



Autumn Examinations 2011

Exam Code(s) CHEMISTRY CH301 and CH315
Exam(s) Third year Chemistry and Third year Biopharmaceutical Chemistry

Module Code(s) CH326
Module(s) ANALYTICAL CHEMISTRY AND MOLECULAR STRUCTURE

Paper No. 1
Repeat Paper

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Instructions: ANSWER FOUR (4) QUESTIONS ONE FROM EACH SECTION

Duration Two (2) Hours
No. of Pages 10
Department(s) Chemistry
Course Co-ordinator(s) Dr. W. M. Carroll

Requirements:

MCQ Release to Library: Yes No

Statistical/ Log Tables x

Graph Paper x

SECTION A

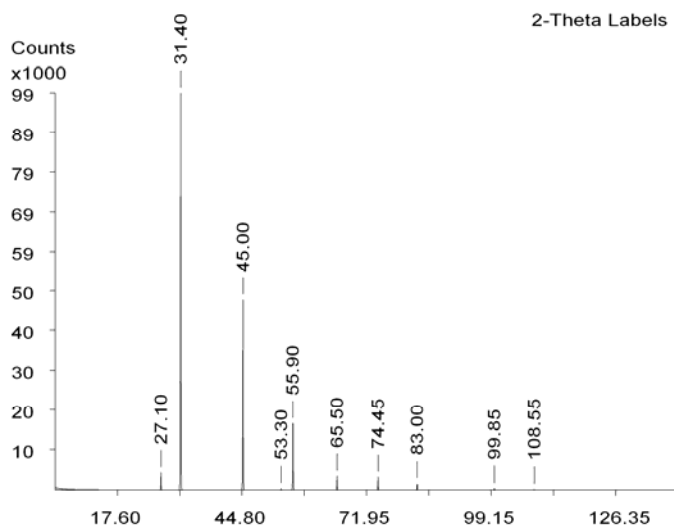
1.

- (a) Consider the molecule HCN.
- (i) Which symmetry group does the molecule belong to?
 - (ii) How many vibrational normal modes does the molecule have, and what do they look like?
 - (iii) How many of the vibrational modes of (ii) are IR-active?
- [15 marks]**
- (b) Specify point groups and draw the symmetry elements for the two molecules cis- and trans-difluorodiazine.
- [10 marks]**

2.

- (a) Define the term "Bravais lattice" **[7 marks]**
- (b) Explain why there is no C-type cell for the tetragonal crystal system. **[8 marks]**
- (c) The X-ray powder diffraction pattern of CaS obtained using radiation of wavelength 1.54 \AA is shown below. The peaks are labelled with 2θ values. On the basis that the structure is cubic and of either the NaCl or CsCl type index the first six reflections.

[10 marks]



SECTION B

3. Describe the operation of the following methods of mass spectrometric analysis.

Magnetic sector

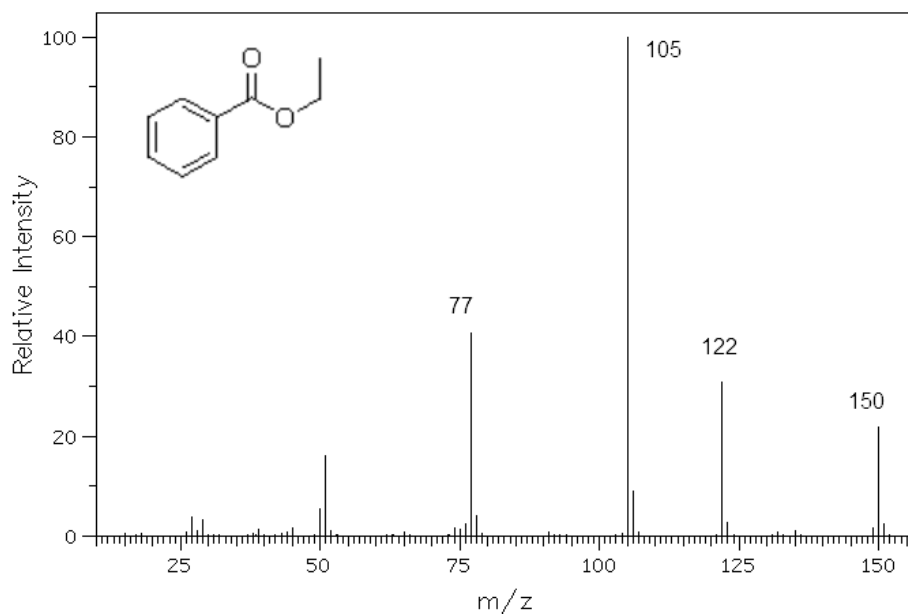
Time of flight

Quadrupolar

The discussion should also cover the advantages and disadvantages of each method.

