Model Answers

AR-7146

M.Sc. (Fourth Semester) Examination, 2013

Chemistry

Paper : Spectrochemical Analysis (CHM:404A)

Section A

1.(i) Conditions for obtaining IR spectra

(a) Molecules should have a dipole moment

(b) Asymmetic molecule

(c) Vibrating molecules should have absorb correct frequency of radiation.

(ii) The technique is based upon the fact that a chemical substance shows a marked selective absorption in the infra-red region. After the absorption of IR radiations, the molecules of chemical substance vibrate at many rates of vibrations, giving rise to absorption bands called as IR spectrum. which will corresponds to the characteristic of functional groups and bands present in a chemical substance.

(iii) Difference between IR and Raman spectroscopy

IR spectroscopy	Raman spectroscopy
(a) It is result of absorption of light by vibrating molecule	(a) Due to the scattering of light by the vibrating molecules
(b) polarizability of the molecule will decide the Raman spectra	(b) the presence of a permanent dipole moment in a molecule
(c) Homonuclear diatomic molecules (H_2, N_2) are found to be Raman active	(c) IR inactive

(iv) Magnetic resonance imaging is a medical imaging technique used in radiology to visualize the internal structure of the body. by measuring the ~~water~~ nuclei of atoms in the body (water contains in the body is more, hence protons

^1H nuclei), which get aligned in a large magnetic field.

(v) Quantitative analysis of NMR:

(a) NMR can be used to determine the molar ratio of the components in a mixture. If the NMR spectrum of a mixture is recorded, it may exhibit a resolved band due to one component and if the number of protons in the molecule giving rise to that band is known, then the integrated area of the band will give a direct measure of relative concentration of that component in the mixture.

(b) Analyte concentration = $\frac{\text{Normalized area of analyte} \times \text{standard concentration}}{\text{Normalized area of standard}}$

(vi) Isolator: It is a non-reciprocal device which minimizes vibrations in the frequency of microwaves produced by klystron oscillator.

Wavemeter: The wavemeter is put in between the isolator and attenuator to know the frequency of microwave produced by klystron oscillator.

(vii) Difference between scanning electron microscopy (SEM) and atomic force microscopy (AFM)

SEM	AFM
(a) SEM measure the interaction of electrons with sample surface	(a) AFM measure the force between sample surface and cantilever
(b) SEM can provide 2-Dimensional information of the surface	(b) 3-Dimensional information
(c) SEM can be faster	(c) slower than SEM

(viii) modes of imaging in AFM: contact mode, intermittent and non contact modes

(ix) principle of ICP-AES: This is a type of atomic emmision spectroscopy, where source of atomization is inductively coupled plasma operated at 7000-15000 K. Plasma sources produces a greater number of excited

atoms in to excited electronic states that subsequently emit light when they return to the ground electronic state, which is measured.

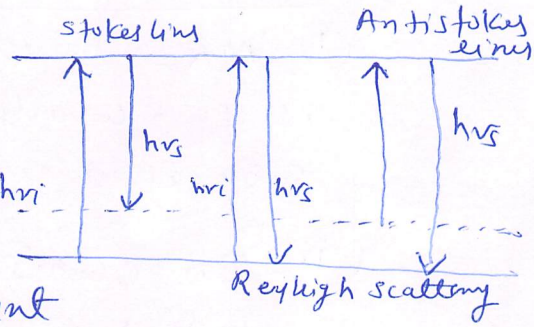
(X) Name of the additives in food products are salicylic acid, saccharin, propionic acid, acetic acid, caffeine, benzoate caramel, cyclamate

Section - B

2. Raman effect: Explained by quantum theory

When a beam of monochromatic exciting radiation passes through a transparent medium, one of the two things can happen. Most of the collisions are elastic and deflected Photons, the scattered radiations have the same energy as incident photon and this called Rayleigh scattering.

