

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHIN 433: INDUSTRIAL PHYSICAL METHOD OF ANALYSIS

STREAMS:

TIME: 2 HOURS

DAY/DATE : WEDNESDAY 22 /09/ 2021

2.30 PM – 4.30 PM

INSTRUCTIONS TO CANDIDATES:

- Answer Question One and any other Two Questions.
- DO NOT WRITE ANYTHING on the question paper.

1.a) (i) Compute the number – average molecular weight for a polystyrene for which the degree of polymerization is 26,000. [1

Mark]

(ii) Explain how the intrinsic viscosity of a polymer can be measured. [3 Marks]

(iii) Calculate the relative viscosity, specific viscosity and reduced viscosity of a 0.5% prepared by dissolving 0.25g of polymer in 50ml of solvent solution and the time for solvent flow between the two appropriate marks was 60s. The time of flow for the solution was 80s.

[3 Marks]

(iv) Outline four conditions required when determining the molecular weight of polymer sample in monomeric or multimeric state solution using small angle x-ray scattering techniques.

[2 Marks]

(v) Write short notes on size exclusion chromatography and its application in polymer science.

[3

Marks]

- (vi) Why is it not possible to have a poly (methyl methacrylate) homopolymer with the following molecular data and of polymerization of 530?

Molecular weight	wi	xi
Range (g/mol)		
8,000 – 20,000	0.02	0.05
20,000 – 32,000	0.08	0.15
32,000 – 44,000	0.17	0.21
44,000 – 56,000	0.29	0.28
56,000 – 68,000	0.23	0.18
68,000 – 80,000	0.16	0.10
80,000 – 92,000	0.05	0.03

The poly (methyl methacrylate) homopolymer consist of each repeat unit having five carbons, eight hydrogens and two oxygens. [3 Marks]

- b (i) Thermogravimetric studies of carbon black filled rubber sample is performed in inert atmosphere upto 950^oc and then quickly changing the atmosphere to air. The observed weight loss is – 66.41% up to 500^oc and the mass becomes constant and further the mass loss between 1300^oc to 2800^oc. Predict the composition of rubber.

[1 Mark]

- (ii) The TGA and DTA data manganese phosphate monohydrate are shown in Table.

TGA	150 ^o C (-H ₂ O)	360 ^o C (-PH ₃)	800 ^o C (-H ₂ O)	NIL	NIL
DTA	160 ^o C (endo)	375 ^o C (exo)	850 ^o c (endo)	590 ^o c (exo)	1180 ^o (exo)

Explain the probable transition of unidentified peaks in TGA. [4 Marks]

- (iii) A mixture of CaCO₃ and CaO is analysed using TGA technique. TG Curve of the sample indicates that there is a mass change from 145.3mg to 115.4 mg between 500 – 900^oC. Calculate the percentage of CaCO₃ in the sample. [3 Marks]

- (iv) State the differences between differential thermal analysis (DTA) and Differential scanning calorimetry. [1 Mark]
- (v) Explain how thermo gravimetric analyzer Gas chromatography/mass spectrometer (TGA – GC/MS) can be used for identification of the components in the sample. [2 Marks]
- (vi) List six common instrumental factors affecting TG curves.

QUESTION TWO (20 MARKS)

- 2a (i) Discuss basic principles and apparatus for Differential thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) [6 Marks]
- (ii) Explain how calibration and interpretation of the DTA and DSC curves are achieved. [8 Marks]
- b) (i) An unknown compound (x) was analyzed by simultaneous TG / DTA in nitrogen. The final residue corresponding to weight loss of 72.5% as measured from the TG curve, was then identified as CoO by x-ray diffraction using the JCPDS reference file. Additional information obtained by EGA-MS revealed that in the first two steps ($1 \Rightarrow 2$ and $2 \Rightarrow 3$ only water was expelled while in the step $3 \Rightarrow 4$ SO₂ and SO₃ were involved in a molar ratio 1:2.

Based on these data calculate the composition of the unknown compound and write the reaction mechanism resolved. [4 Marks]

- b (ii) Explain how thermodilatometry (TD), thermomechanical analysis (TMA) and Dynamic mechanical analysis (DMA) techniques differ in principle from each other. [1½ Mark]
- (iii) Justify the following statement “In situ high -temperature is a true thermoanalytical method”

QUESTION THREE (20 MARKS)

- 3a (i) Discuss characteristic features of neutron activation analysis using a nuclear reactor in relation to other trace analytical methods. [6 Marks]
- (ii) Outline performance characteristics of gamma-ray spectrometers system. [1 Mark]
- (iii) In counting of two samples and background, following data were recorded sample I yielded 4127 counts for 10 min. Sample II 24894 counts for 5 min and the background measurements 2276 counts for 10 min. Calculate the absolute and relative standard deviation of the net counting rates of sample I and sample II. [6 Marks]
- (iv) Explain how activation neutron analysis can be calibrated for quantitative analysis using relative method. [3½ Marks]
- b. Arsenic is determined in high purity silicon by NAA via the $^{75}\text{AS} (n, \gamma) ^{76}\text{As}$ reaction. For this purpose, the silicon sample and standard are irradiated in a nuclear reactor. The experiment and parameters and the physical constants are as follows:

