

ISE

# Analytical Chemistry Sp-1 Theory. Past Papers 2015

## i-Normal phase

- A separation method which allows the distribution of components of a mixture b/w Two phase one is mobile non-polar phase & other is stationary phase is polar.
- Its is evolved in 1970s in the form of liq.
- Uses polar stationary phase which is mainly pure silica.
- Having poor reproducibility of the retention of Time.

## Reverse phase

- It is a separation method which allows the separation b/w mobile phase more polar than the stationary non-polar phase.
- It is recently evolve from HPLC.
- Uses non-polar stationary phase which is modified with silica substrate & long hydrophobic chains.
  - Having higher reproducibility of the retention of Time.

Advantages of

## ii-Gradient Elution

- Mobile phase solvent composition increases with Time.
- Best for complex analysis
- often use for method development
- Increases sensitivity for analyte

## Isocratic Elution

- Mobile phase solvent composition remains constant with Time.
- Best for simple analysis
  - often used for quality control
  - sensitivity does not increase for analyte.

Factor



### iii- Selection criteria for gas in GC:

→ **Stationary phase:** They are close to the polarity of the solvent → **column diameter**

Having small diameter (0.25mm) when sample overloading is not problem → **Thickness of Film:**

If thin then high B.P of the solutes

If thick then low B.P of the solutes.

→ **Column Length:** 30 meters (for most application) 15 meters (for simple samples)

60 meters (for complex samples).

### iv- Func. of programmers in Thermobalance:

A wide variety of fully electronic thermop. controllers & programmers are available commercially. The basic requirements of a balance are accuracy, sensitivity, reproducibility & capacity.

Temp. sensors are either platinum resistance thermometers or thermocouples. Heating rates offered range from fraction of a degree per minute to nearly  $1000^{\circ}\text{C}/\text{min}$ . with facilities for isothermal operations. In a small thermal analysis laboratories one programmer may serve several instruments.

v- **Factors affecting DTA curve:** Most of the factors are associated with instrumental designs sample characteristics include following.

→ Amount of sample → particle size

→ Packing density → Heating capacity



- Thermal conductivity
- Diluent
- Degree of crystallinity
- Swelling & shrinkage

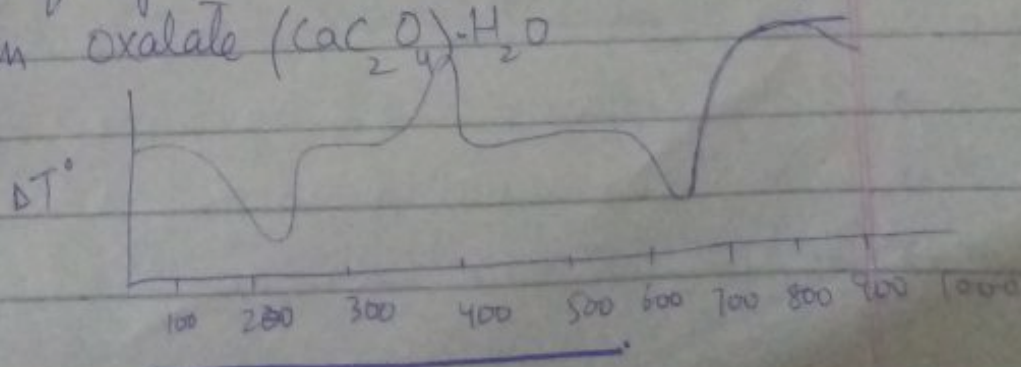
### vi- Packed Column

### Capillary Column

- |   |   |
|---|---|
| → A column that contains fully packed stationary phase made up of fine particles. | A column whose stationary phase is coated on the inner surface. |
| → Has low efficiency.   | Has higher efficiency.  |
| → Require large amount of sample  | Require small amount of sample.                                 |
| → Have high P inside the column   | Have more P. inside the column                                  |
| → Less expensive  | More expensive  |

### vii- Infor. obtained from DSC curve?

DSC measures the energy absorbed or released by a sample when it is heated or cooled. DTA curve of a pure comp. represent the characteristics of a comp. for physical & chemical changes. Using DTA curve one can relate the changes in energy because of thermo-physical & chemical change occurring in a comp. because of heating. Change in DTA curve also gives infor. like M.P, glass Transition & Temp. of crystallization etc. The DTA curve of Calcium Oxalate  $(CaC_2O_4) \cdot H_2O$



$CaC_2O_4 \rightarrow CaCO_3 + CO$



### viii-KCl is ideal electrolyte for Salt Bridge:

KCl is a ideal specie for salt bridge as  $K^+$  &  $Cl^-$  have same no. of  $e^-$  & having approximately same size. As we know charges flow due to the presence of electric field. Electric field is the flow of ions & electrodes. With this principle KCl is used to maintain the neutrality of the soln. - ~~containing~~ So, this reac. reached equilibrium not faster.