However, a small fraction of the collision is inelastic and deflected Photons have either higher frequency ($h\nu_i$) (anti stokes scattering) and lower frequency (stokes lines) than incident Photon of radiation. Both the process is called as Raman Scattering, which is measured in Raman spectroscopy



$$E_i + h\nu = E_S + h\nu_S$$

$$\frac{E_i - E_S}{h} = \nu_S - \nu_i$$

$$\nu_S = \frac{E_i - E_S}{h} + \nu_i$$

$$\boxed{\nu_S = \Delta\nu + \nu}$$

Three conditions:

(i) $\nu_S = \nu_i$, when $\Delta\nu = 0$, molecule deflects without the receiving energy from it. The collision being elastic

(ii) $E_i > E_S$ $\nu_i > \nu_S$ - stokes lines molecules absorbs energy from the incident photon

(iii) $E_i < E_S$, $\nu_i < \nu_S$ - Anti-stokes lines, it means molecules are primarily in excited states

and handed some of the energy to incident photon.

3. Magnetic resonance imaging (MRI): It is advanced analytical technique to visualize the internal structure of the body with perturbing the structure using the nuclei (1H) of the water. The body tissue contains lots of water and each molecule of water has two nuclei or protons. When the person is inside the powerful magnetic field of the scanner, the average magnetic moment of many protons becomes aligned with the direction of the field. The right frequency of radiation is absorbed by these resonating nuclei and thus radiofrequency is measured with receiver coils.

Useful in medicine

(i) MRI is used to image every part of the body and is particularly useful for tissue with many hydrogen nuclei such as brain, muscle, connective tissue and most tumours

(ii) In clinical practise, MRI is used to distinguish pathological tissue (such as brain tumours) from normal tissue

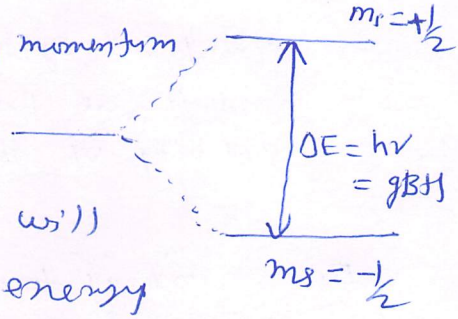
(iii) MRI produces very detailed picture of the brain and commonly used to study the people with problems such as headaches, siezures, weakness, hearing loss and blurry vision.

(iv) Bones and joints can be also studied with MRI to identify injured tendons, ligaments, muscles and cartilage

(v) Spine MRI is most commonly used to ~~look~~ check virtually of a herniated disk or narrowing of the spinal canal in people neck, arm, leg pain.

4. Principle of electron spin resonance spectroscopy

In ESR, the energy levels are produced by the interactions of the magnetic moment of an unpaired electron in a molecule ion with an applied magnetic field. The ESR spectrum results is due to the transitions between these energy levels by absorbing radiations of microwave frequency.



For an electron of spin $S = \frac{1}{2}$, the angular momentum quantum number will have values of $m_S = \pm\frac{1}{2}$. In the absence of magnetic field, the two values of $m_s = +\frac{1}{2}, -\frac{1}{2}$ will give rise to a doubly degenerate spin energy state. If a magnetic field is applied, this degeneracy is removed and this leads two non-degenerate energy levels. The energy will be

$$\Delta E = h\nu = g\beta H$$

Applications

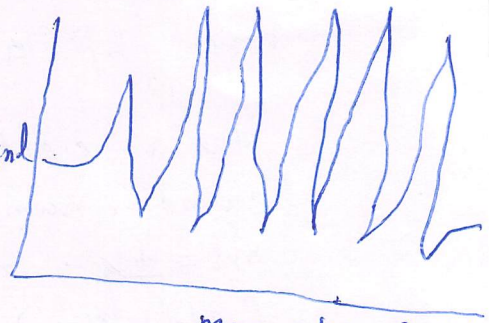
(i) Study of free radicals: Free radicals can readily studied by ESR, even at low concentration. These radicals may produced chemically, photochemically, or high energy radiation. The intensity of ESR signal is directly proportional to the number of the free radical present.

