SG - 482

Total No. of Pages : 3

Seat No.	

M.Sc. (Part - II) (Semester - IV) (CBCS) Examination, March - 2023

ANALYTICAL CHEMISTRY (Paper - XV)

Advanced Methods in Chemical Analysis

Sub. Code : 81582/86573

Day and Date : Friday, 16 - 06 - 2023 **Total Marks : 80**

Time : 10.30 a.m. to 01.30 p.m.

Instructions :
1) Attempt five questions.
2) Question no. 1 is compulsory.
3) All questions carry equal marks.
4) Answer any two questions from Section-I and two questions from section - II
5) Figures to the right indicate marks.

Q1) Write in One sentence.

a) All elements produce Auger electron spectra except H and He why ?

b) State Koopmans Theorem

c) What can be used for depth profiling in AES

d) What are the types of photoelectron spectroscopy.

e) Which spectral observables are used in fluorescence sensing

f) Define Synchronous Fluorescence

g) What is Forster Distance?

h) Give the names of fluorescent Nanornaterials.

i) Enlist the names of analyzing crystals used in X-ray spectroscopy.

j) What is Bremsstrahlung?

P.T.O.

k) Give the meaning of Al Kβ X- radiation.

l) List the detectors used in X ray spectroscopy

m) What is turnover number?

n) What are enzyme inhibitor?

o) Define pseudo first order reaction.

p) What is substrate in enzyme reaction?

SECTION - I

Q2) a) Give a brief account on structural factors of fluorescence. [6]

b) Discuss fluorescence anisotropy. [6]

c) A graph of Io/I verses [Q] gives a straight line with a slope is 2.0×10^{-3} $dm^3\ mol^{-1}$. If the lifetime of a fluorophore is 4 ns, then what will be the collisional quenching rate constant. [4]

Q3) a) Discuss principle and instrumentation of ESCA. [8]

b) Explain application of XPS. [4]

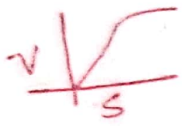
c) In an ESCA experiment Cr Ka- x-rays having 5414.81 eV energy caused ejection of electrons from a compound. The measured K.E. was 4.901 KeV. The work function of spectrophotometer is 4.5 eV. Calculate the B.E. of the electron. [4]

Q4) a) State different quenching mechanim. Explain FRET in detail. [6]

b) Explain static quenching and explain its kineties. [6]

c) Discuss Applications of AES. [4]

enzyme catalysis is ↑ the rate of process by biological molecule as enzyme. Rate = $\frac{-d[S]}{dt} = \frac{d[P]}{dt}$



$E + S \rightleftharpoons ES \xrightarrow{E} E + P$

$V_o = \frac{V_{max}[S]}{K_m + [S]}$ (2)

$V_o = \frac{V_{max}}{2}$ $K_m = [S]$

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SECTION - II

Q5) a) What are enzyme catalysed reactions? Discuss Michalis menten model to describe enzyme catalysed reaction. [6]

b) Explain fixed time method of kinetics of catalyzed reaction. [6]

c) The enzyme urease, which catalyses the hydrolysis of urea, is widely used for determining urea in blood. The michaelis constant for urease at room temp is 2.0 mM & $K_2 = 2.5 \times 10^4\ S^{-1}$ at pH = 7.4. Calculate the initial rate of reaction when the urea concentration is 0.030 Mm and the urease concentration is 5.0 µM. [4]

16

Q6) a) Give a brief account on X-ray generation and their properties. [6]

b) Explain the instrumentation of XRF. [6]

c) Deduce Braggs law and its use in analysis of crystalline compounds. [4]

16. XRD.

Diagram $n\lambda = 2d\sin\theta$

Q.6 a] propⁿ – electromag. waves. wavelength of XRay small. invisible travel in straight line. Measured in Rontgen. X-Ray carries no charge not reflected in mag. field and e⁻ field. they ionizes gas, produces photo electric effect & compton effect.

6b] EDXRF
low cost & fast
poor resolution
simple design

WDXRF.
use crystal.
detector sample
crystal tube
High resolution
sensative to low at. no.

sample
detector
X Ray tube

Bragg law crystalline

Q7) Write a short note (Any Three) : [16]

a) Rotating can phosphoroscope

b) Electron sources in AES

c) Tangent method.

d) Applications of XRF

e) Applications of X-ray diffractions

Fluorescence anisotropy → is a measure mea of the changing orientation of molecule in space w.r.to time bet? the absorption & emission events.

Concept of anisotropy measurement is Brownian motion → watering glass have K.E at rest.

