

Birla Institute of Technology and Science, Pilani, Rajasthan 333031

Midsemester Examination 1st Semester, 2023-2024

CHEM F313: INSTRUMENTAL METHODS OF ANALYSIS

Max. Marks: 25

Time: 45 minutes

Close Book

Date: 07.12.2023

Instructions to the students:

1. There are **three questions** in all. Attempt all the questions in **separate answer sheet**.
2. Start answering each question on a fresh page. **Answer all parts of a question together**.
3. **In a derivation write all the in between steps. In case of missing steps, marks will be deducted.**
4. Write brief answers to the point with proper justifications.
5. Do not exchange your calculator.

$$E^0_{\text{Mg}^{2+}/\text{Mg}^+} = -2.36\text{V}, E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{ V}; F = 96500\text{ C/mol}$$

1. Draw the comparative TGA and DSC curves with proper labelling, clearly showing melting and evaporation processes. [2M]
2. 'Acetylenic protons of R-C≡C-H appear at up field than ethylenic protons of R-CH=C-H in ¹HNMR Spectrum'-justify in two sentences. [2M]
3. The presence of two neighbouring protons in a molecule causes 1:2:1 splitting (¹HNMR). Explain the origin of the splitting. [2M]
4. An organic compound with molecular formula, C₃H₃Cl₅ gave the following ¹HNMR data. (a) a triplet 5.48 τ, (b) a doublet 3.93 τ, 2H. Draw a possible structure with explanation based on the data. [2M]
5. Predict the number of peaks in the ESR spectrum of radical anion of benzene and draw. [2M]
6. Can you separate NaCl and Na₂SO₄ from a mixture using chromatography? How? [2 M]
7. Write down the cell notation for the given reaction and find out the change in free energy at 25 °C. $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$ [2M]
8. Show the variation in 'Voltage' vs 'Time' plot in linear sweep voltammetry with change in scan rate. What is normal pulse voltammetry (NPV)? [2M]
9. Which factors alter the peak current of cyclic voltammetry analysis? If the scan rate is 50 mV/sec and the observed peak current is 76 mA, which scan rate will you maintain to get the peak current 32 mA? [3M]
10. Schematically show how you can purify water from the contamination of As³⁺ using a chromatography technique. [3M]
11. Write down schematically the working process of Atomic absorption spectroscopy. [3M]

*****The END*****

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$k =$ Boltzmann constant ($= 1.38 \times 10^{-23} \text{ J K}^{-1}$), $h = 6.626 \times 10^{-34} \text{ J s}$, atomic mass of Cl = 35.459, H = 1.007, 1 amu = $1.66054 \times 10^{-27} \text{ kg}$

1. (a) Give an example of an organic compound which show all the possible electronic transitions. Compare the intensity of the transitions of 'K' and 'R' bands of the compound and justify your answer. Now if you increase the solvent polarity do you expect any change in the transition energies of those two bands? Justify your answer.

[6M]

- (b) While the addition of one methyl group in '3' position of 3-pentene-2-one results in a bathochromic shift, the addition of one methyl group in '2' position of biphenyl results in a hypsochromic shift in UV-vis absorption spectra. Justify your answer. [3M]

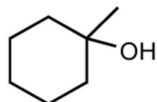
(c) If acetylene shows two C-H stretching vibrations, a symmetrical one at 3374 cm^{-1} ($\overleftarrow{\text{H-C}} \equiv \overrightarrow{\text{C-H}}$) and an unsymmetrical one at 3287 cm^{-1} ($\overrightarrow{\text{H-C}} \equiv \overleftarrow{\text{C-H}}$),

(i) Which of these vibrations will be Raman active and why?

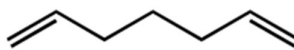
(ii) Calculate the Raman wavelengths for a 4358 \AA exciting line. [4M]

- (d) (i) Determine the number of vibrational modes in each of the following molecules. SO_2 , NO_2^+ , and NO_2 . (ii) Calculate a theoretical absorption frequency in wave numbers for a C-H bond, assuming a force constant of $4.89 \times 10^2 \text{ N/m}$. Calculate the absorption frequency if you substitute hydrogen by deuterium? [5M]

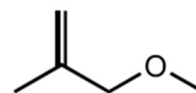
- (e) For each of the following compounds, draw an isomer that differs in functional groups and can be distinguished by IR spectroscopy. Justify in one sentence each. [6M]



(I)

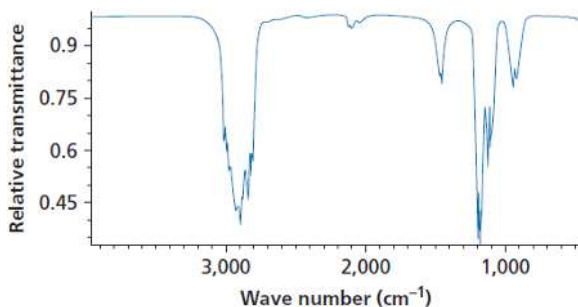


(II)



(III)

- (f) The spectrum shown below belongs to a compound with the formula $\text{C}_2\text{H}_6\text{O}$. Determine the identity of the compound and justify. [3M]



2. (a) A compound with molecular formula, $C_6H_{12}O_2$ shows following four signals: singlet 1.1δ (6H), singlet 2.1δ (3H), singlet 2.6δ (2H), and singlet 3.9δ (1H). It shows an absorption at 1720 cm^{-1} in IR spectrum. Predict a possible structure consistent with given data and explain. [3M]
- (b) Show various fragmentations of methyl butanoate and 3-methyl cyclohexene in Mass analysis. Determine the structure of a compound whose m/e values in mass spectrum are 100, 85, 71, 57, 43(base), 41, 29, 27. [8M]
- (b) (i) Determine the wavelength of X-Ray that causes first order diffraction on [220] planes of gold (Au, cubic system) at $\theta = 5^\circ$ (lattice parameter of Au = 5.23 \AA). (ii) When would you observe a peak shift to a higher angle? (provide two reasons with proper justification) (iii) Why peak broadening is observed in XRD analysis? [7M]
- (c) Suppose you have measured the fluorescence quenching of a solution of tyrosine in presence of quencher iodide ion, which obeys Stern-Volmer equation. Determine the Stern-Volmer Quenching constant using the following data. [5M]

[I ⁻] (M)	0.048	0.076
F/F ₀	0.678	0.512

3. (a) The characteristic yellow emission of potassium vapours consists of a pair of lines at 766.5 nm and 769.9 nm. These arise from the emission of radiation by the gaseous potassium atoms in the 4p excited state to 4s ground state at 3000 K. Find out the number of potassium atoms in the excited state if the number of atoms in the ground state is 5.098×10^{18} . Find out intensity of emitted radiation if the proportionality constant value is 2×10^{19} . [5M]
- (b) (i) Plot the differential thermal analysis curve for an inorganic compound if it undergoes dehydration at 100°C , oxidation at 400°C and melting at 800°C , successively. (ii) How would you distinguish between $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 based on thermogravimetric analysis? Justify your answer. [6M]
- (c) Write down all the involved steps for the separation of NaX, ZnX_2 and AlX_3 from a mixture using a chromatography technique. [5M]
- (d) Write all the associated steps for a cyclic voltammetry experiment to determine unknown concentration of Ascorbic acid which shows an irreversible oxidation peak at 0.6 V vs. Ag/AgCl. [5M]
- (e) Write the significance of R_f value in thin layer chromatography. Why in EPR, the first derivative plot is used but not in NMR? [4M]

*****The END*****