(ii) Study of inorganic compounds: An interesting example is $[NO(SO_3)_2]^{2-}$ yields a triplet in ESR spectrum in chloroform. This arises from the interaction between the spin of the unpaired electron and the spin of of a ^{14}N nucleus ($I = 1$) confirming that this electron is mainly localised on the nitrogen atom.

(iii) Determination of oxidation state of metal: The ESR spectrum of Cu(II) complex (d^9 system) gives a spectrum signal whereas that of Cu(I) complex (d^{10}) system gives a much reduced signal

(iv) Analytical application for the determination of Mn^{2+}: when the ESR spectrum of Mn^{2+} ions in solution is recorded, it shows six lines. The multiplicity is given by $2I+1$, where I is $5/2$ for Mn^{2+} ions, i.e. $2 \times 5/2 + 1 = 6$ - this accounts for six peaks.

(v) Biological systems: ESR variety of biological systems such as leaves, seeds and tissue preparations and the metabolic activity of the material.



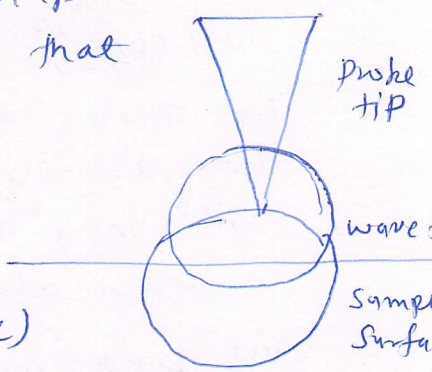
5. Scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level. It can be used for higher resolution of sample of 0.1nm lateral resolution and 0.01nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated.

Theory of STM: In STM operate by scanning a sharp metallic needle over a surface in very close proximity under ultra high vacuum. The wave functions of the electrons of the sample surface and probe tip decay exponentially as the distance away from the surface atoms increases, bringing the probe tip and sample close and allows these probe and surface electrons wave functions to overlap.

Tunneling is a functioning concept that arises from quantum mechanics.

Electrons behaves as beam of energy:

$$-\frac{h^2}{2m}\frac{\partial^2 \psi_n(z)}{\partial z^2} + U(z)\psi_n(z) = E\psi_n(z)$$



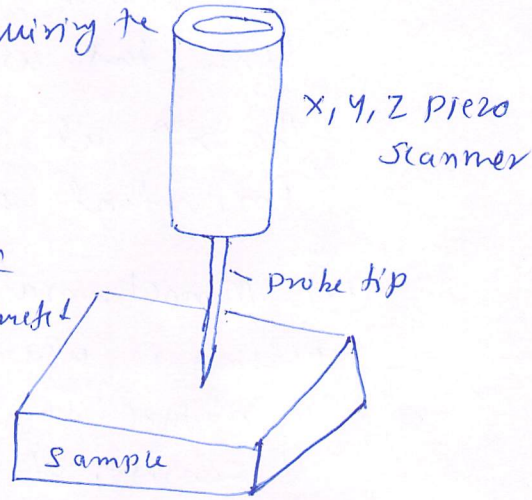
: Probe and sample overlap wave function

ψz - potential energy, $\psi_n(z)$ energy level, h - plancks constant, z, the position, U(z) - barrier of height

Electron wave function $\psi_n(z) = \psi_n(0) e^{\pm ikz}$

Instrumentation of STM:

(i) Probe Tip: The most important component tunneling microscope is its probe tip. The tip is made of tungsten or platinum – irridium. The tip is directly responsible for collecting data. maintaing the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled.

