Course Number: CHEM F313   Course Title: Instrumental Methods of Analysis   Marks: 40
Time: 60 min   Comprehensive Test (Closed Book)   Date: Dec. 30, 2022
Paper I

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1. **Answer all the questions**
2. **Answers written within the box will be considered only**
3. **Each question carries one marks and for every two wrong answers 1 marks will be deducted**
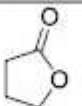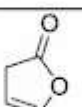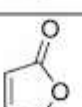4. **Maximum time is 75min**

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Name: ID:

Right answer ☐   **Wrong answer** ☐   **Obtained marks** ☐

_____

Q1. Match the structure of the compound with the carbonyl stretching frequency.

Column A		Column B	
P.	[structure]	X.	1750 cm^{-1}
Q.	[structure]	Y.	1770 cm^{-1}
R.	[structure]	Z.	1800 cm^{-1}

Choose the correct option.

(A) P-Y, Q-Z, R-X;   (B) P-Y, Q-X, R-Z;   (C) P-Z, Q-Y, R-X;   (D) P-X, Q-Z, R-Y   ☐

Q2. The number of signals that appear in the broadband decoupled ^{13}C NMR spectrum of phenanthrene and anthracene, respectively are
(A) 10 and 4;   (B) 10 and 10;   (C) 7 and 4;   (D) 7 and 7   ☐

Q3. The magnetic moment for a spinning nucleus (μ_N) and spinning electron (μ_e), respectively are as follows:
(A) $-g_N\beta_N I_z$ and $g_e\beta_e I_z$;   (B) $g_N\beta_N I_z$ and $-g_e\beta_e I_z$;   (C) $-g_N B_0 I_z$ and $g_e B_0 I_z$; (D) $g_N\beta_N I_z$ and $-g_e B_0 I_z$ (β_N & β_e are the nuclear magneton and Bohr magneton, for the nucleus and electron, respectively; B_0 = applied magnetic field; other symbols are usual notations)   ☐

Q4. Choose the correct option (used symbols denotes the usual notations):
(A) Larmor frequency = $(g_N B_z)/2\pi I = \mu_N \beta_N B_z / h$;   (B) Larmor frequency = $(\mu_N B_z)/2\pi I = g_N \beta_N B_z / h$;
(C) Larmor frequency = $(g_N B_z)/I = \mu_N \beta_N B_z / h$;   (D) Larmor frequency = $(\mu_N B_z)/I = g_N \beta_N B_z / h$;

☐

Q5. Choose the correct option:
- (A) In case of magnetic anisotrophy, the regions where the induced magnetic field is opposed by the applied magnetic field is called the diamagnetic zone and the protons get deshielded in this zone
- (B) In case of magnetic anisotrophy, the regions where the induced magnetic field is opposed by the applied magnetic field is called the paramagnetic zone and the protons get shielded in this zone
- (C) In case of magnetic anisotrophy, the regions where the induced magnetic field is opposed by the applied magnetic field is called the paramagnetic zone and the protons get deshielded in this zone
- (D) In case of magnetic anisotrophy, the regions where the induced magnetic field is opposed by the applied magnetic field is called the diamagnetic zone and the protons get shielded in this zone

Q6. Choose the correct option:
- (A) While recording the ^{13}C NMR spectrum, the both coupling of ^{13}C-^{13}C and ^{13}C-^{1}H are removed by broadband coupling technique
- (B) While recording the ^{13}C NMR spectrum, the both coupling of ^{13}C-^{13}C and ^{13}C-^{1}H are removed by broadband decoupling technique
- (C) While recording the ^{13}C NMR spectrum, the only coupling of ^{13}C-^{13}C is removed removed by broadband coupling technique
- (D) While recording the ^{13}C NMR spectrum, the only the coupling of ^{13}C-^{1}H is removed by broadband decoupling technique

Q7. Which of the following quantities is not changed at a different magnetic field strength:
- (A) Chemical shift (in hertz)
- (B) Nuclear spin population in an energy state
- (C) J coupling constant
- (D) Energy difference between two energy states of nuclei with non-zero spin quantum number

Q8. In a magnetic field, nuclear dipoles (nuclear spins with a spin quantum number of 1 2)
- (A) Precess around the magnetic field direction with random frequency
- (B) are motionless along the direction of the magnetic field
- (C) do not exist
- (D) precess around the magnetic field direction at the Larmor frequency

