

Ex/SC/CHEM/PG/CORE/TH/XII-A/2023

**MASTER OF SCIENCE EXAMINATION, 2023**

(3rd Semester, CBCS)

**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 - A - 3121**

1. Attempt either *A or B*

- A. (i) What is Inversion-Recovery (IR) method? Show how IR method is used for determination of spin-lattice relaxation time ( $T_1$ ). Give the pulse programme used in IR method. 1+3+1
- (ii)  $[\text{SnF}_4(\text{base})_2]$  exists in two isomeric adducts. With the help of NMR spectral measurement how could you identify each of them? [ $^{19}\text{F}$ ,  $I = 1/2$ ;  $^{119}\text{Sn}$ ,  $I = 1/2$ ] 2
- (iii) How could you use  $^{31}\text{P}$  NMR to distinguish between  $\text{PF}_3$  and  $\text{POF}_3$ ? Explain. 2
- (iv) Between  $\text{NH}_3$  and  $\text{NH}_4^+$  which you expect to show sharper  $^{14}\text{N}$  NMR spectrum? Give an explanation in support of your answer. [For  $^{14}\text{N}$ ,  $I = 1$ ] 1

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- B. (i) Discuss the  $^{19}\text{F}$  NMR of  $[\text{TiF}_4]$  in donor solvent at low temperature ( $-30^\circ\text{C}$ ) and high temperature ( $0^\circ\text{C}$ ). 2
- (ii) Discuss the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectrum of the compound  $\text{HPOF}_2$ . 2
- (iii) What are shift reagents? How do they function to modify the NMR spectra? 1+2
- (iv) Discuss the ESR spectrum of (a)  $\text{Co}_3(\text{CO})_9\text{Se}$  (Where  $I=7/2$  for Co), (b)  $\text{K}_3[\text{Mo}(\text{CN})_8]$  (Where  $I=0$  for  $^{94}\text{Mo}$  and  $^{96}\text{Mo}$ ;  $I=5/2$  for  $^{95}\text{Mo}$  (15.78%) and  $^{97}\text{Mo}$ (9.6%) 3

2. Attempt either C or D

- C. (i) With proper explanation compare and contrast the Mossbauer spectra of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ .  $2\frac{1}{2}$
- (ii) With the help of Mossbauer spectroscopy of the  $^{129}\text{I}$  nucleus and use of isomer shift and quadrupole coupling ( $e^2qQ$ ) explain how the structure of  $\text{I}_2\text{Cl}_4\text{Br}_2$  was established. [Given quadrupole splitting parameter  $e^2qQ$  for  $\text{I}_2\text{Cl}_6$  is 3040 while that for  $\text{I}_2\text{Cl}_4\text{Br}_2$  are 3040 and 2916].  $2\frac{1}{2}$
- (iii) Identify number of transitions for an NQR active nuclei having  $I=7/2$  in an axially symmetric field ( $\eta=0$ ). Draw the nuclear quadrupole energy level diagram for the same. What happens to the drawn diagram when asymmetry parameter  $\eta$  has a finite value.  $2\frac{1}{2}$

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- (c) Discuss the standard addition method used to remove matrix interference in AAS. 2
- (d) Write the principle of hollow cathode lamp (HCL). 2
- (e) Describe the principle of hydride generation technique for the estimation of As. 2

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## UNIT - A - 3122

3. Answer the following questions : 2x5

- (a) The fundamental and first overtone bands of  $^{14}\text{N}^{16}\text{O}$  appeared at  $1876.06\text{ cm}^{-1}$  and  $3724.20\text{ cm}^{-1}$ , respectively. Calculate the equilibrium vibration frequency, the anharmonicity and the force constant of the molecule.
- (b) By utilizing appropriate IR data, how will you prove the occurrence of Jahn-Teller distortion in  $[\text{Mn}(\text{DMSO})_6]^{3+}$  (DMSO=dimethylsulfoxide) complex?
- (c) Vibrational measurements of the Raman technique have several advantages over infra-red. Evaluate the correctness of the statement.
- (d) The symmetrical stretching mode of  $\text{CO}_2$  is infrared inactive but Raman active. Explain.
- (e)  $\nu_{\text{NO}}$  stretching frequencies of  $[\text{M}^{\text{II}}(\text{CN})_5(\text{NO})]^{2-}$  (M=Fe, Ru, and Os) are 1938, 1927 and  $1905\text{ cm}^{-1}$ , respectively ... Rationalize the trend.

4. Answer the following questions :

- (a) Discuss what happens when a liquid (MX) aspirates to the flame in AAS.  $1\frac{1}{2}$
- (b) Name the various interferences present in flame AAS. Discuss the chemical interference.  $1+1\frac{1}{2}$

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- (iv) Only one line in the halogen NQR spectrum of the compounds  $\text{K}_2\text{SeCl}_6$ ,  $\text{Cs}_2\text{SeBr}_6$ ,  $\text{K}_2\text{PtCl}_6$  is recorded. What does it indicate? What is the cause of splitting of the  $^{127}\text{I}$  nucleus in the NQR spectrum of  $\text{HIO}_3$ .  $1\frac{1}{2}+1$
- D. (i) While ion-exchange of Sn(II) into zeolite is done, aerial oxidation of tin occurred. It is almost impossible to determine the ratio of Sn(II)/Sn(IV) in zeolite chemically. What experiment do you expect to be of help to estimate the relative amounts of tin (II) and tin (iv) in solid sample? Explain the basic principle of the method.  $1+2$
- (ii) Explain why  $[\text{Co}(\text{NH}_3)_6]^{3+}$  shows NQR resonance for  $^{14}\text{N}$  but not for  $^{60}\text{Co}$  though both the isotopes are having quadrupole nuclei (satisfying the condition  $I \geq 1$ ).  $2$
- (iii) Four branches of peaks each consists of eleven lines with the intensity ratio  $1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1$  are obtained in the EPR spectrum of bis-salicylaldimine copper (II) complex although a total of sixty lines are expected. Explain why? [For  $^{63}\text{Cu}$ ,  $I=3/2$ ]  $3$
- (iv) Derive the energy level diagram for nuclei with spins  $I=5/2$  and  $7/2$  in axially symmetrical systems. Show all possible NQR transition(s) in each case assuming the selection rule,  $\Delta m_1 = \pm 1$ .  $2$

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