NUI Galway
OÉ Gaillimh

Semester I Examinations 2010-2011

Exam Code(s)	**3BS9; 3BPM**
Exam(s)	**Third year Chemistry and Third year Biopharmaceutical Chemistry**
Module Code(s)	**CH326**
Module(s)	**ANALYTICAL CHEMISTRY AND MOLECULAR STRUCTURE**
Paper No.	
Repeat Paper	
External Examiner(s)	**Prof. Kieran Molloy**
Internal Examiner(s)	**Prof. P. Murphy, Dr. W.M. Carroll, Prof. L. Eriksson, Dr. A. Erxleben, Dr. N. Geraghty, Dr. T. Higgins, Dr. D. Leech, Dr P. O'Leary and Dr. A. Ryder.**
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	Yes				
Graph Paper	Yes				

SECTION A

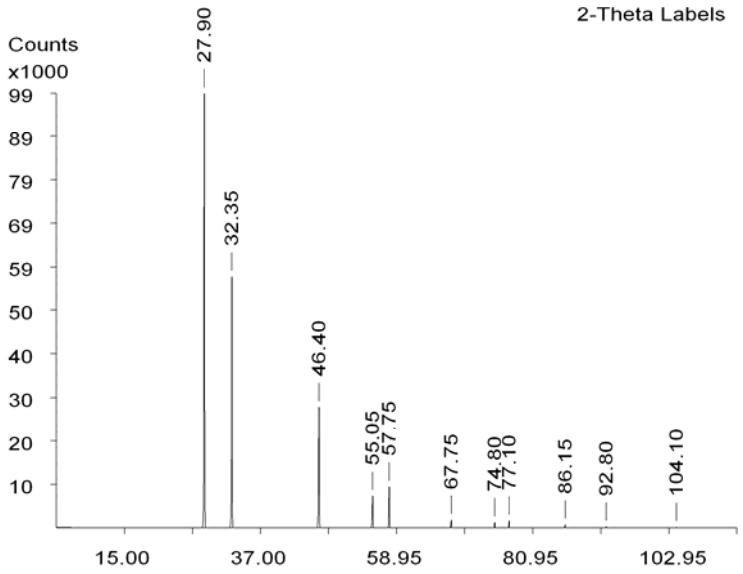
1.

(i) Specify the point groups for the following molecules:
H_2O, CH_4, NH_3, H_2O_2, C_2H_4 **[5 marks]**

(ii) Which symmetry elements are present for trigonal planer molecules (D_{3h} symmetry) such as BF_3? **[10 marks]**

(iii) Draw the vibrational normal modes for a molecule of D_{3h} symmetry. Which of these are IR-active, and why? **[10 marks]**

2. The X-ray powder diffraction pattern of CdO obtained using radiation of wavelength 1.54 Å is shown below. The peaks are labelled with 2θ values. CdO crystallizes with the NaCl lattice.