Q9. Which of the following electromagnetic radiation used in ESR?
- (A) IR radiation; (B) Radio waves; (C) Microwaves; (D) X-ray radiation

Q10. The hyperfine splitting in an ESR spectra observed (given below) may be due to single nuclei of
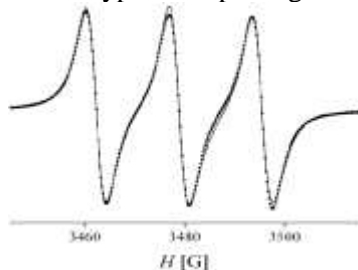
(A) ^{1}H; (B) ^{19}F; (C) ^{14}N;(D) ^{13}C

Q11. The hyperfine splitting pattern that can be observed with three equivalent protons:
- (A) 1 : 1; (B) 1:2:1; (C) 1:3:3:1; (D) 1:1:1:1

Q12. ESR sensitivity increases with _____temperature and with _____magnetic field strength.
- (A) Increasing, increasing; (B) Increasing, decreasing; (C) Decreasing, decreasing; (D) Decreasing, increasing

Q13. ESR involves detecting of a physical phenomenon of _____electromagnetic radiation.
- (A) Adsorption; (B) Absorption; (C) Radiation; (D) Reflection

Q14. Unit for measurement of hyperfine splitting constant in ESR is

(A) Gauss / mm;   (B) Tesla/sec;   (C) Gauss;   (D) No units

Q15. Glass transition temperature is related to a transition of
(A) One form of amorphous to another form of amorphous; (B) Amorphous to Crystalline;
(B) Crystalline to Amorphous; (D) One form of crystalline to another form of crystalline

Q16. DTA records the
(A) Absolute temperature variation of the sample with the temperature of reference
(B) Temperature difference of sample and reference with the temperature of reference
(C) Enthalpy change of the sample with the temperature of reference
(D) Enthalpy change of the sample and reference with the temperature of reference

Q17. In a TGA plot, it was seen two observations (i) initially it shows parallel to X-axis; (ii) then the line comes down with a slope. What these represents?
(A) (i) compound is stable; (ii) compound is losing some part of it
(B) (i) compound is unstable; (ii) compound is losing some part of it
(C) (i) compound is stable; (ii) compound is gaining some part of it
(D) (i) compound is unstable; (ii) compound gaining some part of it

Q18. The temperature difference between sample and reference in DTA is measured using
(A) Thermister;   (B) Thermocouple;   (C) Voltmeter;   (D) Ammeter

Q19. Melting and oxidation peaks in DTA are
(A) Exo and exo;   (B) Endo and exo;   (C) Endo and endo;   (D) Endo and exo

Q20. DSC curves are used to check the purity of drugs and polymers. How it is determined?
(A) By studying dimensional changes; (B) By analyzing gases formed in the thermal analysis
(B) By studying melting point; (D) By studying oxidative stability

Q21.

M	Working Electrode	X	potential is varied linearly with time
N	Reference electrode	Y	Serves as source or sink for electrons
Q	Counter electrode	Z	potential remains constant with time

Choose right combinations for all cases:
(A) MY; NX; QZ;   (B) MZ, NY, QX;   (C) MX, NZ, QY;   (D) MX, NY, QZ

Q22. Primary use of cyclic voltammetric is
(A) Quantitative analysis;   (B) Qualitative analysis;
(C) Study the mechanism of redox process;   (D) Structural analysis

Q23. For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46V at 25°C. The value of the standard Gibbs energy, $\Delta°G$ will be (F = 96500coulomb mol^{-1}).
(A) -98kJ;   (B) -98J;   (C) 89kJ;   (D) -89kJ

Q24. The electrode potentials for
$Cu^{2+}(aq) + e \rightarrow Cu^{+}(aq)$ and $Cu^{+}(aq) + e \rightarrow Cu(s)$ are +0.15V and +0.5V, respectively. The value of $E°_{Cu2+/Cu}$ will be
(A) 0.65V;   (B) 0.15V   (C) 0.50V   (D) 0.325V

Q25. In atomic absorption spectroscopy with what material is the cathode in hollow cathode lamp constructed?
(A) Tungstein;   (B) Quartz;   (C) Elements to be investigated;   (D) Aluminium

Q26. Choose the correct sequence in flame photometry
(A) Desolvation, Excitation, Atomization, Emission; (B) Atomization, Desolvation, Excitation, Emission
(C) Atomization, Excitation, Desolvation, Emission;   (D) Desolvation, Atomization, Excitation, Emission