[10 Marks]

The electron impact ionisation spectrum of ethylbenzoate is given below. Account for the major peaks (as indicated) in the spectrum and the fragmentation mechanisms which lead to the formation of the respective ions. The peak at m/z 122 arises from a rearrangement; name the rearrangement.



[15 Marks]

4.

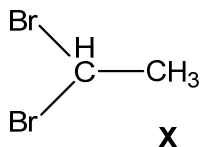
Stainless steels often undergo passivation treatments in order to improve their corrosion resistance in chloride environments. An increase in the level of chromium in the passive film, a change in the thickness of the passive film and the removal of inclusions or impurities from the surface have all been suggested as reasons for the increased stability of the steel. Show how these effects could be quantified using both surface analytical and imaging techniques.

[25 Marks]

SECTION C

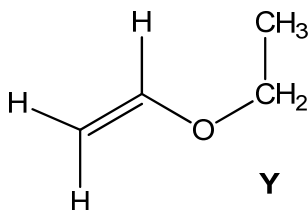
5. Answer all parts

- (a) Draw a simple schematic diagram of an NMR spectrometer and briefly explain how a sample is prepared for NMR analysis. **[7 marks]**
- (b) Explain in general terms how coupling (splitting) arises in a $^1\text{H-NMR}$ spectrum, basing your answer on the splitting pattern you would expect for the molecule **X**.



[6 marks]

- (c) Using the correlation tables provided, assign approximate chemical shifts to the groups of chemically equivalent protons in the molecule **Y**. The three alkene hydrogens should be considered to be equivalent. Explain briefly why the chemical shift values are as you have suggested.

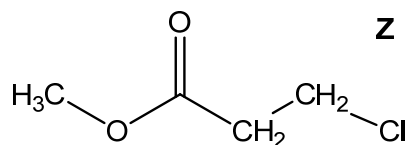


[6 marks]

- (d) Discuss the use of NMR spectroscopy in medicine. **[6 marks]**

6. Answer all parts; correlation tables are attached to the back of the examination paper

- (a) Sketch the $^1\text{H-NMR}$ spectrum you would expect for the molecule **Z**:



The sketch should indicate the approximate chemical shift and the splitting pattern of each signal in the spectrum. **[10 marks]**

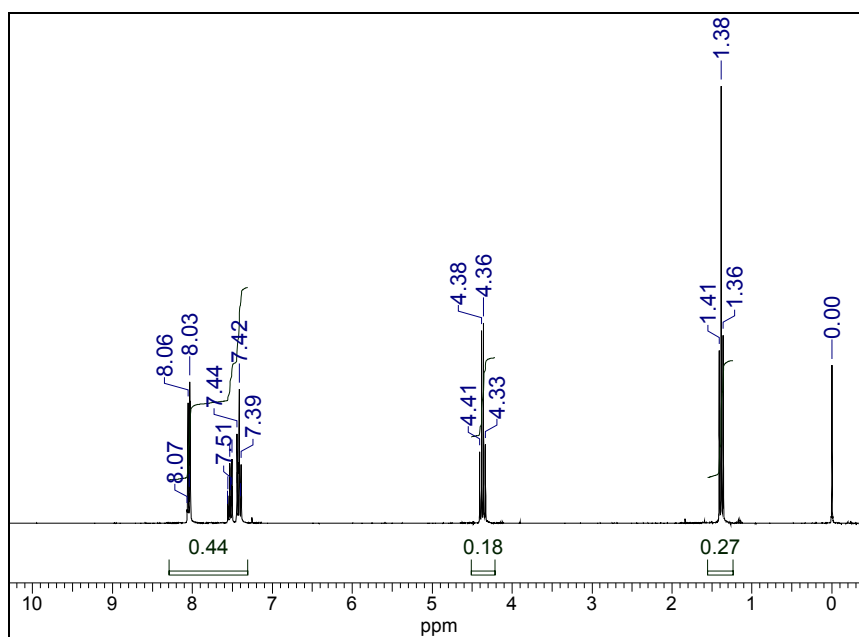
- (b) The IR spectrum of a liquid **M**, whose molecular formula is $C_9H_{10}O_2$, contains strong bands at 1721 and 1200 cm^{-1} . The ^1H - and ^{13}C -NMR spectra (solvent CDCl_3) obtained for **M** are reproduced below. An analysis of its DEPT spectrum produced the information given in the following table:

Signal	166.54*	132.73	130.56*	129.51	128.27	60.90	14.33
Number of hydrogens attached to C-atom responsible for signal	0	1	0	1	1	2	3

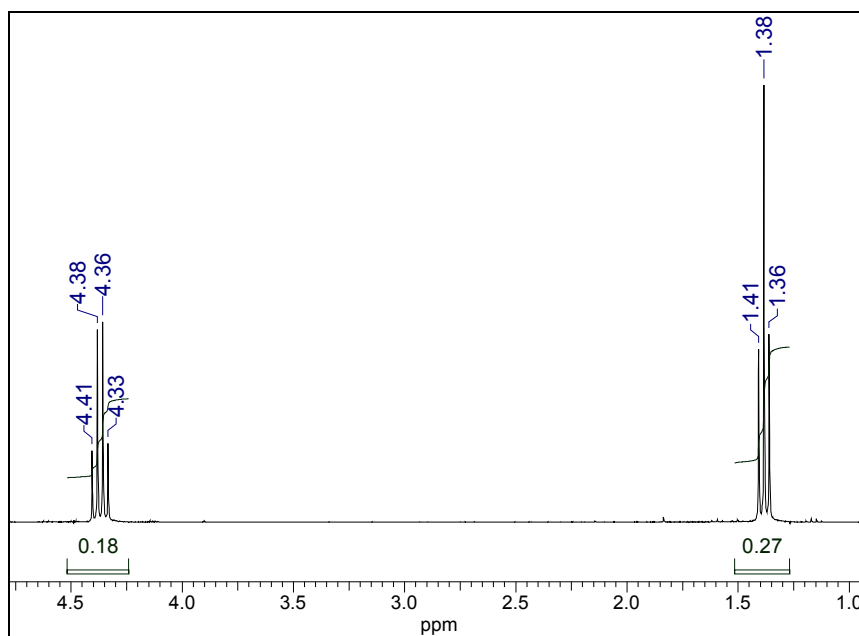
*unlabelled in the ^{13}C -NMR spectrum below

- (i) If the signals between $\delta 8.2$ and $\delta 7.3$ are taken together, the ^1H -NMR spectrum contains three signals: $\delta 8.2 - 7.3$, 4.37 and 1.38; how many protons are involved in each of the three signals? **[5 marks]**
- (ii) What C,H grouping is indicated by the signals at $\delta 8.2 - 7.3$? **[2 marks]**
- (iii) What C,H grouping is indicated by the signals at $\delta 4.37$ and 1.38 which are coupled to each other? **[3 marks]**
- (iv) Determine the structure of the molecule **M**. **[5 marks]**

