Model Answers

M.Sc (Second Semester) Examination, 2013 Chemistry   ①

Paper : CMT-201 (Analytical Chemistry)

SECTION-A

1. (i) (B) ICP-AES

(ii) (B) Helium

(iii) Advantages of dropping mercury electrode :

(a) It surface area is reproducible with any given capillary

(b) Posses property of forming an amalgam with many metals

(c) The diffusion current assumes steady value almost instantly and is reproducible.

(d) The surface area of mercury can be calculated from the weight of drops.

(iv) standard addition calibration method : In AAS, suppression of the signals due to sample matrix, high viscosity or chemical reaction with analyte. This can be overcome by standard addition method, where known concentration of analyte is added to the unknown solution. A curve is plotted between absorbance and concentration added. The curve is extrapolated, the intercept obtained is equivalent to the concentration of analyte present in unknown sample.

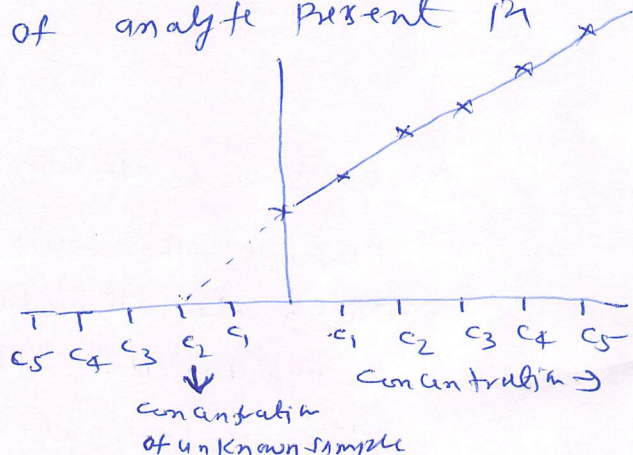(v) Working of proportional counter detector in x-ray absorption :

A proportional counter is filled with a heavier gas like xenon or krypton. The heavier gas is preferred because it can easily ionized. A proportional counter is operated at high voltage below Gieger plateau. The output pulse of

Proportional counter is dependent upon the intensity of x-rays falling on a proportional counter.

(vi) Fluorescence quenching: The decrease in the fluorescence intensity arises when the excited state of fluorophore collide with surrounding molecule, is called fluorescence quenching.
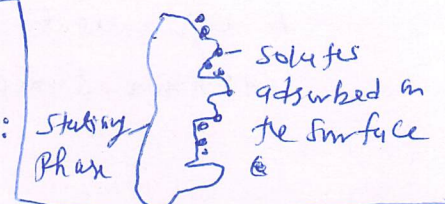
$$M^* + Q \longrightarrow Q^* + M \text{ (molecule lose energy)}$$

Excited molecule   quencher   Excited quencher

(vii) Size exclusion chromatography: This is type of chromatography in which the separation of molecules is based on the molecular size and shape in the pores of packing material (in column). Bigger molecules not retained on the column and passes first than smaller molecules.

(viii) Principle of adsorption Chromatography: The stationary phase is a solid on which the solutes are adsorbed. The mobile phase can be liquid or gas. Separation of components by this method depends on the differences both in their degree of adsorption by the adsorbent and solubility in the solvent used for separation.

Stationary Phase — Solutes adsorbed on the surface

(ix) Procedural decomposition temperature (PDT): PDT is the lowest temperature at which the cumulative weight mass change reaches a magnitude that the thermobalance can detect this is indicated in the curve as (Ti)

weight → / temp →

A   A'   Ti   B'   B   TF
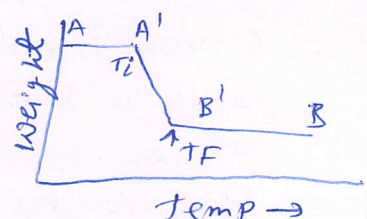
(x) Factors affecting DTA curve:
(a) Environmental (static atmosphere, Dynamic atmosphere)
(b) Instrumental (sample holder, Differential temps, furnace and Temperature controller)

③

SECTION B

2. Ilkovic Equation (Derivation)

The current flow in polarizable electrode is given by

$$i = K(c-c_0) = nFAD\frac{(c-c_0)}{\delta} \quad -(i)$$

Where n is no. of electron transfered, F is Faraday (96500 columb)
A is surface area of polarizable electrode, D is diffusion
coefficient, c and c_0 are the concentration of species in
bulk of solution and at the surface of electrode. δ is the
thickness of diffusion layer.

