M. SC. CHEMISTRY EXAMINATION, 2025

(3rd Semester)

PAPER : XII-A

(Analytical Chemistry Special)

Time : *Two Hours* *Full Marks* : 40

(20 *marks for each Unit*)

Use a separate Answer Script for each Unit.

UNIT—3121-A

Answer either **Question No.1** or **Question No.2**

1. *(a)* Explain why $J_{13_{C-H}}$ coupling constant of $-CH_2$-group in $(C_6H_5)_2CH_2$ and $(CH_3)_2CH_2$ differ from their corresponding carbonium ions. 2

(b) How could you identify all possible isomers of the compound $[SnF_4(base)_2]$ from their NMR spectra? [^{119}Sn, $I = ½$]. 3

(c) Availing the following Bloch equation derive the required relation between T_1 and FID height which can be used in IR method :

$$\frac{dM_Z}{dt} = -\gamma(M_x H_1 \sin \omega t + M_y H_1 \cos \omega t) - (M_Z - M_0)/T_1$$

(All symbols have their usual meaning)

Mention all conditions applied while deriving equation. 4+1=5

(d) "While the compound PCl_4F preserves molecular symmetry in the solid state but not PCl_4Ph". Defend the statement on the basis of their NQR spectral results. 2

(e) Explain why four branches of peaks each consists of eleven lines with an intensity ratio 1:2:3:4:5:6:5:4:3:2:1 are obtained in ESR spectrum of bis-salicylaldimine copper(II) complex although fifteen lines are expected for each branch. 4

(f) Enumerate the reasons for Mössbauer spectrum of ^{57}Fe showing multiple lines. 3

(g) What is nutation? 1

2. *(a)* The $[PtBrCl(PR_3)_2]$ ($R = CH_3$) exists in two isomers. How could you identify each of them using NMR spectral measurement? ($I = ½$ for both ^{31}P and ^{195}Pt). 2

(b) Sketch the expected number of ^{19}F NMR spectral lines, including satellites, for $[XeF_5]^-$. [Abundance of ^{129}Xe ($I = ½$ for 26%)]. 2

(c) Write a short note on 'Shift reagent'. 2

(d) Define axial EPR spectrum and how does it look? 2

(c) Taking ν_{CO} as a probe, how will you monitor the oxidative addition reaction in Vaska's compound? 2

(d) How will you prove the occurrence of linkage isomerism in $[Ru(dmso)_6]^{2+}$ (dmso = dimethylsulfoxide) with the help of IR spectroscopy? 2

(e) Justify the infrared stretching frequencies observed for the following isoelectronic species : 2

$[Mo(CO)_6]^+$: 2090 cm^{-1}

$[Cr(CO)_6]$: 2000 cm^{-1}

$[V(CO)_6]^-$: 1858 cm^{-1}

2. *(a)* Discuss what happens when a liquid sample (MX) is aspirated to the flame in AAS? 1½

(b) Write the principle of Hollow Cathode Lamp (HCL) and Electrodeless Discharge Lamp (EDL). 1½+1½=3

(c) Describe the principle of hydride generation technique used for the estimation of As(III)/As(V) mixture. 1½

(d) Write short notes on : 2+2=4

(i) Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

(ii) ICP Torch

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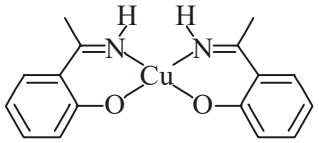
(e) For complex **A**, deuteration of NH protons does not alter the ESR spectrum. How many hyperfine lines will be expected in the EPR spectrum of **A**. [^{63}Cu (I=3/2)]. 2



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(f) A particular Mössbauer nucleus has spins of I = 1/2 and I = 3/2 in its excited and ground states respectively. Show through proper a diagram into how many lines will the γ ray spectrum split if (a) the nucleus is under the influence of an internal electric field gradient but no magnetic field; (b) there is no electric field gradient at the nucleus but an external magnetic field is applied; (c) both an internal electric field gradient and an external magnetic field are present. 4

(OR)

Using suitable equation(s) related to Nuclear Quadrupole Resonance spectroscopy for energies of the 0 and ±1 levels of a nucleus with I = 1 in an asymmetric field, calculate the frequency in terms of e^2Qq and η for the $0 \rightarrow = 1$ and $0 \rightarrow = -1$ transitions. [Symbols have their usual meaning] 4

(g) Answer *any* **two** questions :

(i) With particular reference to Mössbauer spectroscopy, discuss 'Chemical Shift'. How does it help to realize types of bonds present in a series of tin compounds having the isotope ^{119}Sn? 1+2=3

(ii) Draw the Mössbauer spectrum of Fe in $FeSO_4.7H_2O$ and explain it. 3

(iii) What is the cause of splitting of ^{127}I nucleus in the NQR spectrum of HIO_3? 3

(iv) In the bromine NQR spectrum of K_2SeBr_6 one line is obtained at room temperature but two lines at dry ice temperature. What does it indicate about the compound and what is the large significance of this observation? 2+1=3

UNIT—A: 3122a and 3122b

1. Answer the following questions :

(a) Using classical theory, explain the occurrence of Stokes and anti-Stokes Raman scattering. Why are the Stokes lines in the vibrational Raman spectrum of a molecule more intense than anti-Stokes? 3

(b) The selection rule for pure rotational spectrum of a diatomic molecule is $\Delta J = \pm 1$, while that of the rotational Raman spectrum is $\Delta J = \pm 2$. Suggest a reasonable explanation for the observation. 1