Q27. Which of the following is the principle of atomic absorption spectroscopy?
(A) Radiation is absorbed by non-excited atoms in vapour states and are excited to higher state
(B) Medium absorb radiation and transmitted radiation is measured
(C) Colour is measured; (D) Colour is simply observed

Q28. The correct order for the basic features of a mass spectrometer is

3

(A) Acceleration, Deflection, Detection, Ionization; (B) Acceleration, Ionization, Deflection, Detection
(C)Ionization, Acceleration, Deflection, Detection; (D) Ionization, Acceleration, Detection, Deflection

Q29. The base peak in a mass spectrum is
(A) The peak corresponding to the parent ion;   (B) The lowest mass peak
(C)The peak set to 100% relative intensity;   (D) The peak showing molecular weight of a compound

Q30. Which of the following statements is wrong?
(A) The energy required for removing an electron from a molecule varies in the given order: lone pair < conjugated electron < non conjugated electron
(B) Isotopic ratio is particularly useful for the detection and estimation of number of S, Cl and Br atoms in the compound
(C) Neutral fragments and molecules do not get detected in the detector in mass spectroscopy
(D) The most intense peak in the mass spectroscopy is called the molecular ion peak

Q31. The Raman spectrum is said to consist of anti-stokes line when
(A) $\Delta\upsilon = 0$; (B) $\Delta\upsilon > 0$; (C) $\Delta\upsilon < 0$; (D) either $\Delta\upsilon > 0$ or $\Delta\upsilon < 0$ (υ = wavenumber)

Q32. Raman Scattering is observed because of
(A) Atmospheric scattering; (B) Rayleigh scattering; (C) Elastic collision; (D) Inelastic collision

Q33. In IR spectrum, the absorption band corresponding to the transition from v=0 to v=2 is called as
(A) Fermi resonance; (B) Overtone; (C) Fundamental absorption band; (D) Combination band

Q34. Which of the following shows bathochromic shift in polar solvents?
(A) Water;   (B) Ethanol;   (C) Ethylene;   (D) Chloroform

Q35. Two samples each containing same analytes at equal concentration are irradiated with I and 2I intensities of radiation. Choose the correct option regarding the absorbances of A1 (irradiated at I) and A2 (irradiated at 2I).
(A) A2 = 4A1; (B) A2 = 2A1; (C) A2=A1; (D) A2=1/2A1

Q36. Which one is the incorrect option.
(A) Absorptivity varies with changing the wavelength
(B) Absorptivity varies with changing the intensity of light
(C) Absorptivity varies with changing the temperature
(D) Absorptivity varies with nature of the compounds

Q37. Anti-Kasha's rule describes the following transition.
(A) S_1 to S_0;   (B) S_2 to S_0;   (C) S_1 to T_1;   (D) T_1 to S_0

Q38. Which one is the correct expression of quantum yield (Q) and excited state life time (t) of a fluorophore
(A) Q = kr / (kr + knr)   and t = 1 / (kr + knr);   (B) Q = kr / (kr + knr)   and t = 1 / kr;
(C) Q = 1 / (kr + knr)   and t = kr / (kr + knr);   (D) Q = 1 / (kr + knr)   and t = 1 / kr

Q39. In the Stern-Volmer equation,

$$\frac{F_0}{F} = 1 + k_q\tau_0[Q]$$

(A) k_q = Stern-Volmer constant and τ_0 = quenched life time;
(B) k_q = Bimolecular quenching constant and τ_0 = quenched life time
(C) k_q = Stern-Volmer constant and τ_0 = unquenched life time
(D) k_q = Bimolecular quenching constant and τ_0 = unquenched life time

Q40. Lippert-Mataga equation cannot measures
(A) the difference between the maxima of the absorbance and emission spectra of a fluorophore
(B) the difference of dipole moment of excited and ground electronic states of a fluorophore
(C) the excited state life-time of a fluorophore
(D) the sensitivity of a fluorophore towards solvent polarity

-END-

Answer all the questions:

Q1. (i) The chemical shift of the CH_3 protons in acetaldehyde is $\delta = 2.2$ and that of the CHO is 9.8. What is the difference in local magnetic field between the two regions of the molecule when the applied field is 15T (consider, difference in shielding constant $(\Delta\sigma) \approx$ difference in chemical shift $(\Delta\delta)$?