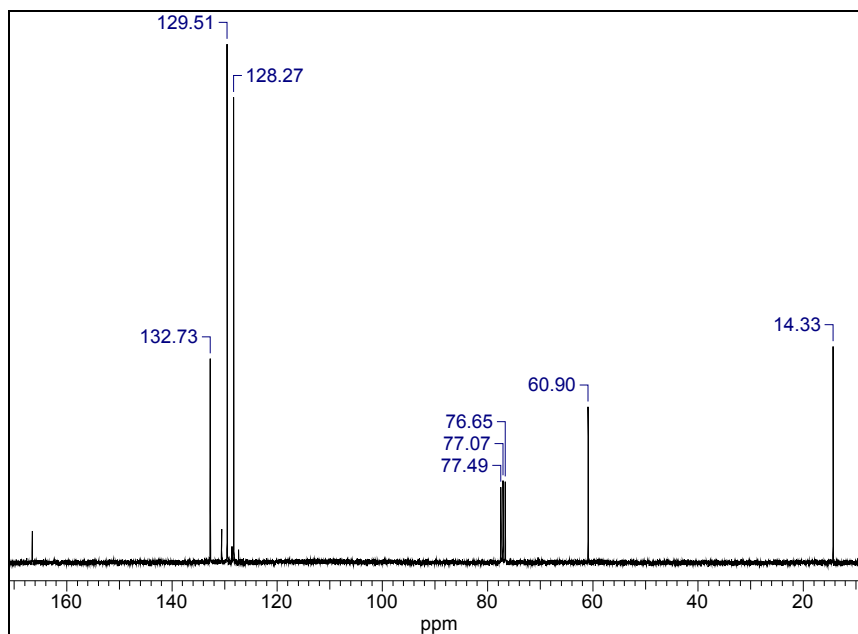
¹H-NMR spectrum of M



Expanded ¹H-NMR spectrum of M



^{13}C -NMR spectrum of M*

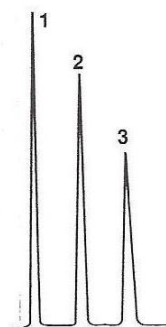


*There are unlabelled signals at 166.54 and 130.56 ppm; the signals at approximately 77 ppm are due to the solvent, CDCl_3

SECTION D

7.

Vitamins



1. Vitamin C
2. Vitamin D₃
3. Vitamin K₁

0 8 16 min

Column: 250mm x 4.6mm

Packing: Econosil C18, 10 μ

Flowrate: 1.0mL/min

Mobile Phase: 97% Methanol, 3% H₂O

The details of the analysis of a multi-vitamin preparation using HPLC are provided above.

(a) Explain why HPLC is used more frequently than GC in the analysis of pharmaceuticals.

[5 marks]

(b) Given a chromatogram of a sample (HPLC or GC), what feature of the chromatogram (i) provides information about the number of components in the sample, (ii) allows a component to be identified and (iii) provides information about the concentration of a component in the sample.

[5 marks]

- (c) Draw a schematic diagram of a HPLC system that could be used to carry out the above analysis. **[5 marks]**
- (d) A variable wavelength UV detector, set at 240 nm, was used in the analysis. Draw a schematic diagram of the detector and explain how it works. **[5 marks]**
- (e) What type of column is used in the analysis? Draw a diagram showing a section of the surface of the stationary phase particles involved. **[5 marks]**

8. Answer (a) and (b).

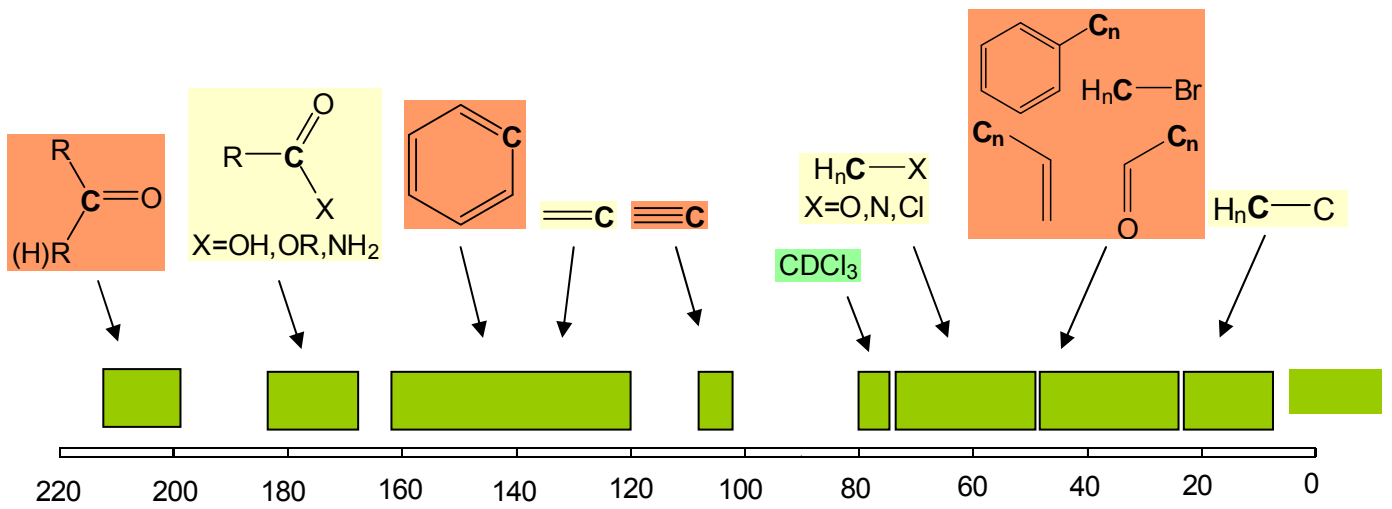
- (a) Answer all parts.
- (i) Compare the thermal conductivity detector with the electron capture detector for gas chromatography. Describe how their uses differ. **[4 marks]**
- (ii) With reference to gas chromatography write brief notes on each of the following;
- (i) columns **[2 marks]**
- (ii) stationary phase **[2 marks]**
- (iii) A packed column is 2250mm in length and has a height equivalent of a theoretical plate of 1.5mm. Calculate the width of chromatographic peaks with retention times (t_r) of 2.5min and 3.2min. **[4.5 marks]**
- (b)
- (i) Briefly give an overview of the principal disadvantages of the XRF technique. **[6 marks]**
- (ii) Explain with the aid of diagrams why the calibration plot for the iron content of a manganese steel is linear whereas plots for chromium and nickel steels are non-linear. **[6.5 marks]**