(a) Index the first six reflections. **[12 marks]**

(b) Calculate the unit cell parameter. **[6 marks]**

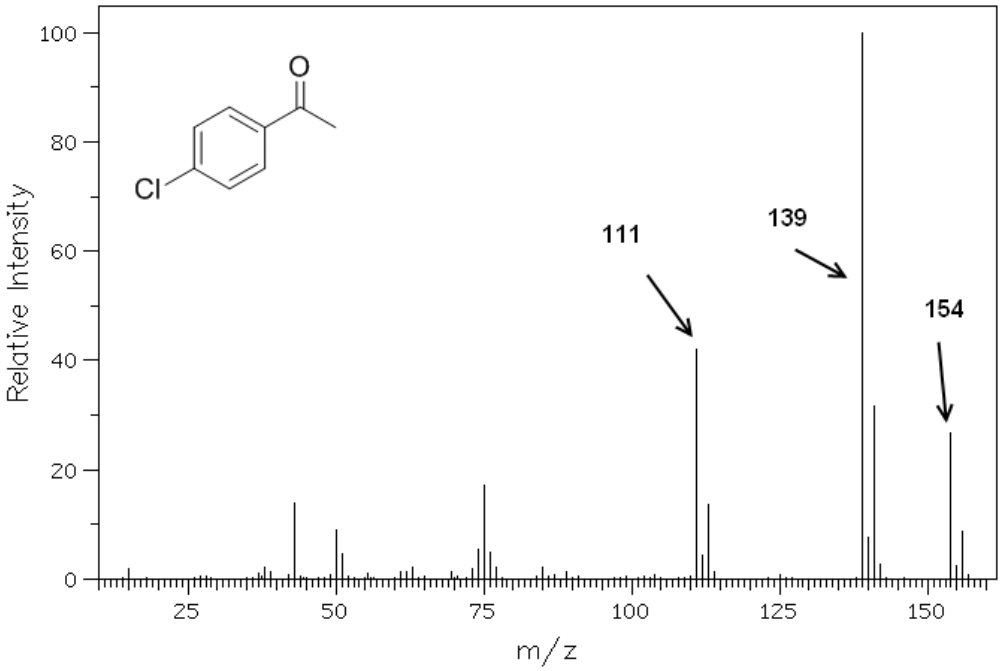
(c) Calculate the density of CdO. **[7 marks]**

Assume the following atomic weights: Cd, 112.41; O, 15.999. Avogadro's number is 6.022×10^{23}.

SECTION B

3. Describe the operation of the following types of ionisation methods.
Electron impact ionisation
Chemical ionisation
MALDI
The discussion should also cover the advantages and disadvantages of each method. **[10 Marks]**

The electron impact ionisation spectrum of 4'chloroacetophenone 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. Chlorine possesses two common isoptopes ^{35}Cl and ^{37}Cl evidence of which can be seen in the spectrum: outline the evidence for the two isotopes.



[15 Marks]

4. **Answer (a) and (b).**

(a) Secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS) are two very important techniques that can provide valuable chemical and structural information about materials. Discuss.
[15 marks]

The following number of X-rays were counted over the same period from a specimen containing iron and nickel and two elemental standards using a SEM-EDX spectrometer. The background has already been subtracted.

X-ray line	Unknown	Element
Fe $K_{\acute{a}}$	31906	106602
Ni $K_{\acute{a}}$	72062	103853

The beam voltage was 20kV and the X-ray take-off angle was 45^0. Show how this information can be used to give quantitative data concerning the alloy composition.

[10marks]

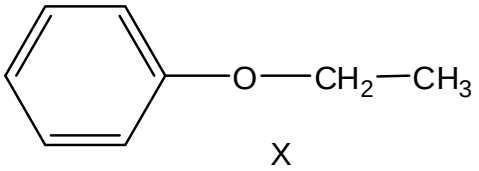
SECTION C

5. Answer all parts

(a) You have just obtained the ^{1}H-NMR spectrum of a molecule whose structure is unknown. Outline the kind of information about the molecule that you would be able to obtain from the spectrum. **[8 marks]**

(b) In terms of ^{1}H-NMR spectroscopy, explain what is meant by shielding and how it is related to the chemical shift of a proton in a spectrum. **[7 marks]**

(c) Using the correlation tables provided assign approximate chemical shifts to the groups of chemically equivalent protons in the following molecule X. The five aromatic hydrogens should be considered to be equivalent. Using the ideas you have discussed in (b) account for the chemical shift values you suggest.



X

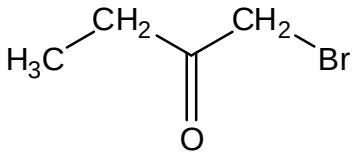
[6 marks]

(d) In terms of ^{13}C-NMR spectroscopy, explain what is meant by a DEPT spectrum and how it is used in working out the structure of a molecule.