Second concept → photoselection by used of a polarized light

Application – It is used to measure ~~K.E~~ binding constant & kinetic of reaction that cause change in ~~rational~~ rotational time of molecule.

used in microscopy, study aggregation of protein in response to signaling

Answer Key Set -I

Q. 1

1. All elements produce Auger electron spectra except H and He why?
   Ans: Because Auger process requires at least three electrons while H and He have one and two electrons respectively.
2. State Koopmans Theorem
   Ans: The ionization energy of a molecule is equal to the negative of the energy of the highest occupied molecular orbital (HOMO)
3. What can be used for depth profiling in AES
   Ans: Inert ion Source
4. What are the types of photoelectron spectroscopy
   Ans: Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS)
5. Which spectral observables are used in fluorescence sensing
   Ans: Fluorescence Intensity, lifetime, Intensity ratios etc.
6. Define Synchronous Fluorescence
   Ans: The fluorescence which is obtained through simultaneous scanning of excitation and emission wavelength with a fixed wavelength difference.
7. What is Forster Distance?
   Ans: It is a distance between donar and acceptor at which 50% of energy is transferred.
8. Give the names of fluorescent Nanomaterials.
   Ans: Cadmium sulphide quantum dots (CdS), Graphene Quantum dots (GQDs), Carbon Dots (CDs), Lead Sulphide quantum dots (PbS_2)etc.
9. Enlist the names of analyzing crystals used in X-ray spectroscopy.
   Ans; Topaz, LiF, NaCl, Ammonium Dihydrogen phosphate (ADP)
10. What is Bremsstrahlung ?
    Ans: It is radiation that arises from retardation of particles.
11. Give the meaning of Al Kβ X- radiation.
    Ans: The vacancy in K shell is fulfilled when an electron from the M shell to the K shell, the X-ray radiation emitted is called a Kβ X- radiation.
12. List the detectors used in X ray spectroscopy
    Ans: Geiger Muller tube, Scintillation counter, solid state detector etc.
13. What is turnover number?
    Ans: It is defined as the maximum number of molecules of substrate is converted to product per catalytic site per unit time by an enzyme.
14. What are enzyme inhibitor?
    Ans: An enzyme inhibitor is a molecule that binds to an enzyme and blocks its catalytic activity
15. Define pseudo first order reaction.
    The reactions that have higher order true rate law but are found to behave as first order are called pseudo first order reactions

Enzyme operate

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M. Sc. II, Sem-IV (CBCS)
Examination April -2024
(Analytical Chemistry)
Paper No. XV- Advanced Methods in Chemical Analysis
Subject Code: 81582 / 86573

12037

Day and Date : Saturday, 20-04-2024 **Total Marks : 80**

Time : 10.30 a.m. to 01.30 p.m.

Instructions :

1) Attempt five questions
2) Question No. 1 is compulsory
3) Attempt any two questions from section-I and two questions from section -II
4) All questions carry equal marks
5) Figures to right indicates full marks

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Q.1 Write in One sentence **(16)**

1. Write the reaction between H_2O_2 and thiosulphate
2. Give the meaning of steady state approximation
3. What is temperature coefficient.
4. Give the unit of rate constant of first order reaction.
5. State the Frank-Condon principle.
6. Give the names of fluorescent nanomaterials.
7. Enlist two conditions for FRET.
8. Define fluorescence lifetime.
9. What is Bremsstrahlung?
10. What is CuKa- X radiation.

11. Define diffraction phenomenon.
12. Name the detectors used in X-ray spectroscopy
13. Analysis of solid surfaces can be achieved by ESCA. True/False
14. What is KLL transition in Auger electron spectroscopy.
15. How we can distinguish between Cu, CuO and Cu_2O by using X-ray photoelectron spectroscopy
16. What is satellite peak observed in Auger electron spectroscopy

Section -I

Q.2) a) What are enzyme catalysed reactions? Discuss Michalis - Menten model to describe enzyme catalysed reaction. **(8)**

b) Explain fixed time method of following kinetics of catalysed reaction. **(4)**

c) X-ray of wavelength 1.54 A^0 are diffracted at an angle of 14.22^0 by crystalline silicon. Using the Bragg's equation. calculate the distance between the planes of atoms responsible for diffraction in this crystal, assuming n=1. **(4)**

Q.3) a) Draw the schematic of X-ray absorption spectrometer and explain with reference to principle, working and applications. **(6)**

b) State Bragg's equation and explain how it is used to identify the crystal structures of crystalline materials. **(6)**

c) How X-rays are generated? Explain properties of X-rays. **(4)**

Q.4) a) Discuss fluorescence resonance energy transfer between suitable donor-acceptor pair in solution. **(6)**

b) "Ultra high vaccum chambers are required for the photoelectron spectrometer" Justify the statement. **(6)**

c) The fluorescence lifetime of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1 calculate the rate constant of fluorescence decay. **(4)**