### ix-Why Calomel Electrode preferred over SHE:

The potential of standard Calomel electrode containing an unsaturated soln. of KCl is less Temp. dependant. But its potential change due to change in  $Cl^-$  ions & change in its activity. So, Calomel electrode is preferred over SHE.

### x-Liq. Junction potential in potentiometry:

Liq. Junction interface b/w two soln. containing different electrolytes or same electrolytes. A junction potential occurs at every liq. junction. It is caused by unequal +ve & -ve ions.

— (2019) —

### i-Advantages of Thermal conductivity:

Advantages of Thermal conductivity detectors are:-

- General response to both org. & inorg. species
- Large linear dynamic range ( $-10^5$ )
- less sensitivity



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→

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70





as the time from injection to detection-  
The RT for a comp. is not fixed as many factors  
can influence it even if the GC column is  
used. These include the gas flow rate.

**Factors affecting:** It depends upon many factors:

- Analyte condition
- degradation of column-
- Existence of active part such as contamination
- Types of column

Principle  
of:-

#### v- DTA

The basic principle of DTA is change in Temp. DT b/w Test sample & an inert reference sample under controlled & identical conditions of heating or cooling is recorded continuously as a func. of Temp. or Time. Thus the heat absorbed/emitted by a chemical system is determined.

#### TGA

The plot of weight change against Temp. called TGA

In TGA analysis, sample is heated in a given environment at controlled rate.

The change in the weight of the substance recorded as a func. of Temp. or Time. The Temp. is increased at constant rate of known initial weight of the substance & the changes in weights are recorded as a func. of Temp. at different Time interval.

viii- **Ideal reference Electrode.** Ideal reference electrode that has half cell potential known constant & incompletely insensitive to the composition of ~~study~~ soln. under study.

vi- Repeat  
vii-



In conjunction with the reference is the indicator working electrode whose response depends upon the analyte conc. Basic func. of reference electrode is to maintain a constant electrical potential against which deviations may be measured.

ix - Potentiometric Titration: Potentiometric titrations the equivalence point is determined by the measurement of an indicator electrode potential against a convenient reference electrode potential and plotting the difference against volume of Titrant, called potentiometric Titrations.

x - DTA curve: DTA is a thermoanalytical technique that is similar to DSC. DTA curve provides data on the transformation that have occurred such as glass transition, crystallization, melting & sublimation.

### Characteristics of DTA curve:

DTA curve are not helpful in the identification of material but the peak areas provide quantitative information regarding mass of sample, heat of reac. & factors such as sample geometry & Thermal conductivity.

→ Two factors are expressed by a factor  $K$ , called calibration factors then peak areas can be expressed as Peak area =  $\Delta H_{mk}$ .



i-Thermobalance In analytical chemistry,

a balance is used for thermogravimetric analysis known as thermobalance. It involves the measurement of weight associated with the transformations of matter when heated.

ii-Evolved gas detection: Evolved gas analysis is a method used to study the gas evolved from the heated sample that undergoes decomposition or desorption. It is either possible just to detect evolved gases by using evolved gas detection (EGD) or to analyse the explicitly when gases evolved using evolved gas analysis.

iii - WCOT

SCOT

→ Wall coated open Tubular column was first introduced by Galay in 1957

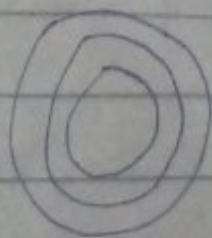
Support coated open Tubular column was first introduced by Hala'sz & Harvath in 1963

→ In this column wall is directly coated with stationary phase layer at a film thickness  $0.05-3\mu\text{m}$

In this column, an adsorbed layer of very fine solid support coated with the liquid phase.

→ WCOT has low sample capacity.

SCOT columns hold more liquid phase & have higher sample capacity.





## iv- DTA

- Differential Thermal analysis
- The Temp. difference developed b/w a sample & reference comp. is increased at identical heat measurements
- Uses to analyze the thermal properties of minerals for the characterization of polymers & biological materials
- Sample can be used as a solid substance.

Differential scanning calorimetry  
The heat flow is measured against the Temp. change at a particular time - used To analyze proteins, anti-bodies etc -  
Sample can be always used as liquid.

v- Precolumns in HPLC: A precolumn is also called a guard column it protects the column by plugging or contamination by samples & mobile phase.