[4 marks]

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

(a) Sketch the ^{1}H-NMR spectrum you would expect for the following molecule:



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 Z, whose molecular formula is $C_4H_8O_2$, contains strong bands at 1735 and 1200 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra (solvent $CDCl_3$) obtained for Z are reproduced below. An analysis of its DEPT spectrum produced the information given in the following table:

Signal	174.85	51.47	27.42	9.14
Number of hydrogens attached to C-atom responsible for signal	0	3	2	3

(i) The ^{1}H-NMR spectrum contains three distinct signals: how many protons are involved in each of the three signals?

[5 marks]

(ii) What C,H grouping is indicated by the signals at δ3.67 in the ^{1}H-NMR spectrum? **[2 marks]**

(iii) What C,H grouping is indicated by the signals at δ2.35 and 1.15 in the ^{1}H-NMR spectrum which are coupled to each other?

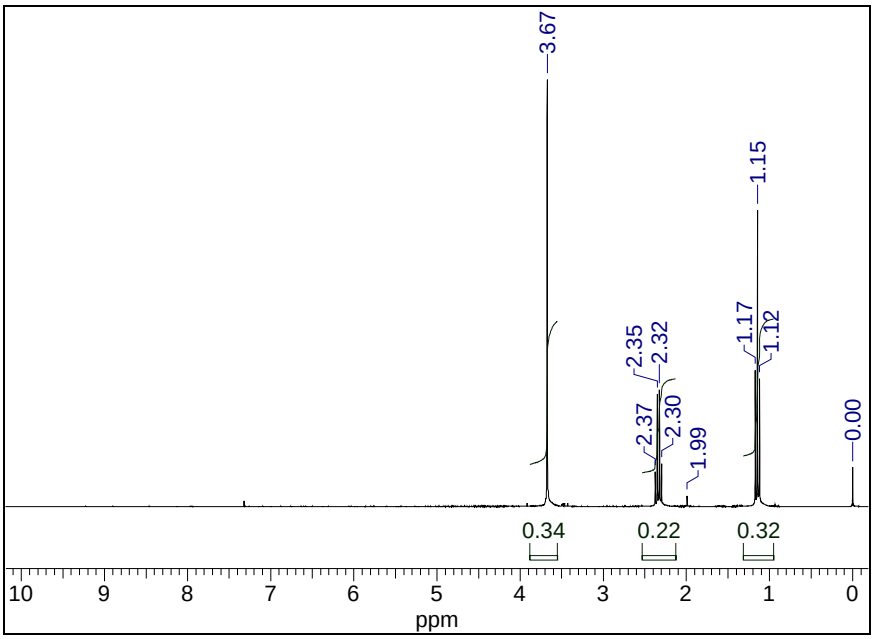
[3 marks]

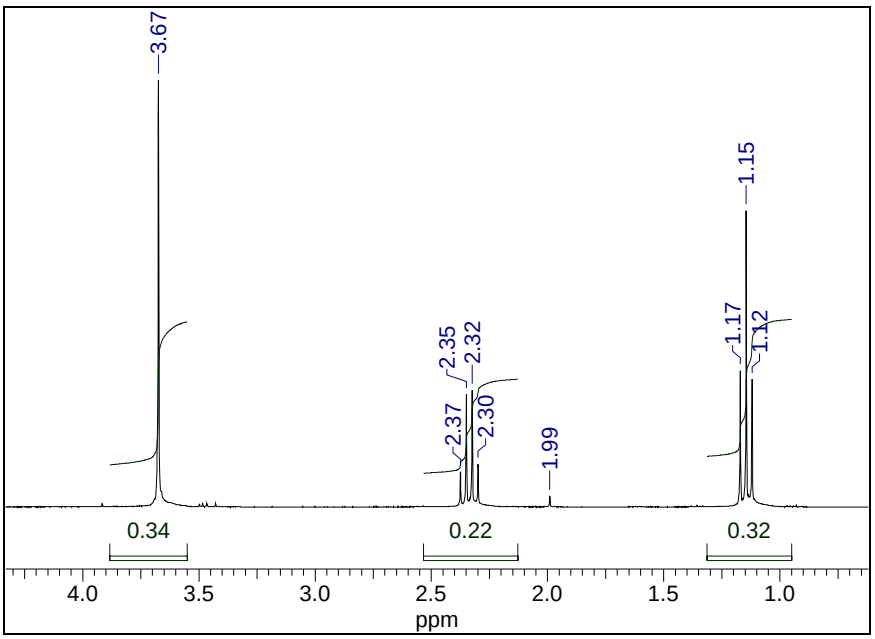
(iv) Determine the structure of the molecule Z.