The value of c_0 is zero, when diffusion current is maximum
limiting diffusion current (i_d)

$$i_d = nFAD\frac{c}{\delta} \quad -(ii) \qquad\qquad \delta = (\pi D t)^{1/2}, \quad -(iii)$$

where t is time taken
for analyte to reach the surface of
electrode from the bulk solution.

on substituting the value of δ in eqn of i_d (ii)

$$i_d = \frac{nFADc}{(\pi D t)^{1/2}} \quad -(iv)$$

The surface area of dropping mercury electrode can be
determined. suppose the volume of single drop can be
related to flow rate m in a drop. Find (t)

$$V = \frac{mt}{\rho} = \frac{mt}{13600} \quad (n) \qquad [\rho = \text{density of mercury } (\rho = 13600 \text{ mg cm}^{-3})$$
$$\text{density of mercury } 13.6 \text{ g cm}^3]$$

The drop is assumed to be spherical

$$V = \frac{4}{3}\pi r^3 \text{ (ii)} \qquad r = (mt)^{1/3} \quad \text{(iv)} \quad ① \text{ and } ⑪$$

Equating ① and ⑪

$$r = \left(\frac{3}{13600 \times 4\pi}\right)^{1/3}(mt)^{1/3}$$

$$r = 0.028 (mt)^{1/3}$$

(c) Sample characteristics (Particle size)

The surface area of drop:

$$A = 4\pi r^2 = 4\pi(0.026)^2 . mt^{2/3} = 8.43 \times 10^{-3}(mt)^{2/3}$$

However, the value of A should be corrected accorty to Ilkoic, because the area of drop change during the coarse of its formation from minimum value of zero to maximum. $\sqrt{7/3} = 1.528$

$$A = 8.43 \times 10^{-3}(mt)^{2/3} \times 1.528 = 0.013 (mt)^{2/3}$$

Substituting the value of A in equation (iv)

$$id = \frac{0.013 \; n \; F \; D^{1/2} m^{2/3} t^{1/6}}{\pi^{1/2}} c = 706 \; n \; c \; D^{1/2} m^{2/3} t^{1/6} \quad (v)$$

The expression (v) is instaneous limiting diffusion current at time t. the average limiting diffusion current can be shown be $6/7$ of the instaneous current

$$Id = 6/7 \times id = \frac{6}{7} \times 706 \; n \; c \; D^{1/2} m^{2/3} \times t^{1/6}$$

$$\boxed{Id = 607 \; n \; D^{1/2} m^{2/3} t^{1/6} c}$$

* Applications of polarographic technique

(i) Application to inorganic compound: this can be used for the estimation of cations and anions in the presence of interfrences. In the separation of zinca and nickel, which have nearly identical half wave potential in neutral chloride solution, an alkali hydroxide can be used as supporting electolyte. zincate ions are reducible, where nickel is precipitated as the hydroxide. Also used for the determination of anions such as bromate, iodate vandate and selenite.

(ii) Application to organic compounds: Polarography can be used for the determination of structure, for the quantitative identification of compounds.

The estimation of sugars have been carried out in the range of 10^{-3} to 10^{-2} M using PH of 2.3 and hydrazine as supporting electrolyte. The general reaction of organic in polargraphy is $R + nH^+ + ne \rightarrow RH_n$ (Reduced form)

(Oxidized) form
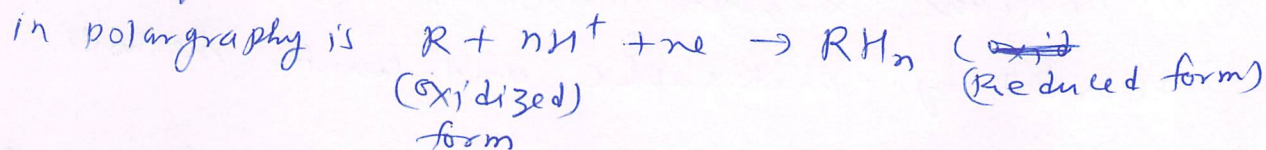
(iii) Determination of dissolved oxygen:
Dissolved oxygen produces two reaction wave in the figure correspondy to —

