
O-H (free	~3600 (v)
O–H (intermolecular H-bond)	3200–3500 (s)
O–H (intramolecular H-bond)	3400–3600 (s)
O–H	1260–1400 (s)
C–OH	1020–1200 (s)
Aryl-O–H	~3600 (m), 1180–1390 (s), 600–700 (s)
COO–H (dimer)	2500–3300 (s)
COO–H (chelated)	2500–2700 (s)
C–O–C (all kinds)	1050–1250 (v)
N–H	3200–3500 (m), 1500–1600 (s), 650–900 (s)
C–N	1020–1200 (m)
C(=O)N–H (amide)	3200–3400 (s), ~1450 (s), 1590–1650 (m)
C–F	1000–1400 (s)
C–Cl	600–800 (s)
C–Br	500–750 (s)
C–I	~500 (s)
NO_2	1660–1490 (s), 1390–1260 (s)
C≡N	~2250 (s)

Table 3: IR Correlation table for carbonyl groups

Functional group	**Type**	**band (cm^{-1}) (all strong absorptions)**
RC(=O)R′ ketones	saturated aliphatic	1715–45
	aryl	1650–1700
	α-β unsaturated	1660–1700
	cyclobutanone	~1780
	cyclopentanone	~1750
	α halo	1730–50
	β-diketone (enol form)	1580–1640
RC(=O)H aldehydes	sat aliphatic	1720–40
	α-β unsat	1685–1705
	aryl	1685–1715
	β-keto (enol form)	1645–70
	α-halo	1730–65
COOH carboxylic acids	sat. aliphatic (dimer)	1700–25
	sat. aliphatic (monomer)	1740–1800
	aryl (dimer)	1680–1710
	α-βunsat	1690–1715
	a halo (dimer)	1715–40
	H-bonded (intramolecular)	1650–80
	anion	1550–1610, 1300–1420
C(=O)-O-C=O acid anhydrides	sat aliphatic	1800–40, 1740–80
	α-β unsat, aryl	1780–1830, 1710–55
C(=O)X acid halides	X = Cl sat aliphatic	1790–1815
	X = Cl α-β unsat, aryl	1735–50, 1765–90
COOR Esters	sat aliphatic	1725–50
	α-β unsat, aryl	1705–40
	RCOOC=C	1750–1800
	α-keto	1740–60
	β -eto	1635–55
	α-halo	1740–70
	lactone (5 ring)	1760–80
C(=O)-N Amides	1º amide I	~1690
	amide II	~1600
	2º amide I	1670–1700
	amide II	1510–50
	3º amide	1630–70
	lactam	1700
amino acids	Free	1390–1425, 1560–1600
C=N	oxime	1640–90