[5 marks]

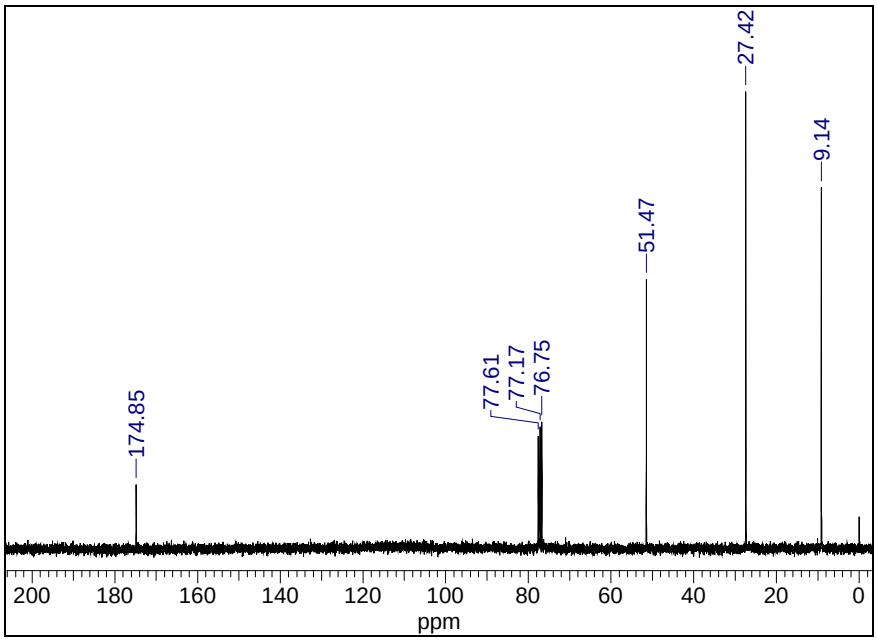
[Spectra appear in the pages that follow]

^{1}H-NMR of Z


3.67
2.35
2.32
2.37
2.30
1.99
1.17
1.12
1.15
0.00
0.34
0.22
0.32
10
9
8
7
6
5
4
3
2
1
0
ppm

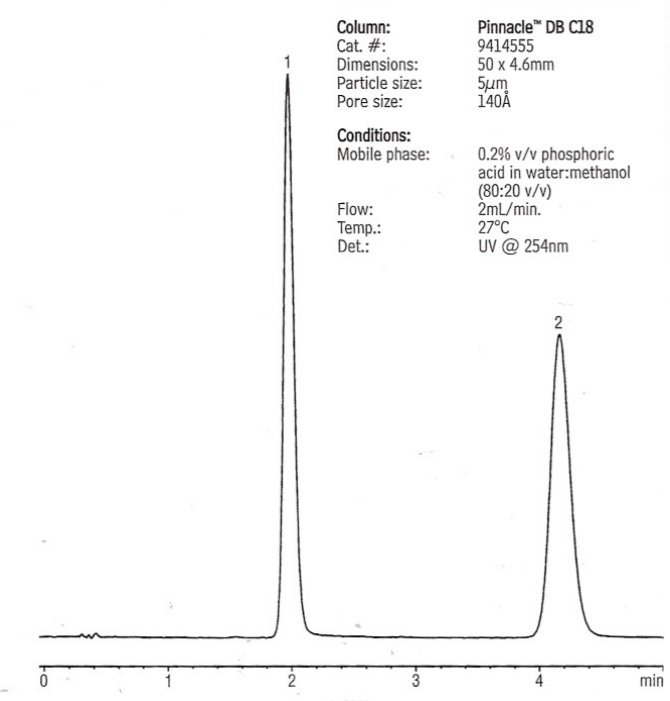

3.67
2.35
2.32
2.37
2.30
1.99
1.17
1.12
1.15
0.34
0.22
0.32
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{13}C-NMR of Z