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$$
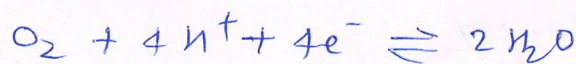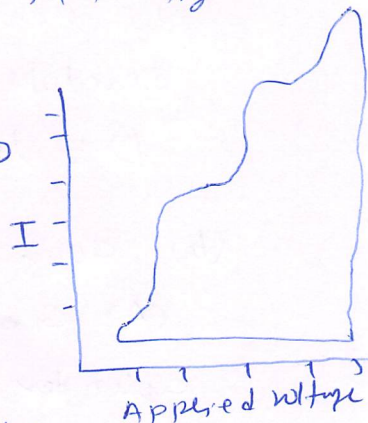$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$
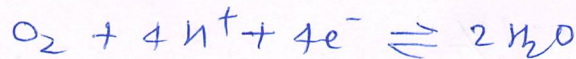
Figure shows the reduction of oxygen in air-saturated 0.1 M KCl solution.

I
Applied voltage

3. Different components of X-ray absorption spectroscopy

(i) X-ray sources: X-rays are generated when high velocity electrons impinge on a metal target (anode) tungsten heated with betry to emmit thermonic electrons, when these electron strike target anode and transfer their energy to its metallic surface to gives off X-ray radiation.

X-ray Hot Cathode
Anode
X-ray Source

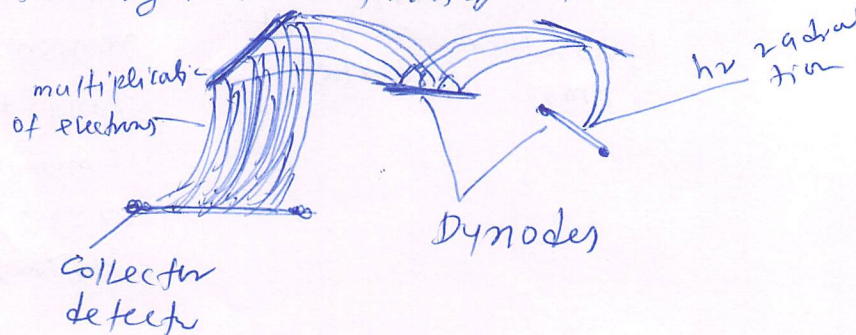Beam blocked
Collimator gap
→ X-ray beam
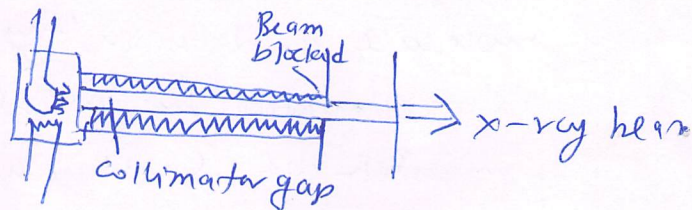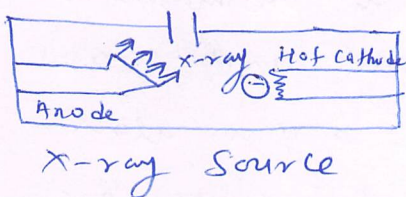
(ii) collimater: is device which absorbs unwanted radiation and passes the narrow beam of light.

(iii) Monochromator: (a) Filter: is window of material that absorbs undesirable radiations and allows required wave length to pass.

