CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 405: ANALYTICAL CHEMISTRY II

STREAMS: BSC. CHEM **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 23/04/2025 **11.30 A.M. – 1.30 P.M.**

INSTRUCTIONS

Answer Question **ONE** and any other **TWO** Questions

QUESTION ONE (30MARKS)

a. (i)Discuss the major advantages of an FTIR spectrometer compared with a dispersive instrument? ***(3 marks)***

(ii)The first FTIR instruments used three different interferometer systems. Briefly, describe how it has been possible to simplify the optical systems in more contemporary instruments ***(3 marks)***

(iii)Nondispersive IR instruments often used for the determination of gases rather than dispersive IR spectrometers. Discuss. ***(3 marks)***

(iv)Explain the source of an FID signal in FT-NMR. ***(3 marks)***

(v)Explain why ^{13}C-^{13}C spin-spin splitting is not observed in ordinary organic compounds? ***(2 marks)***

b. Explain the following terms ***(5 marks)***

i. Larmor frequency

ii. magnetic anisotropy

iii. the shielding constant

iv. the chemical-shift parameter

v. CW-NMR measurements coupling constants

c. Figure 20-29 shows the mass spectrum of the same compound from an EI source and a CI source.

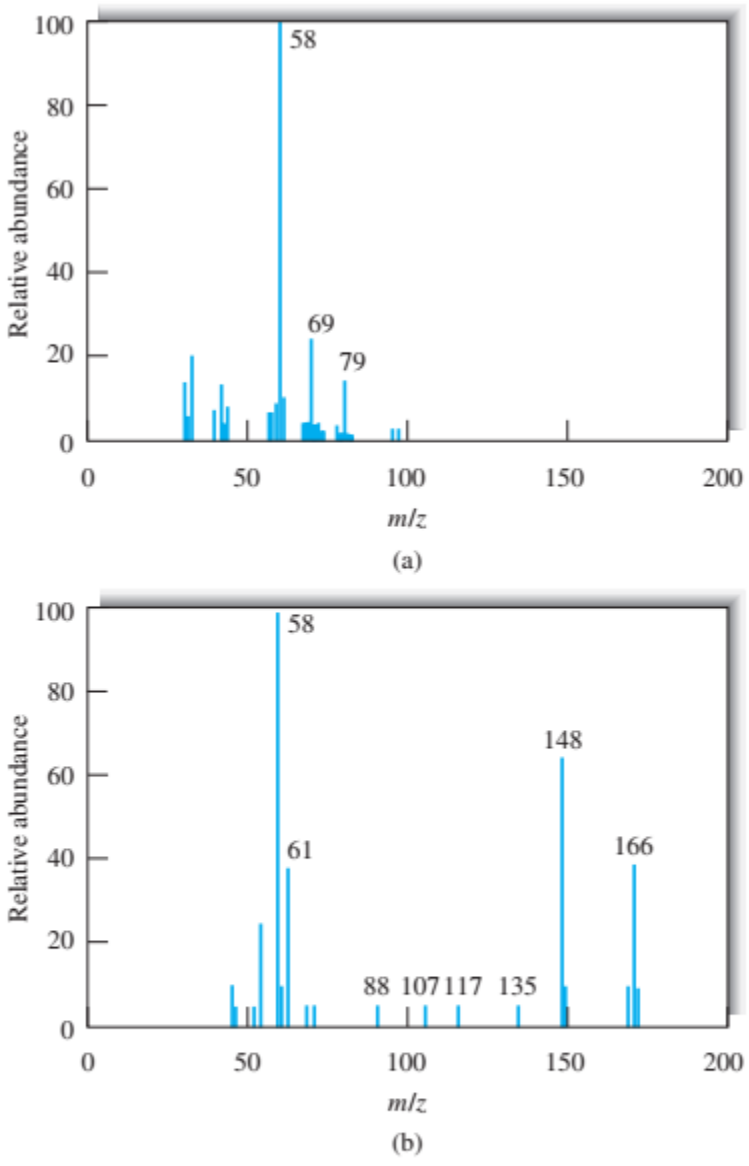


FIGURE 20-29 EI spectrum (a) and CI spectrum (b) of the same biologically important compound. (From H. M. Fales, H. A. Lloyd, and G. A. W. Milne, *J. Amer. Chem. Soc.*, **1970**, *92*, 1590–1597, **DOI**: 10.1021/ja00709a028. American Chemical Society.)