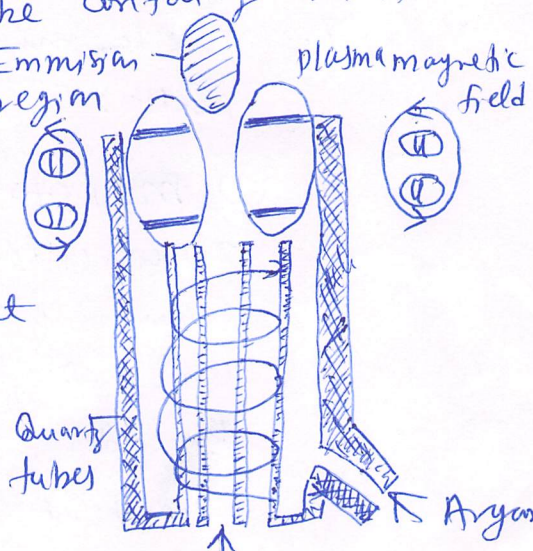


(ii) Piezoelectric actuator: Piezoelectric actuators that control the movement of the scanning tip, most commonly constructed of lead zirconium titanate. The most conceptually simple arrangement of these actuators is in the form of three mutually perpendicular bars that corresponds to the x, y, z movement of probe tip.

(iii) Computer Controller: computer controllers required to process the current data and produce useful data.

6. Inductively coupled plasma - Atomic emmision spectroscopy (ICP-AES):

(i) Induced coupled plasma (ICP): Is a very high temp (7000 – 8000 K) excitation source that efficiently desolvates vaporize, excites and ionizes atoms. The plasma source consists of concentric quartz tubes, with the inner tube containg ~~an Ar gas flow~~ the sample aerosol and Ar support gas and the outer tube containg an Ar gas flow to cool the tubes.



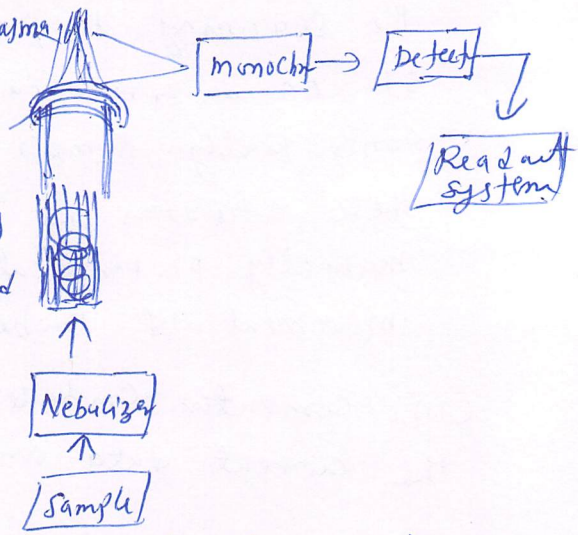
(ii) Nebulizer: It is device that converts solution of the analyte into finely derided droplets that are carried into the atomizer.

(a) pneumatic nebulizer: the sample solution is aspirated through a capillary by the nebulizing gas.

(b) Frit nebulizer: the sample solution is pumped to a glass frit.

(iii) Radio frequency generator: the majority of radiofrequency (rf) power generator are crystal controlled radiofrequency generators. which operated at 27.12 & 40.68 MHz. the rf at which the torch operates is an important parameter in sustaining plasma operation.

(iv) Monochromators: Emmision from plasma is usually polychromatic in nature that implies that it consists of large number of radiations of different wavelengths these needs to be suitably dispersed to analyse for the possible elements in the analyte..



the complex spectra is achieved by using ruled grating monochromators having a large number of grooves on the grating.

(v) Detectors: the detectors used in ICP-AES are Photomultiplier tubes (PMT), photodiode arrays and charged devices.

7. Determination of moisture, proteins and fats in milk:

(i) Moisture: moisture values find aticity in product specifications and standards of identity. the most common procedure employs a vacuum oven drying at 100°c for about 5 hrs. & hot plat method.

Procedure: (1) weigh 10gm of milk in dried beaker and heat the sample on the electric hot plate stirring continously with glass rod.

3. Avoid sputtering during heat
4. stop heating after all the milk evaporated and put into the desicator for cooling. weigh the beaker.

Calculations: moisture present in milk = $\frac{w_1}{w_2} \times 100$

where w_1 = weight of the milk after heating (in gm)

w_2 = weight of the milk for the test (in gm)

(ii) Determination of proteins:

Protein is a very common ingredient of all the food material. Protein content in butter is determined by calculation method. the total percentage of moisture, salt, lactic acid and fat is subtracted from 100.