(iv) Detector: three types of detectors are used for the detection of uv-radiation, such as photovoltaic cell, Phototubes and photomultiplier tube. But PMT is most sensitive detector used in uv-visible spectro-photometer. A photomultiplier tube consists of an electrode covered with a photoemmisive material. this tube contains large number of dynodes, which emmits several electrons when uv-visible radiation falls on it, which enhances the signal intensity of the Instrument.

multiplication of electrons

Collector detect

Dynodes

hv radiation

6. **Instrumentation of gas chromatography**

(i) carrier gas, which must be chemically inert include helium, nitrogen and hydrogen. carrier gas should not react with sample and stationary phase, high purity and should not be explosive.
Helium is generally excellent because of its conductivity, inertness. Hydrogen gas can be react with unsaturated compounds and causes fire.
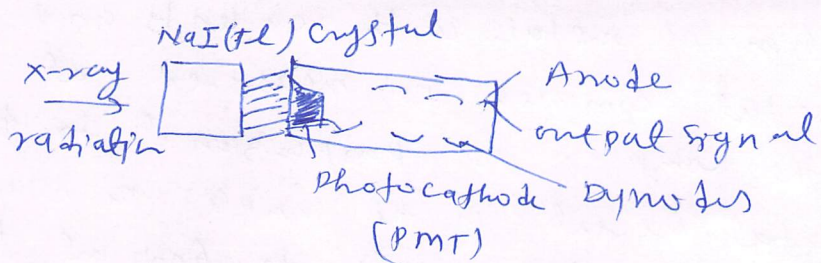
(ii) Column: column can be made from copper, stainless steel, aluminium and glass. two types of column

(a) packed column : 2-6 mm (id) , 3-10mm (od) and coating of silica particles < 100-300 mm.

(b) capillary / open tubular column: they are again two types — wall-coated tubular (WCOT): 30-90 meters id (0.025 − 0.075 cm)
support − coated open tubular (SCOT): coaty of 30 mm particle size.

X-ray radiation → NaI(Tl) crystal → Photocathode → Dynodes → Anode output Signal

(PMT)

(D) Semiconductor: Si(Li) and Ge(Li) used as semiconductor where x-ray falls, it generates an electron (-e) and hole (+h) in a fashion same as the proportional counter detector.

4. Application of UV-visible spectrophotometer

(i) Determination of composition of the complex: Job's method of continuous variation is used to determine the composition of the complex formed. The total concentration of metal and ligand is fixed but their ratio varies.

$$n M + pL \rightleftharpoons M_n L_p$$
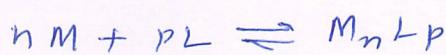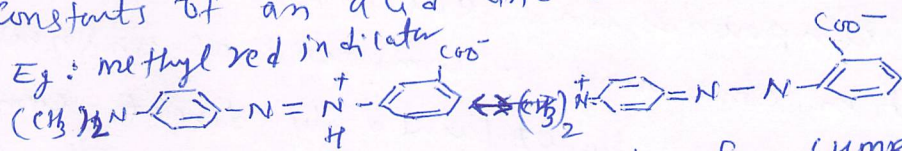
$$\frac{p}{n} = \frac{x}{1-x}$$

*The ratio of ligand to metal can tells about the composition of complex

where M – is metal ion and L – is ligand & m, n – are number of metal and ligands required.
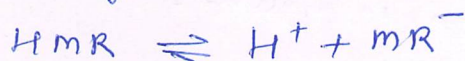
(ii) Determination of PK value of indicator:
Spectrophotometry is used for determination of the dissociation constants of an acid and bases.
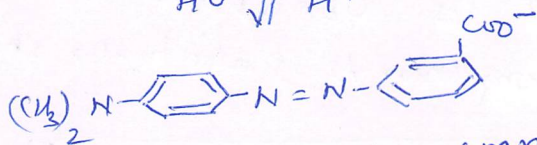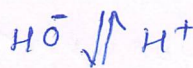
Eg: methyl red indicator

$$(CH_3)_2 N - \langle \rangle - N = \overset{+}{\underset{H}{N}} - \langle \rangle \rightleftharpoons (CH_3)_2 \overset{+}{N} \langle \rangle = N - N - \langle \rangle$$