9.

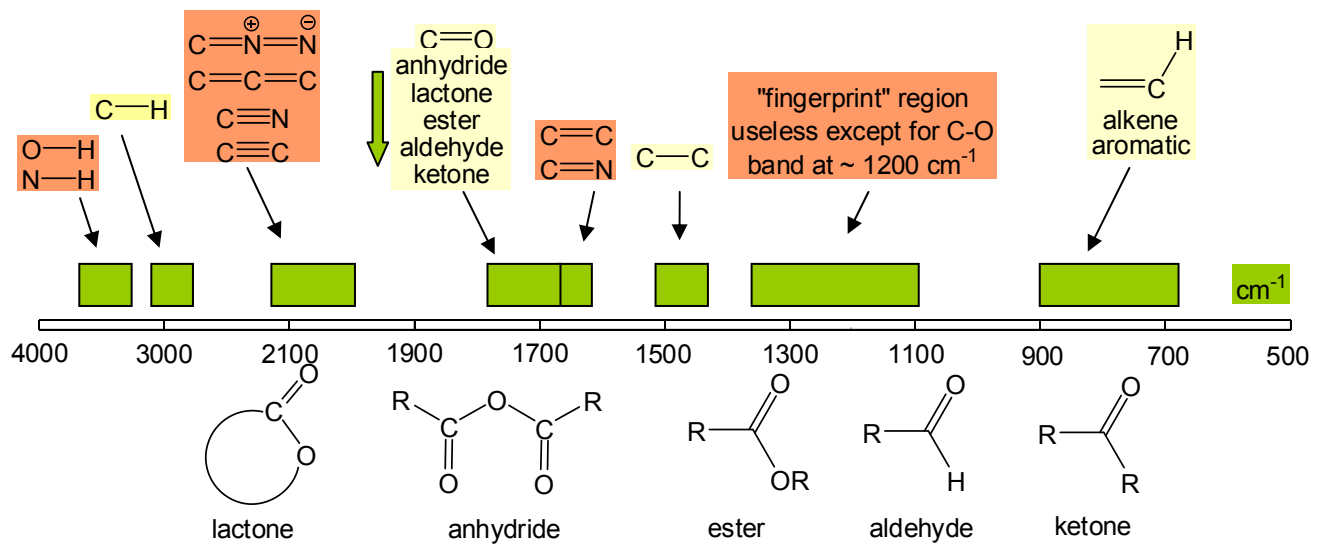
- (a) Describe the basic principles involved in Differential Scanning Calorimetry (DSC) and the type of information obtained by the application of this technique. What additional information, over that obtained by thermogravimetry, may be obtained using DSC? **[10 marks]**
- (b) A thermogram of an iron(II)sulphate sample weighing 64.3 mg shows a loss of mass between 500 and 560°C of 33.8 mg. Identify the residue (presume it contains iron). What gas(es) may be evolved? (atomic masses, Fe 55.85, S 32, O 16). **[5 marks]**
- (c) Describe briefly the principles, mechanism and applications of one type of gas sensor. **[10 marks]**

Correlation Tables for Spectroscopy

¹³C-NMR (ppm)



IR



¹H-NMR