In other words it is a protective column or cartridge installed b/w the injector & analytical column. It serves to remove impurities & suspended solids from reaching the column.

vi- Electrode Potential: It is an electric potential ~~current~~ in an electrode component.



In a cell, there is an electrode potential for the cathode & an electrode potential for an anode. The difference b/w the 2 electrodes potential equal to the cell potential.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

vii- Nernst Equation:

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \log K$$

→ Helpful for determining cell potential, equilibrium constants, etc.

$E^{\circ}$  = Standard cell potential,  $R$  = universal gas constant.  
 $n$  = valence of ions,  $F$  = Faraday,  $T$  = absolute Temp.  
 $\log = K$  at equilibrium.

viii- Stepwise Elution: Process in which composition of mobile phase changes in steps during single chromatographic run. SE can work as a purification & composition of proteins at the same time. The conc. factors by SE with ion exchange chromatography columns were measured as a func. of the feed volume & feed concentration.

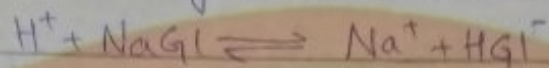
ix- Standard Columns in HPLC: The most important part in HPLC is column which is made up of glass, plastic & steel. <sup>Mostly</sup> Stainless column is used to withstand pressure as well as chemical action of solvent. Mostly 2 columns are used in HPLC  
① Guard column ② Analytical column.



Guard column contains some stationary phase as the main column, so it protects the main column, extends the life of main column. Analytical column has large size than guard column & has more stationary phase b/w them.

x-Eq. for pH measurement in glass electrode:

The ion exchange reac. can be written as:-



NaGI = Glass, HGI = silica acid

GI represents many -vely charged sites of glass surface the eq. constant for this purpose is so large that the surface of glass membrane mainly consist of silicated ( $HGI^-$ )

2016.

i- Thermal Analysis: Thermal analysis is the branch of material science where the properties of the material & their change with temp. can be studied.  $\rightarrow$  Several methods are used these are distinguished from one another by the property which is measured.  $\rightarrow$  It depends upon physical properties of certain substances.  $\rightarrow$  Physical properties include mass, Temp. enthalpy etc. these are Techniques of thermal analysis.

ii- Application of DSC:  $\rightarrow$  composition of polymers can be determined  $\rightarrow$  M.P & Glass Transition Temp. can be determined  $\rightarrow$  Thermal degradation & impurities  $\rightarrow$  The polymer degradation by lowering the M.P can be determined.



→ Compare additive effects on materials-

iii - Resolution in HPLC: The resolution of an elution is a quantitative measure of how much two elution peaks can be differentiated in a chromatographic separation. It is defined as an ability to separate two signals i.e. separation of 2 constituents → Higher the resolution it is easier to achieve the baseline separation b/w 2 peaks

v-G.T.T.  
vi-G.I.E  
(2015)

iv-Characteristics of Detectors in HPLC:

→ High sensitivity → low dead volume → large linear response range → Reliable & easy to use non-destructive

vii-Derivatization is necessary in GC:

Derivatization is the process of chemically modifying a comp. to produce new comp. with having same properties <sup>which are suitable</sup> that used for analysis in GC. The ~~structural~~ chemical formula of comp. is same while there is just modification in func. group reacting chemically with derivative and derivatizing chemical & physical properties ~~that~~ in order to make them detectable & analyzable.

Derivatization also <sup>reduces</sup> ~~improves~~ analyte adsorption used in GC system. It also make the improve of detectors quality, peak operation & peak symmetry

viii-Thermal Conductivity Flame Ionization

- It is a sample detector. Universal detector for organics
- General responses Both. Does not respond to common inorganic comp.
- Used for org. & inorg. species. Linear & dynamic range than TC.
- Large linear dynamic range.
- Non-destructive solutes can be collected after detection. Carrier gas not detected.



ISE

## ix - Advantages

- These Type of electrodes are un-affected by sample colour or Turbidity
- Non-destructive & non-consumption
- Non-contamination & <sup>response</sup> short interval time in sec, minute, useful in industries
- ISEs are of few electrodes that measure both +ve & -ve ions.

## Disadvantages

- Electrodes are fragile & have limited shelf life.
- Interference occurs by other ions.
- Electrodes can be fouled by proteins & other organic solutes.
- Electrodes respond To activity of uncomplexed ions. So ligands must be absent.

FL - F  
Structure Diagrams works:



## Packed column

- S.P is directly coated in the column
- Applicable for both GSC - GLC
- L.P is adsorbed on the surface of beads in a thin layer or onto the solid inert packing.

## Capillary column

- S.P is coated on the inner walls of column
- Applicable for GLC
- Liq S.P is immobilized on the capillary tubing walls.

PUACP

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