Sample = 0.2g

Thermal neutron flux, $\phi_{\text{th}} = 9 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$

Epithermal flux, $Q_{\text{ep}} = 1.6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$

irradiation time $t = 24 \text{ hrs}$

Atomic weight of arsenic $A_w = 75 \text{ g mol}^{-1}$ Iso topic abundance of ^{75}AS , $j_a = 1$ thermal neutron cross section $\sigma_{\text{th}} = 4.3 \text{ b} = 4.3 \times 10^{-24} \text{ cm}^2$

Resonance integral. $I = 60 \text{ b} = 60 \text{ b} = 60 \times 10^{-24} \text{ cm}^2$ half life of ^{76}As , $t^{1/2} = 26.3 \text{ h}$

- (i) Considering the detector efficiency, the minimum detectable ^{76}As radioactivity is 5.5 Bq. Estimate the limit of detection MLOD of arsenic for the above given experimental conditions. [1½ Marks]
- (ii) The radioactivity of the irradiated sample counted via the 559.1 keV photopeak after a decay time of 5 h was 18 counts per second (cps). For the standard containing 10 ng As, assuming rate of 1036 cps was measured after a decay time of 16 h. Calculate the content of arsenic in the silicon sample. [2 Marks]

QUESTION FOUR (20 MARKS)

- 4a. (i) If you were given a choice between using the Al OR Ag anodes in a monochromatic source (from which the Al- $K\alpha$ OR Ag- $L\alpha$ x-rays are used) which would you use if you were interested in ascertaining the B.E xps value of the Si-2s core electrons from Si? [1 Mark]
- (ii) Describe if and how the work function of a sample of interest can be derived using x-ray photoelectron spectroscopy (XPS) OR ultraviolet photoelectron spectroscopy (UPS) [3 Marks]
- (iii) In typical XPS spectra both photo electron peaks and Auger electron peaks are present.
- (I) What instrumental parameter can be used to distinguish the two. [1 Mark]
- (II) Explain how the results can be obtained. [1 Mark]
- (vi) Describe what happens to all the photo electron peaks observed in the spectra collected from an insulating sample when ineffective charge neutralization conditions are used. [1 Mark]
- b (i) A compound containing C 14 -CO- and CF- based organics. Using the knowledge that the B.E xps shifts for the C-1s level can be ascribed to typical initial state effect (intra-atomic). List these with a reason the expected B.E xps order from lowest to highest. [1 Mark]
- (ii) Explain unusual initial state effect causes core-level B.E xps values of certain metal atoms / ions such as Sr, Ba etc to decrease during oxidation. [1 Mark]

- (iii) What could cause the spin orbit splitting value of photoelectrons from a specific level OR a specific element to deviate from that typically observed. [1 Mark]
- (iv) The analysis of an unknown but homogeneous sample is carried out with photoelectrons collected at some off normal take off angle. On rotating the sample a round its normal axis (azimuth rotation) reproducible periodic spikes are noted in various core level photoelectron signals.
- (I) What are these variations indicative of ? [1/2 Mark]
- (II) How may they be useful [1 Mark]
- (i) Outline the differences and similarity between cylindrical mirror analyser (CMA) and the hemispherical sector analyser (HAS) [2 1/2 Marks]
- (ii) Comment on the following statement.
 "X-ray photoelectron spectroscopy (XPS) are used to define film thickness" [1 Mark]
- (iii) Explain why Quantification of sputter depth profiles of even the most stable metal oxides (e.g perovskites) with 0.5 keV Ar⁺ ions at an angle of 45° relative to the sample surface, using sensitivity factors defined from unsputtered surfaces tends to reveal less than stoichiometric amount of oxides nitrides etc. [2 Marks]
- (iv) Scanning electron microscopy (SEMI), which records secondary electrons (these peak in energy within 1 to 10 eV range). is often used in conjunction with Auger electron spectroscopy (AES) and/ OR XPS to visualize the area of interest (this is done since SEM provides the best spatial resolution of the three, even though it does not provide elemental characterization capabilities). Explain which of these three techniques exhibit the greatest surface specificity to the formation of carbon over layers (this could be in the form of adventitious C, self-assembled monolayers a morphous carbon layers etc) on gold Assume that in all cases, the data are collected at normal take off angles C-1s photoelectron emissions resulting from Al-K α irradiation are examined in XPS and C KVV Auger emissions are examined in AES. [3 Marks]
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