(ii) Calculate the magnetic field at which ^2H come into resonance at 250MHz (data for ^2H: $g_N = 0.85745$; $\mu_N = 5.0508$ x 10^{-27} JT^{-1})   **[3M+ 3M]**

Q2. (i) The centre of the EPR spectrum of atomic hydrogen lies at 329.12mT in a spectrometer operating at 9.2231GHz. What is the g-value of the electron in the atom ($\mu_B = 9.27402$ x 10-24 JT^{-1})

(ii). Determine the (a) number of EPR lines and (b) intensity distribution of $^{\cdot}CD_3$ (radical).

(iii) Sketch and demonstrate (in one line) the EPR spectrum of XH_2 radical (I for X = 5/2; odd electron remains on X) (each transition should be shown by line only; derivative plot should be avoided)   **[3M + 3M + 4M]**

Q3. TGA thermogram is shown for $CuSO_4 5H_2O$ complex. It shows a total four distinct losses which is shown below.
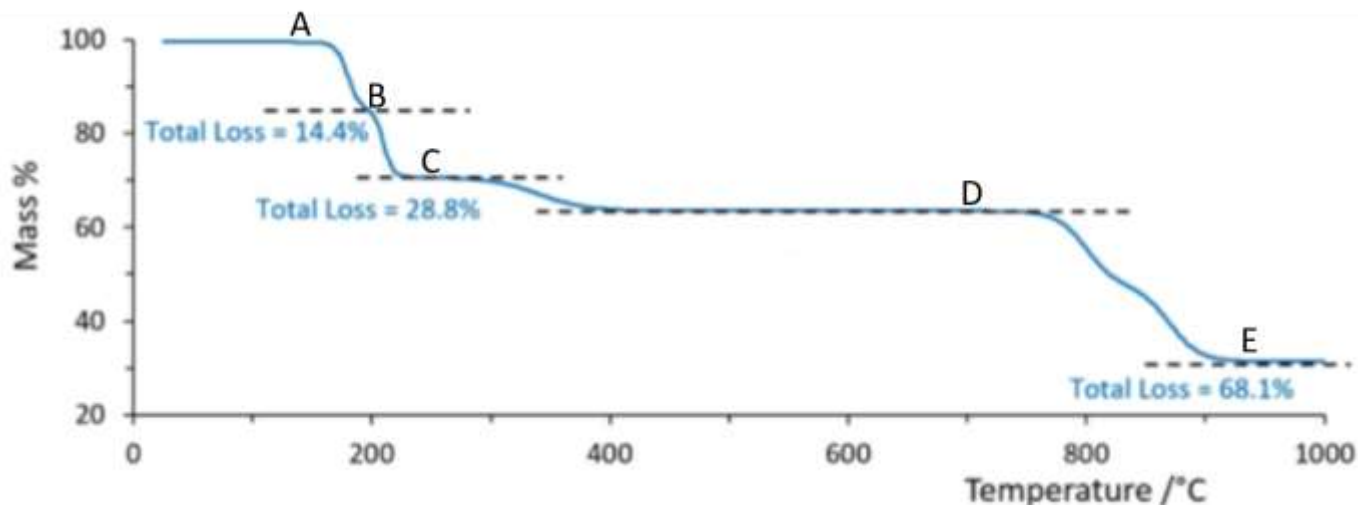
Here, A = $CuSO_4 5H_2O$ and the loss from A to B = 14.4%, loss from A to C = 28.8% and loss from A to E = 68.1%.
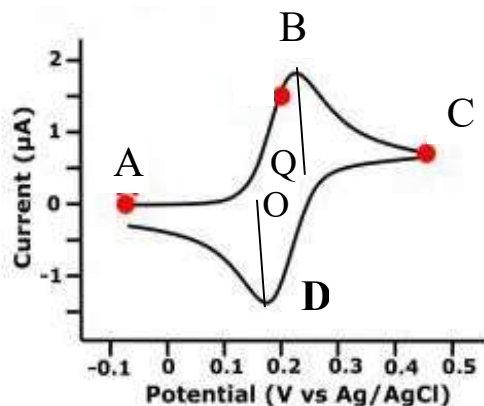**(i)** Find out the molecular formula at B, C, D and E (write the compounds inside the box drawn at the answerscript).

Molecular formula at B	Molecular formula at C	Molecular formula at D	Molecular formula at E

?	?	?	?

(ii) Calculate the expected total percent loss from A to D.   **[4M + 2M]**

**Q4.** The cyclic voltammogram of a redox couple is shown below:

Answer the following questions.

