Loughborough University

Structural Characterisation, Spectroscopy and Analysis

22CMB104

Semester 1 2022/23 In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **2 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

Help during the exam

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

1. a) Turmeric has recently gained interest for its possible anti-inflammatory properties, particularly in the treatment of arthritis. The darker the orange colour, the more active the material is claimed to be. Unfortunately, the growing market for turmeric has resulted in the natural yellow material being cut with red pigments to make it look more orange. The most common diluents used are the toxic lead oxide (Pb_3O_4) crystallising with a body-centred structure and the non-toxic (γ-Fe_2O_3) crystallising with a face-centred structure.

(i) Draw a body-centred cubic unit cell and mark on the 123 plane.

[3 marks]

(ii) While turmeric is normally amorphous, both red diluents used to make the material more marketable are crystalline. The powder diffraction pattern of turmeric collected with iron radiation of wavelength 1.936 Å gives the following reflections:

23.21, 26.86, 38.35, 45.30, 47.44, 55.35, 60.82, 74.23, 86.78, 100.76°

Index the data, determine the lattice type, and hence determine whether the turmeric is safe to use. [12 marks]

b) Sr_2FeO_4 crystallises with a body-centred tetragonal unit cell where a = 3.860 Å and c = 12.39 Å

(i) Draw a primitive tetragonal unit cell and mark on the 110 plane.

[3 marks]

(ii) What are the two equivalent positions in a body-centred unit cell?

[2 marks]

(iii) Given the fractional coordinates of iron is at (0,0,0) and the two oxygen are at (0,½,0) and (½,½,0.3427). Determine the two different Fe–O bond lengths and the coordination geometry of the iron. [5 marks]

2. a) An organic addition reaction is attempted in which $Ni(acac)_2$ is used as a catalyst. A slow evaporation of the reaction solution results in green/blue crystals. Sketch the apparatus used for a slow evaporation crystallisation and describe the pros and cons of this method of crystallisation. [4 marks]

b) The crystallisation described in (a) produced the coordination compound $[Ni(acac)_2(MeOH)(OH_2)]$ (FW = 306.98 g mol^{-1}) which crystallised with unit cell dimensions: a = 10.6500, b = 5.1496, c = 12.3686 Å, β = 106.470°. The density is 1.567 g cm^{-3}.

(i) Calculate the unit cell volume. [2 marks]

(ii) State the crystal system with a brief justification. [2 marks]

(iii) Calculate the number of nickel complex molecules per unit cell and hence say how this calculation strongly suggests there is no solvent of crystallisation. $N_A = 6.022 \times 10^{23}$. [4 marks]

(iv) For each Ni ion at position x, y, z in the unit cell, the space group symmetry requires that there is another at –x, y+½, –z. Construct a Patterson vector table for this space group. [4 marks]

Continued…

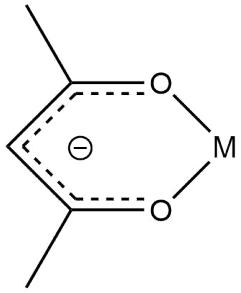
(v) In this space group, the y coordinate can take any value. Use your vector table and the list of largest Paterson peaks in the table below to determine the x and z coordinates ONLY for all of the Ni ions within the unit cell.

[5 marks]

Peak	Coordinates			Relative height	Vector length /Å
	x	*y*	*z*		
1	0.0000	0.0000	0.0000	999	0
2	0.9797	0.5000	0.4228	332	5.89
3	0.1395	0.2204	0.0940	106	1.97
4	0.8747	0.1755	0.0687	104	1.99
5	0.0323	0.2704	0.1203	85	1.99

(vi) The mode of coordination of acac to a metal ion is shown in the figure below. Use this information and the chemical formula from part (b) to sketch the two possible isomers for this metal complex. On your sketches indicate the likely vectors associated with peaks 3, 4, and 5.

[4 marks]



3. In this question you will need to use the following equation.

$$D = \frac{K_D[H_3O]^+}{K_a + [H_3O]^+}$$ Equation 1

a) Aspirin (Acetylsalicylic acid) is a weak acid which has an acid dissociation constant K_a of 2.8 × 10^{-4}. In a suspected poisoning case, you have been asked to extract aspirin from an aqueous sample medium (plasma) using liquid/liquid extraction with diethyl ether before analysis by gas chromatography. The distribution coefficient K_D which describes the partitioning of aspirin between diethyl ether and water is 3.5.

Plot a graph which shows how the Distribution ratio (D) varies with pH, and using this information suggest what pH should be used for the extraction giving clear justification for your decision. [13 marks]

b) The analysis method for the extracted aspirin uses gas chromatography.

(i) Sketch a schematic diagram of the gas chromatograph system you would use for this analysis. [6 marks]

(ii) Illustrate, using a labelled diagram, the essential features of the detector you would propose for the analysis of the aspirin extract; justify your selection of detector. [6 marks]

4. a) A 6-coordinate, octahedral transition metal complex (**A**) was found to have a magnetic moment of 5.95 BM.

(i) What would you expect to see in terms of d-d transitions in the UV/visible spectrum of (**A**)? [3 marks]

(ii) How would this spectrum change if the complex underwent a one electron reduction reaction to give a new octahedral complex (**B**)? [2 marks]

(iii) How would this spectrum change again if complex (**B**) was further reduced by addition of one more electron, giving a new octahedral complex (**C**)? [5 marks]

b) The mixed metal oxide system $CuMn_2O_4$ is a synthetic spinel material containing Cu^{2+} ions. Show whether crystal field stabilization arguments can be used to definitively predict whether this would be a “normal” or “inverse” spinel arrangement. For the purposes of your answer, assume $\Delta_t = 0.5\ \Delta_o$ and that all metal ions are high spin. [10 marks]

c) Fully account for the fact that while zinc sulfate, $Zn(SO_4)$, is colourless, zinc chromate, $Zn(CrO_4)$, is an intense yellow pigment. [5 marks]

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