Calculation = % of protein = percentage of moisture + Lactic acid + Fat − 100

Procedure: ① Dilute 200 ml fush milk to 1000 ml by adding DW in 2-Litre beaker and add 1g glacial acetic acid, white PPT settle down.

(ii) Decant aqueous layer and wash the precipitate several times with water by decantation.

(iii) Transfer the ppt in to mortar and grind with minimum amount of 0.1 N NaOH to neutralize

(iv) check with litmus paper for neutality of the substance

(v) Filter the resultant suspension through muslin cloth by pressing the liquid comming out is finitly turbid.

(vi) Acidify the ~~liquid~~ filtrate by adding glacial acetic acid

(vii) wash the ppt with water and neutralize with 0.1 N. NaOH soln and filter through muslin cloth.

(viii) Finally the ppt is made past with rectified Spirit and again ~~filter~~ wash it first with and then with ether (to remove fats)

(ix) Dry it in oven when casein (protein) is obtained as a white amorphous powder.

(x) Weigh the yield and find out the amount of Protein gm.

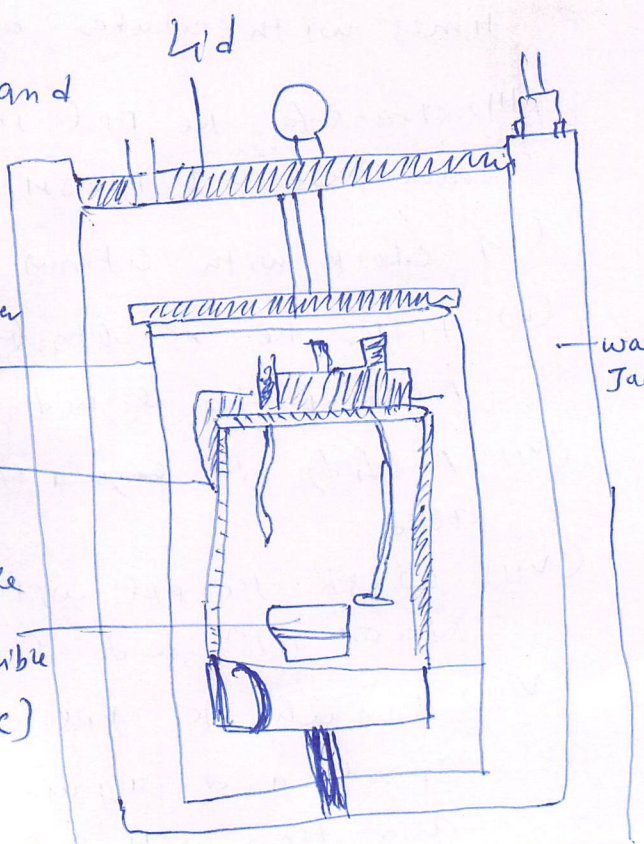
8. The calorific value of fuel is defined as the "amount of heat obtained by complete combustion of a unit mass of a fuel.

Determination of calorific value:

The calorific value is determined by the use of a bomb calorimeter. It is used for the determination of a calorific value of solid and liquid fuels. It consists of the following steps to get calorific value of fuel.

A weighed quantity of the fuel is placed in the crucible and supported over the ring. A fine platinum wire is tightly stretched across the pole pieces of the bomb and one end of a piece of sewing cotton thread is tied around the wire. The crucible is placed in position and the loose end of cotton is so arranged as to be in contact with the liquid fuel.

Make the electrical connection and then place the cover in position and switch on the stirrer. Initial temperature of the water is noted with help of a thermometer. Now connect the electrode with battery and complete the circuit so that the sample burns and heat is liberated.



$$\text{Calorific value} = \frac{(W + w)(t_2 - t_1 + t_c) - (C_s + C_N + C_F + C_c)}{m}$$

equivalent, m is