Acidic form (HMR) Red

Applying mass action:

$$HMR \rightleftharpoons H^+ + MR^-$$

$$k = \frac{[H^+][MR^-]}{[HMR]}$$

$$pk = pH - \log \frac{[MR^-]}{[HMR]}$$

$$(CH_3)_2 N - \langle \rangle - N = N - \langle \rangle$$

Basic form (MR⁻)
Yellow

(iii) Quantitative determination of metals: visible spectrophotometry can be used for the determination of metals such as iron, lead, Cu, zinc, cadmium, arsenic or mercury from water, soil, food samples by
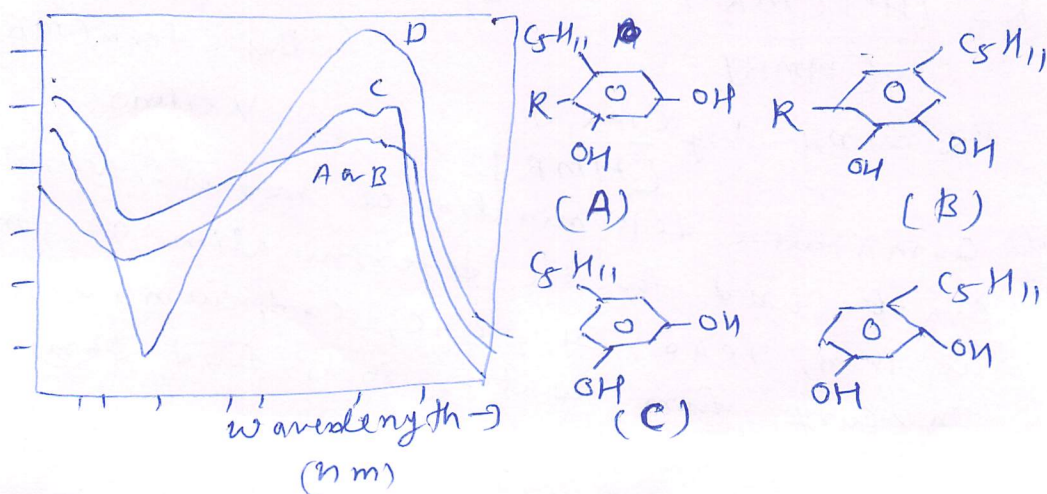
the complex formation of metals with reagents and then the color of the metal complex is measured at λ_{max}. the intensity of the complex is proportional to the concentration of metal present in the sample. The beer's law is used for calibration points to find out the concentration of metal present in unknown sample.

(iv) structure of inorganic complexes : spectrophotometry has been used to distinguish between cis and trans complex. The geometrical isomers of transition complex can be easily distinguished from their visible spectra. the cis isomer of $[Co(en)_2F_2]NO_3$ is violet, whereas the trans isomer is green. The spectra of cis and trans isomers are shown in fig.
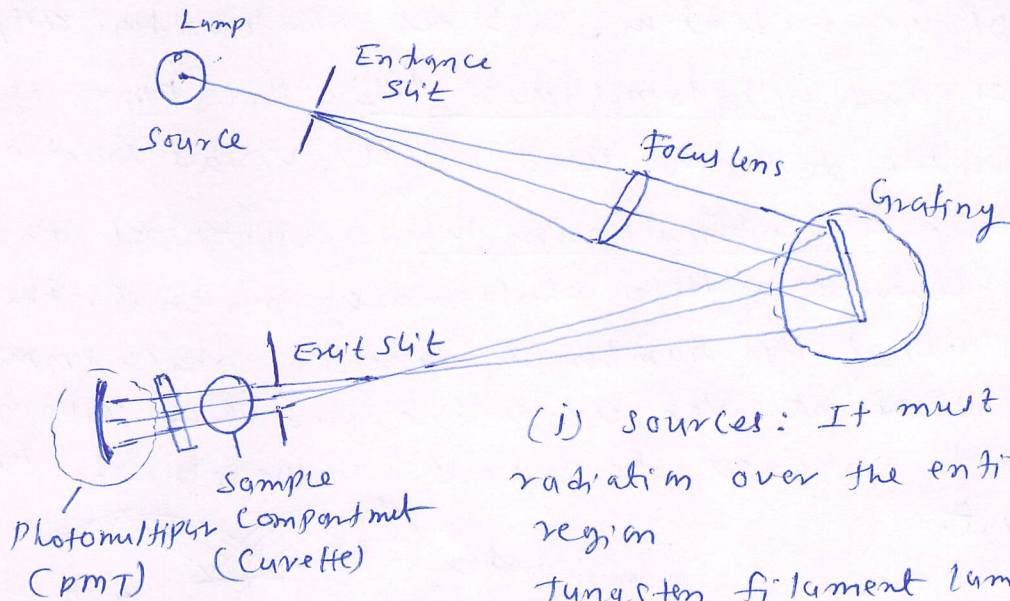