Q5) a) Describe construction and working of Auger electron spectroscopy. (6)

b) What is chemical shift in ESCA. How this value helps in identification of substances. (6)

c) What is ASTM card? How these cards are useful for the characterization of solid materials? (4)

Q.6) a) Discuss construction and working of filter fluorometer. (8)

b) What are the structural factors affecting fluorescence, discuss in detail. (4)

c) An XPS electron was found to have a K. E. of 1052 ev when ejected with an Al K*a* source (486.6 ev) and measured with work function 27.8 ev. Calculate

a) B. E. of electron

b) kinetic energy of electron if a MgK*a* source (12.54.6 ev) used. (4)

Q7) Write notes on (any three) **(16)**

a) Applications of Koopman's theorem.

b) Indexing XRD peaks

c) Enzymatic determination of urea.

d) Delayed Fluorescence

e) Application of XRD in crystal analysis.

□□□

SET I Answer Key

1. Reaction between H2O2 and thiosulphate-
2. Steady state approximation- It is based on assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.
3. Temperature coefficient.- It is defined as ratio of the rate constant at two temperatures differ by 10^0C
4. Give the unit of rate constant of first order reaction.- **time^{-1} i.e. min^{-1}or sec^{-1}**
5. Frank-Condon principle. – It states that electron rearrangements occur so rapidly that nuclei can be considered as stationary until the rearrangement is complete.
6. Fluorescent nanomaterials- silica nanoparticles, nanodiamonds, hydrogels, metal nanoparticles
7. Enlist two conditions for FRET-

   The donor molecule must be fluorescent and exhibit sufficiently long lifetime in order for resonance energy to occur.

   The fluorescence emission spectrum of the donor molecule must overlap the absorption or excitation spectrum of the acceptor chomophore.
8. Define fluorescence lifetime -fluorescent lifetime is the mean time spent in the excited state. $\tau_f = 1/k_{fluoro}$ +
9. Bremsstrahlung -continuous radiation are called bremsstrahlung.These radiation arises from retardation of particles.
10. What is CuKα- X radiation- -When an electron vacancy in theK shell is filled by an electron from the L shell,the characteristic radiation emitted is Cu-Kα radiation
11. Diffraction phenomenon- Diffraction is slight bending of light as it pass around the edge of an object.
12. Detectors used in X-ray spectroscopy – Scintillation counter, Geiger-muller counter.
13. ESCA can identify elements in the periodic table above helium. **True**/False
14. KLL transition – The K level electron undergoes initial ionization An L level electron moves into fill the K-level vacancy and at the same time , gives up energy of that transition(L to K) to another L-level electron, which then becomes the ejected Auger electron
15. How we can distinguish between Cu, CuO and Cu_2O by using X-ray photoelectron spectroscopy – one can clearly distinguish between metallic copper and copper oxide CuO. But difficult to distinguish between between Cu and Cu2O. However by also observing the oxygen 1s spectrum(530.8 ev for Cu2O and 530.1 ev for CuO)one can easily distinguish between metallic copper and its two oxidation states.
16. Satellite peak in Auger spectroscopy – Satellite peaks provide information about the electronic structure and chemical bonding in the material.

Q2 **c)** X-ray of wavelength 1.54 A^0 are diffracted at an angle of 14.22^0 by crystalline silicon. Using the Bragg's equation. calculate the distance between the planes of atoms responsible for diffraction in this crystal, assuming n=1.

$n\lambda = 2d\sin\theta$

d = 1.54/2 sin14.22 =1.54/2x0.9965 = 1.54/1.9931= 0.7726

4 c) The fluorescence lifetime of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1 calculate the rate constant of fluorescence decay.

$\phi_F = 0.1$

$\tau_{F= 10\ ns = 10 \times 10^{-9}}$ $k_F = ?$

$\phi_F = k_F \times \tau_F$

$k_F = \phi_F / \tau_F = 0.1/10 \times 10^{-9}$

$k_F = 0.1/10^{-8}$

$k_F = 10^7\ s^{-1}$

Q 6) c)An XPS electron was found to have a K. E. of 1052 ev when ejected with an Al Kα source (486.6 ev) and measured with work function 27.8 ev. Calculate a) B. E. of electron b) kinetic energy of electron if a MgKα source(12.54.6 ev) used

Answer – 406.2 ev and 820.6 ev.

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