(i) Which mass spectrum would be best for determining the molecular mass of the compound? Explain. ***2 marks***

(ii) Which mass spectrum would be best for determining the chemical structure? Explain. ***2 marks***

(iii) The EI source was a pulsed source used with a TOF mass analyzer. If the flight tube were 1.0 m long and the accelerating voltage were 3000 V, what would the flight time be for the ion at m/z = 58? ***3 marks***

(iv) For two ions of m/z values m_1/z and m_2/z, derive an equation for the difference in flight times Δt_F as a function of the two masses, the charges, and the accelerating voltage. ***3 marks***

(v) For the same TOF analyzer as in part (iii), calculate the difference in flight times between ions of m/z =59 and m/z = 58. ***3 marks***

d) How many fundamental vibrational modes would you predict for ***(2 marks)***

i. Methane,
ii. Benzene,
iii. Toluene,
iv. Ethylene,

QUESTION TWO (20MARKS)

a) Predict the appearance of the high-resolution proton NMR spectrum of ***(3 marks)***

i. cyclohexane.
ii. diethyl ether.
iii. 1,2-dimethoxyethane, $CH_3OCH_2CH_2OCH_3$.

b) (i) Describe sources of folded spectral lines ***(2 marks)***

(ii) What resolution is needed to separate the ions $C_2H_4^+$ and CH_2N^+, with masses of 28.0313 and 28.0187, respectively? ***(2 marks)***

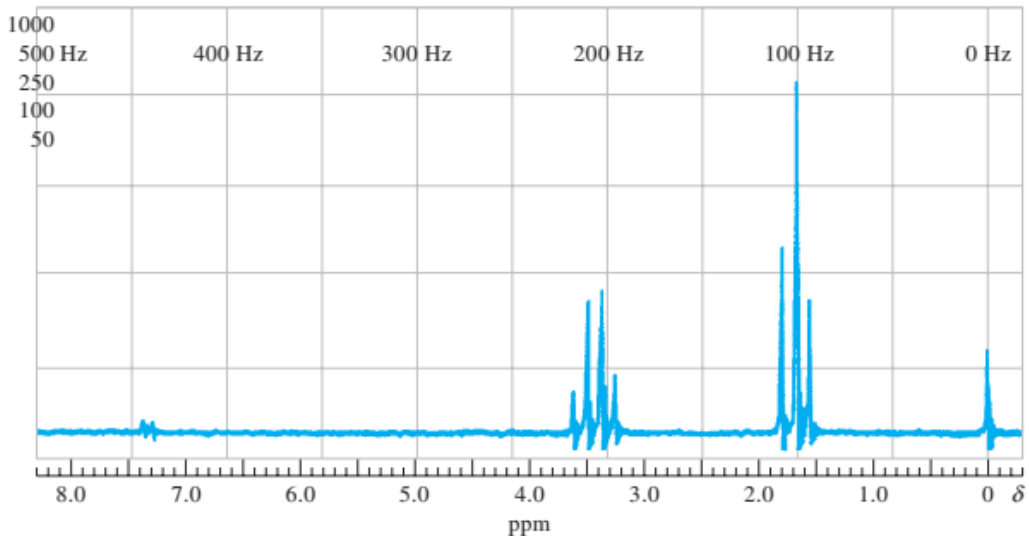
(iii) What accelerating voltage is required to direct a singly charged water molecule through the exit slit of a magnetic sector mass spectrometer if the magnet has a field strength of 0.240 T (tesla) and the radius of curvature of the ion through the magnetic field is 12.7 cm? ***(3 marks)***

(iv) Calculate the ratios of the $(M + 1)^+$ to M^+ peak heights for the following two compounds: dinitrobenzene, $C_6H_4N_2O_4$ (M= 168), and an olefin, $C_{12}H_{24}$ (M = 168). ***(3 marks)***

c) (i) Describe the difference between gaseous field ionization sources and field desorption sources. ***(3 marks)***

(ii) The ion-accelerating voltage in a particular quadrupole mass spectrometer is 10.00 V. How long will it take a singly charged cyclohexane ion to travel the 15.0 cm length of the rod assembly? Assume that the initial velocity of the ion in the *z* direction is zero. ***(2 marks)***

(iii) The proton NMR spectrum in Figure below is for an organic compound containing a single atom of bromine. Identify the compound. ***(2 marks)***



QUESTION THREE (20marks)

a) Calculate the resolution required to resolve peaks for

(i) CH_2N (M = 28.0187) and N_2^+ (M =28.0061). ***(2 marks)***

(ii) $C_2H_4^+$ (M = 28.0313) and CO^+ (M = 27.9949). ***(2 marks)***

(iii) $C_3H_7N_3^+$ (M = 85.0641) and $C_5H_9O^+$ (M = 85.0653). ***(2 marks)***

(iv) androst-4-en-3,17,-dione (M^+) at m/z = 286.1930 and an impurity at 286.1240. ***(2 marks)***

b) (i) Discuss the major differences between a tandem-in-space mass spectrometer and a tandem-in-time mass spectrometer ***(3 marks)***

(ii)Outline the advantages and disadvantages of x-ray Fluorescence method ***(4 marks)***

(iii)Describe various sample handling techniques pertaining the sample in solid state ***(5 marks)***

QUESTION FOUR (20marks)

a) (i) Using IR spectroscopy, how will you distinguish the following isometric compounds.