Wavelength →
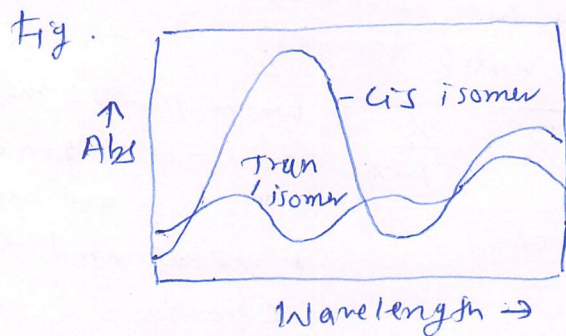
(v) structural analysis : uv-visible spectrophotometry provide a valuable tool in the identification of unsaturated organic compounds and elucidation of their structure. Information concerning a compound of unknown structure can be sometimes be obtained by direct comparision of its obsorption spectrum with those of known compounds structure, shown in figure.

Wavelength →
(nm)

(A) (B) (C)

5. Diagram of UV-visible spectrophotometer

Lamp
Source
Entrance Slit
Focus lens
Grating
Exit slit
Sample Compartment (Cuvette)
Photomultiplier (PMT)

(i) Sources: It must supply continous radiation over the entire wavelength region.
Tungsten filament lamp is the most common source of visible radiation. (400 - 750nm range)
Hydrogen lamp is used for UV region.

(ii) Filters and monochromators: A source is generally emmiting a continous spectra. Therfore a device is required to select a narrow band from wavelength of the continous spectra. For this selection, filters or monochromators both are used.
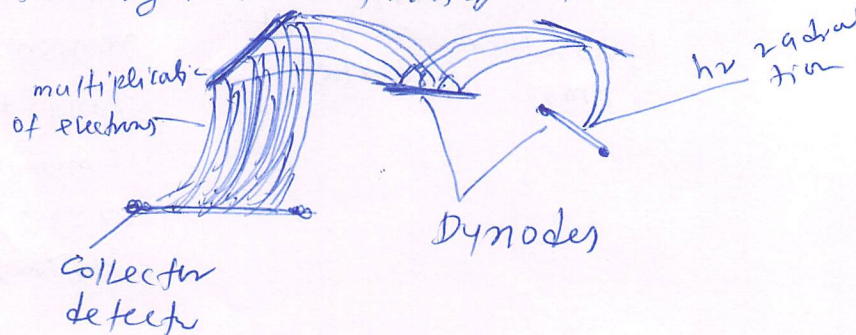
(a) Filters: suitable filter can select desired wavelength band

(b) monochromators: A monochromator successfully isolates band of wavelengths usually much more than narrower filter. the essential elements of monochromators are an entrance slit, a dispersing element (prism or grating) and exit slit. The function of a prism or grating is to disperse the heterochromatic radiation into its component wavelengths.

(iii) sample cells: The cell holding the sample should usually transparent to light incident. The thickness of cell is 1 cm length. Cell or cuvette is made from glass or quartz. The ~~sample~~ shape of cuvette is rectangular or cylindrical.

(iv) Detector: three types of detectors are used for the detection of uv-radiation, such as photovoltaic cell, phototubes and photomultiplier tube. But PMT is most sensitive detector used in uv-visible spectrophotometer. A photomultiplier tube consists of an electrode covered with a photoemmisive material. This tube contains large number of dynodes, which emmits several electrons when uv-visible radiation falls on it, which enhances the signal intensity of the instrument.

multiplication of electrons

hv radiation

Dynodes

Collector detect

6. **Instrumentation of gas chromatography**

(i) carrier gas, which must be chemically inert include helium, nitrogen and hydrogen. Carrier gas should not react with sample and stationary phase, high purity and should not be explosive.
Helium is generally excellent because of its conductivity, inertness. Hydrogen gas can be react with unsaturated compounds and causes fire.