SECTION D

7. Details of a HPLC analysis of the flavouring compound vanillin (Peak 1) are provided below:



(a) Draw a schematic diagram of a HPLC system that could be used to carry out the analysis. An indication of the type of detector and pumping system required should be given. **[5 marks]**

(b) What type of stationary phase is used in the analysis? Briefly describe the retention mechanism that operates with such a stationary phase.

[5 marks]

(c) What type of detector is used in the analysis? Draw a simple diagram showing how this type of detector works.

[5 marks]

(d) Outline the advantage associated with reducing the retention times of the analytes further and outline two changes that could be made, in terms of the chromatographic conditions and/or hardware, in order to bring this about. Explain your answer.

[5 marks]

(e) A food sample is to be tested for the presence of vanillin. How would you use HPLC to confirm that the sample does contain vanillin? Two pieces of evidence should be provided.

[5 marks]

8. Answer (a) and (b):

(a)

(i) Describe the operation of the flame ionization detector used in gas chromatography. Comment on the advantages/disadvantages of the detector. **[3marks]**

(ii) With reference to gas chromatography write brief notes on each of the following;

packed columns **[2marks]**

theoretical plates **[2marks]**

(iii) For a packed column with 2000 theoretical plates, calculate the width of a chromatographic peak when the retention time (tr) is 2.00min. Taking this width as average, calculate the maximum number of chromatographic peaks that can be resolved per minute from tr=1.5 min to tr=2.5min without overlap at the peal base.

[5.5marks]

(b)

(i) Describe with the aid of diagrams the two types of detectors that are used in wavelength dispersive X-ray fluorescence spectrometers.

[6 marks]

(ii) Outline the construction and mode of operation of basic single channel wavelength dispersive, and energy dispersive, X-ray fluorescence spectrometers. **[6.5 marks]**

9.

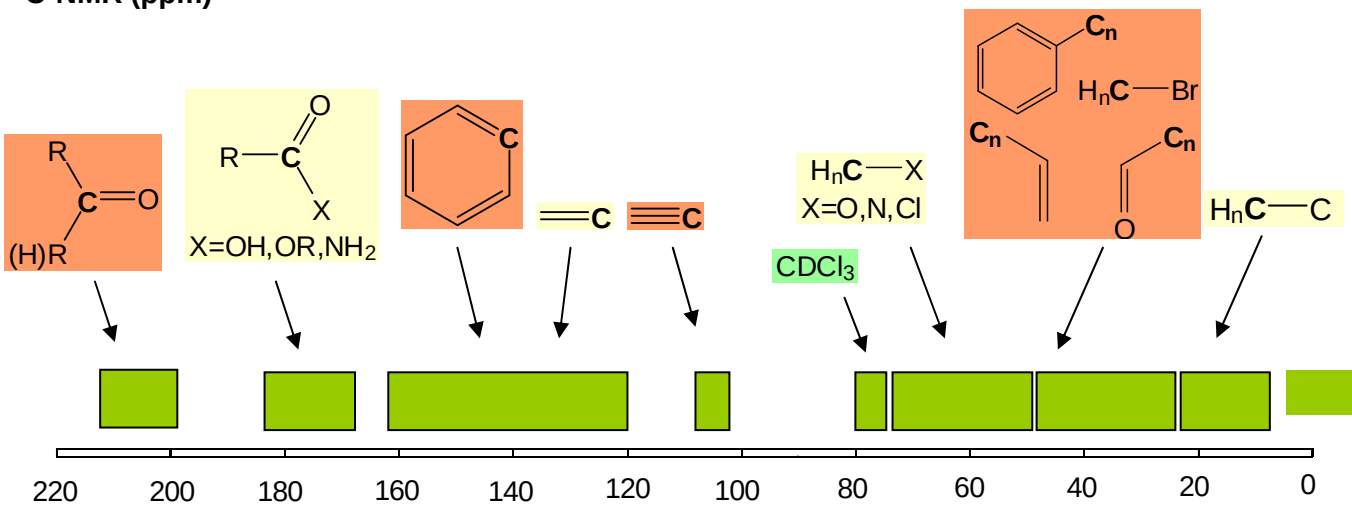
(a) Describe the basic principles involved in Thermogravimetry (TG) and the type of information obtained by the application of this technique. What additional information, over that obtained by TG, may be obtained using Differential Scanning Calorimetry (DSC)? **[10 marks]**