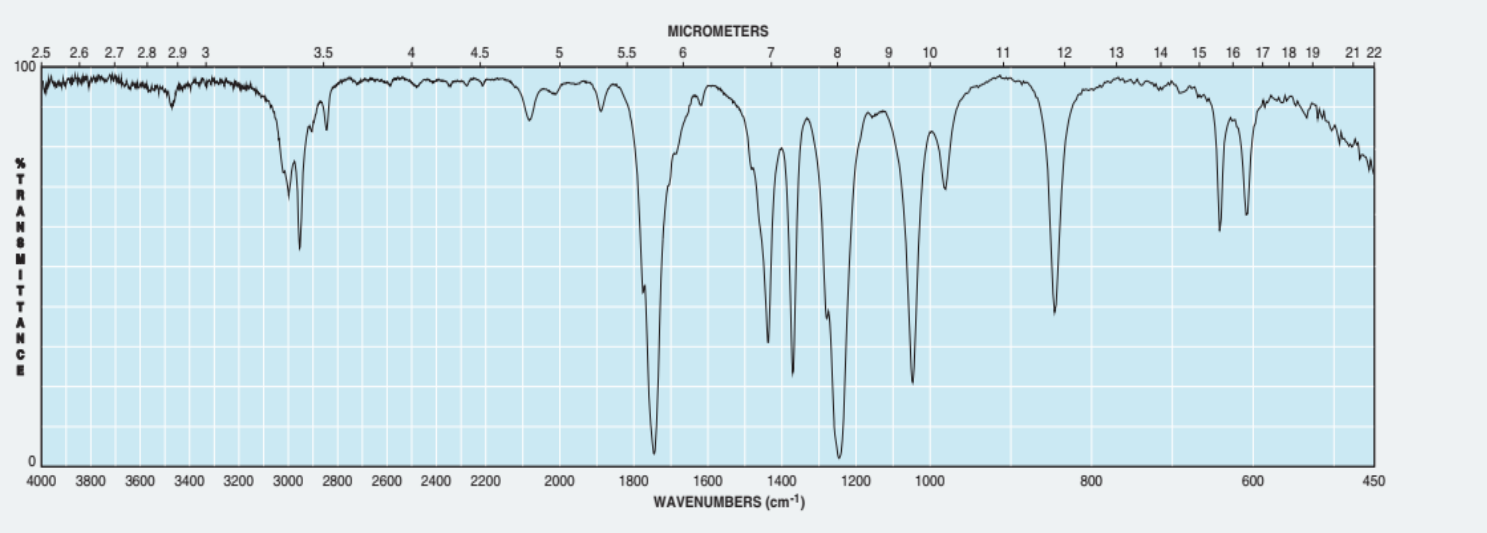
$CH_3CH_2 \equiv CH$ and $CH_3C \equiv C\ CH_3$ ***(2 marks)***

(ii)What is the short-wavelength limit of the continuum produced by an X-ray tube having a tungsten target and operated at 50 kV? ***(2 marks)***

(iii) Calculate the minimum tube voltage required to excite the following lines. The numbers in parentheses are the wavelengths in Å for the corresponding absorption edges.

1. K lines for Ca (3.064) ***(2 marks)***
2. Lα lines for As (9.370) ***(2 marks)***
3. Lβ lines for U (0.592) ***(2 marks)***
4. K lines for Mg (0.496) ***(2 marks)***

b) An unknown compound with the molecular formula $C_3H_6O_2$ yields the following IR

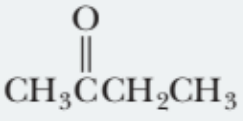


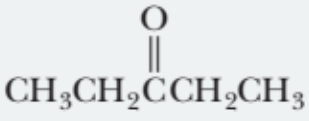
spectrum. Draw possible structures for the unknown. ***(2 marks)***

c) Each of the following compounds gives only one signal in its ^1H -NMR spectrum. Propose a structural formula for each. ***(3 marks)***

(i) C_2H_6O (ii) $C_3H_6Cl_2$ (iii) C_6H_{12}

d) Predict the number of signals and the splitting pattern of each signal in the 1H NMR spectrum of each compound. ***(3 marks)***

(a) 

(b) 

(c) 

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