(ii) Column: column can be made from copper, stainless steel, aluminium and glass. two types of column

(a) packed column : 2-6 mm (id) , 3-10mm (od) and coating of silica particles < 100-300 mm.

(b) capillary / open tubular column: they are again two types — wall-coated tubular (WCOT): 30-90 meters id (0.025 — 0.075 cm)
support - coated open tubular (SCOT): coating of 30mm particle size.

(iii) ovens: Column oven temperature is important variable that must be controlled for the separation of components in GC. The temperature of the oven is kept near to boiling point of compound. For the separation of compounds, the programming of temperature in oven is needed.

(iv) Detectors: The ideal detector for gas chromatograph has following characteristics.
* Adequate sensitivity * Good stability and reproducibility
* a linear response to solute that extends over several orders of magnitude.

(a) Flame ionization detector: most widely used detector. The effluent from the column is mixed with hydrogen and air, then ignited electrically that can conduct electricity.

(b) thermal conductivity detector (TCD): Based on the changes in the thermal conductivity of the gases stream brought about by the presence of analyte molecules.

(c) Electron capture detector: organic molecules capture electrons and there is decrease in the current is measured.

Applications:
(i) pesticides in foods: Gas chromatography can be used for the determination of pesticides in fruits, vegetables and other food products. Thus, the contamination of pesticide can be known.

(ii) Drugs analysis in clinic: The drugs present in urine and blood samples of clinical purpose can be studied.

(iii) Many volatile organic pollutants such as Benzene, chlorofluoro carbon can be determined.

7. (a) Normal phase chromatography : In this chromatography, the stationary phase is polar and mobile phase used are non-polar in character. Here most non polar organic compounds, first eluted from the column followed by increasing polar compounds.

(i) stationary phase : silica or alumina can be used as main component of normal phase chromatography. This is also modified to polar group on the surface of silica/alumina.

(ii) mobile phase : Non polar organic solvents such as, C_6H_6 hexane, CH_2Cl_2, $CHCl_3$ can be used as mobile phase for the elution of polar compounds from the polar column.
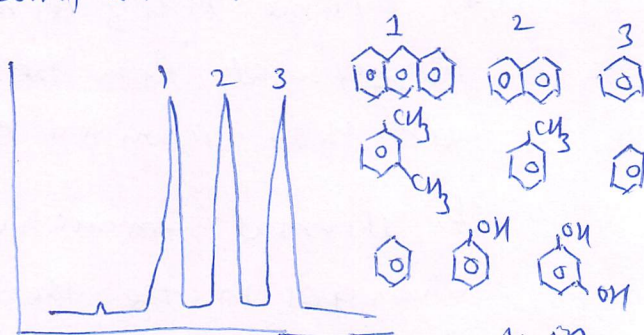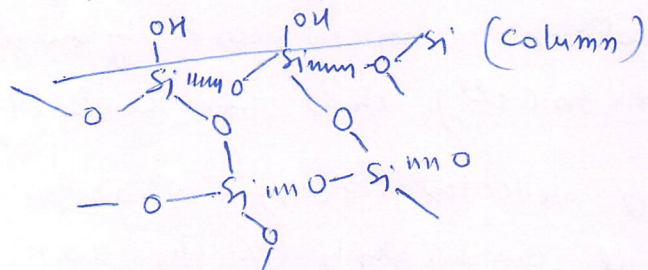
* most polar solute highly retained on the polar column (stationary phase) and thus non-polar compound elute first.

seperation of compounds in normal phase chromatography

(b) Reverse Phase chromatography : In this chromatography, the stationary phase is non-polar and mobile phase used is polar organic solvent. for the elution of compounds from the column.