Show the **(i) (a)** anodic peak potential; **(b)** cathodic current; **(c)** Switching potential; **(ii) (a)** oxidation peak;

(b) cathodic trace (represents these by the alphabets indicated in the cyclic voltammogram). **[1.5M + 2M]**

Q5. **(i)** State the principle of Atomic Absorption Spectroscopy (AAS) (3 points); **(ii)** Write the specific function of

nebulizer used in AAS (in one line).   **[2M + 1M]**

Q6. (i) The mass spectrum of 4-methyl-3-pentene-2-one is given below. Determine the molecular formula of the

fragmented masses corresponding to 83, 55 and 43.
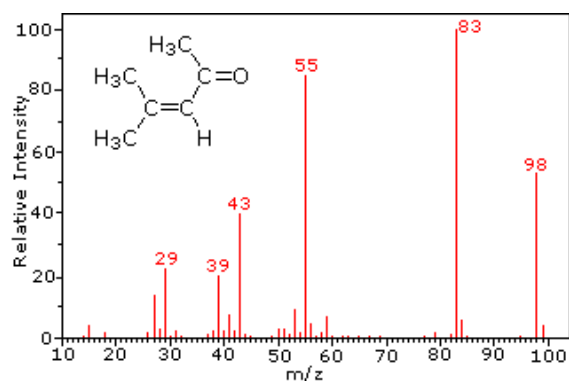
(ii) The mass spectrum of bromine is given below. There are five peaks are observed. Identify each of the five species as per their observed masses. **[1.5 + 5M]**
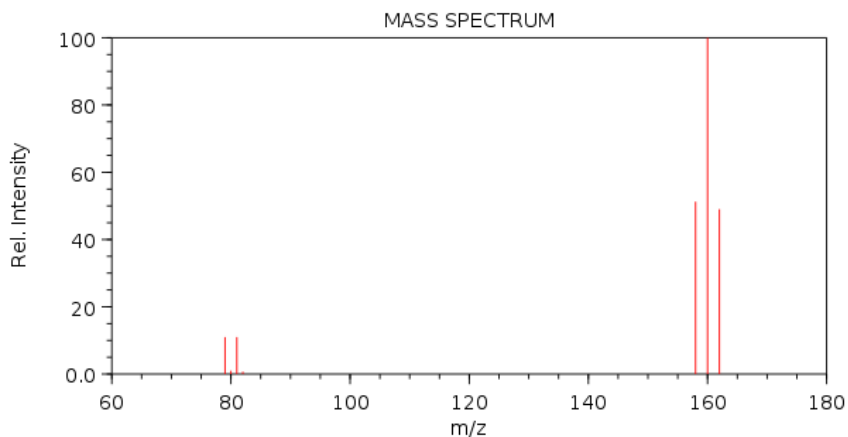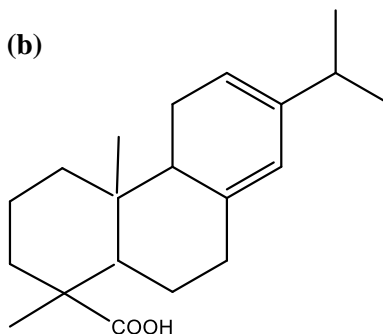

Q7. (i) The excitation wavelength of LASER in a Raman effect experiments is 546nm if the Stokes line observed at 552nm, then determine the wave number of anti-stoke line (in cm^{-1}).

(ii) Calculate the absorption positions of the following compounds using Woodword-Fieser rule.
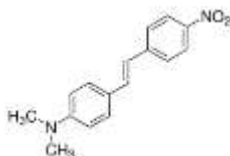
(a)
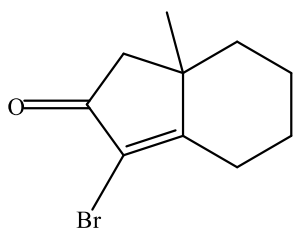
(b)

[3M + (3M + 3M)]

Q8. The chemical structure of a fluorophore molecule is given below. The absorption and emission spectra of this molecule was recorded in hexane and acetonitrile and the observed peak in acetonitrile is red-shifted in both cases. It is observed that the shifting of emission peak in these two solvents is higher than the shifting in absorption peak in the same solvents. **(i)** Show the time frame for absorption, vibrational relaxation and fluorescence in hexane and acetonitrile by drawing the Jablonski diagram. **(ii)** Why does the shifting of emission peak is higher than the shifting in absorption peak?

[4M + 2M]

END