(b) A sample of sapphire, mass 110 mg, yielded an endothermic deflection of 50 mm from baseline upon heating at a heating rate of 20 K/min between 400 and 500k. A polymer sample, mass 21.5 mg, yielded a deflection of 27 mm under the same conditions. Given that the heat capacity of sapphire at 445 K is 0.997 J/(K.g) calculate the heat capacity for the polymer sample. **[5 marks]**

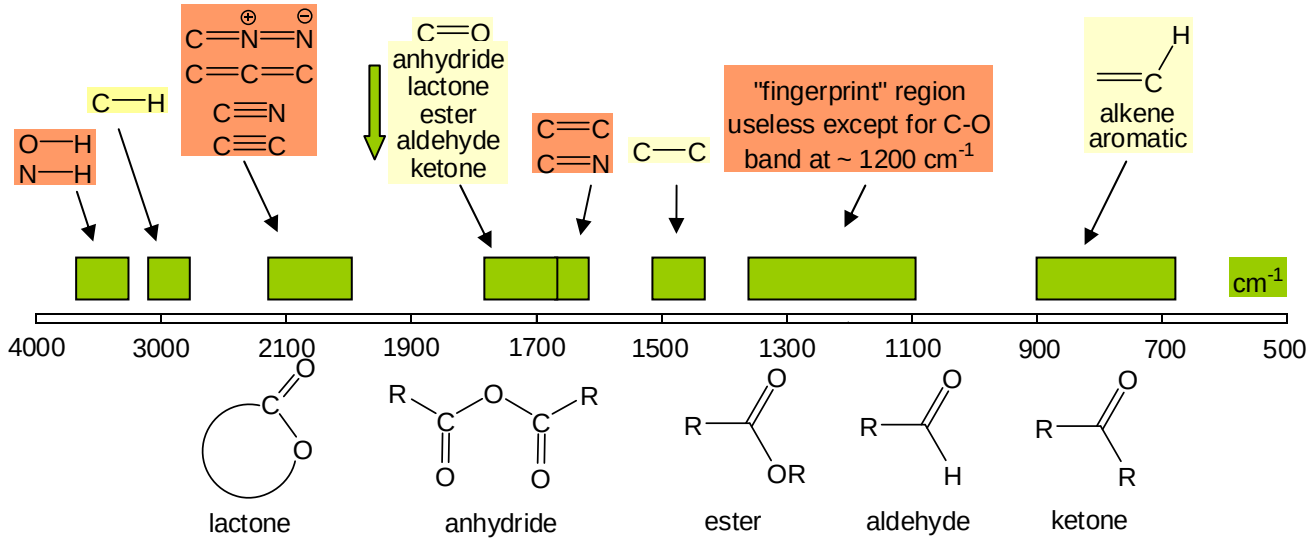
(c) The Universal Exhaust Gas Oxygen (UEGO) sensor combines amperometric and galvanic (lambda) oxygen sensors to monitor automobile combustion efficiency, in particular in "lean-burn" engines.
Describe the operating principle of either sensor
What advantage is gained by combining the sensors to provide the UEGO?
[10 marks]

Correlation Tables for Spectroscopy

^{13}C-NMR (ppm)



IR



^{1}H-NMR