(i) stationary phase : C_{18}, C_8, C_5, Phenyl can be coated as hydrophobic surface on silica, as shown
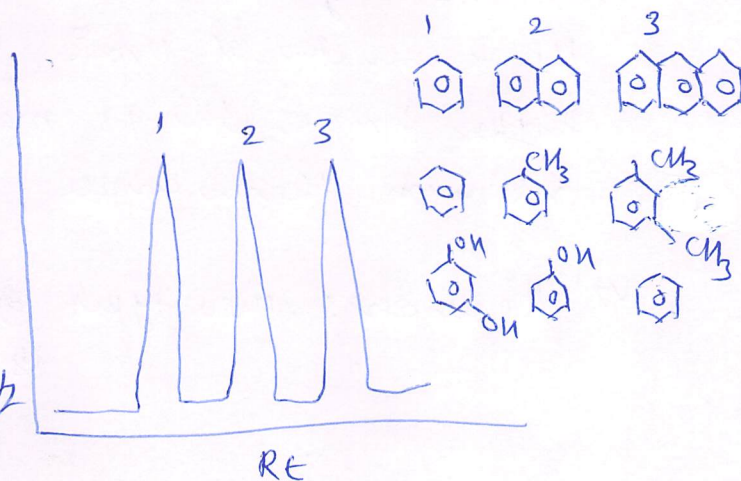
C_{18} column ($- C_{18}H_{37}$: octadecyl)

C_8 column ($- C_8H_{17}$: Hexadecyl)
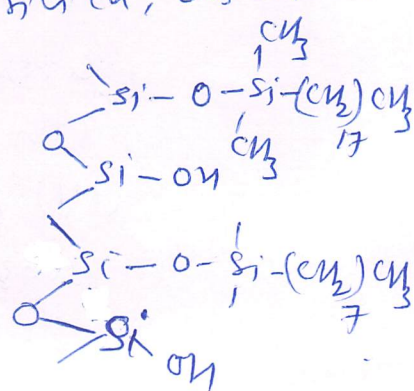
(ii) mobile phase: methanol, acetonitrile, tetrahydrofuran (13) water can be used as mobile phase in reverse phase chromatography.

Seperation of compounds in RPC: In RP the separation of organic compounds based on their degree of hydrophobicity of stationary phase.

RE

8. Instrumentation of thermal gravimetric analysis (TGA)

(i) the balance: the important components of TG is a good thermobalance. It should have accuracy, sensitivity and reproducible. two types of balances:

(a) Deflection balances: Beam, cantilever, spring and torsion

(b) Null point balances

(ii) Sample holders: the geometry, size and material of the sample holder have important effect on the shape of TG curve. sample holders are made up of glass, quartz, alumina and platinum. The shape of holder are shallow pan, Deep crucible, loosely curved crucibles

(iii) Furnace: the furnace and control system should be designed to produce a linear heating rate over the whole working temperature range of furnace. Different temp. range is made up of different materials
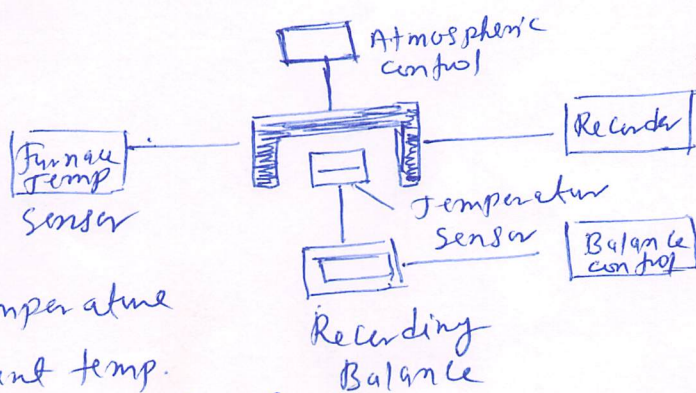
< 1100 °C — kanthal or nichrome wire

1100 - 1500 °C — platinum or alloy of platinum and rhodium

(iv) Temperature Sensor: Temperature of the TG can be controlled by the use of thermocouple. For measuring the temperature of $1100°C$, chrome or alumel is used and higher temperature is measured using tungsten and rhenium thermocouple.

(v) Recorder: Two types @ time base potentiometric

@ x-y recorder.