# B.Sc. Part – I
# Year: 2020-21

## Online Teaching

# Analytical Chemistry
# (Paper: IV)

**Dr. Arjun S. Kumbhar**
**Department of Chemistry**
**P.D.V.P. College, Tasgaon**

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# Shivaji University, Kolhapur: CBCS Syllabus Chemistry
# B.Sc. Part –I Semester (I and II)
# To be implemented from June -2018

## Nature of Syllabus

### ▪ Semester I

- Paper – I : Inorganic Chemistry
- Paper – II : Organic Chemistry

### ▪ Semester II

- Paper – III : Physical Chemistry
- Paper – IV : Analytical and Industrial Chemistry

- Theory: 200 (50+50+50+50 =200 marks for each semester)
- Practical : 50
- Total : 250

# Nature of Examination



| Q. No | Details | Marks | Marks option |
|---|---|---|---|
| 1 | (a) Select the most correct alternative among those given below<br>(b) ) Answer the following in one sentence | 05<br>05 | - |
| 2. | Long answer type questions (2 out of 4) | 20 | 10 |
| 3. | Short answer type questions (4 out of 6) | 20 | 10 |
| | 5 | 50 | 20 |

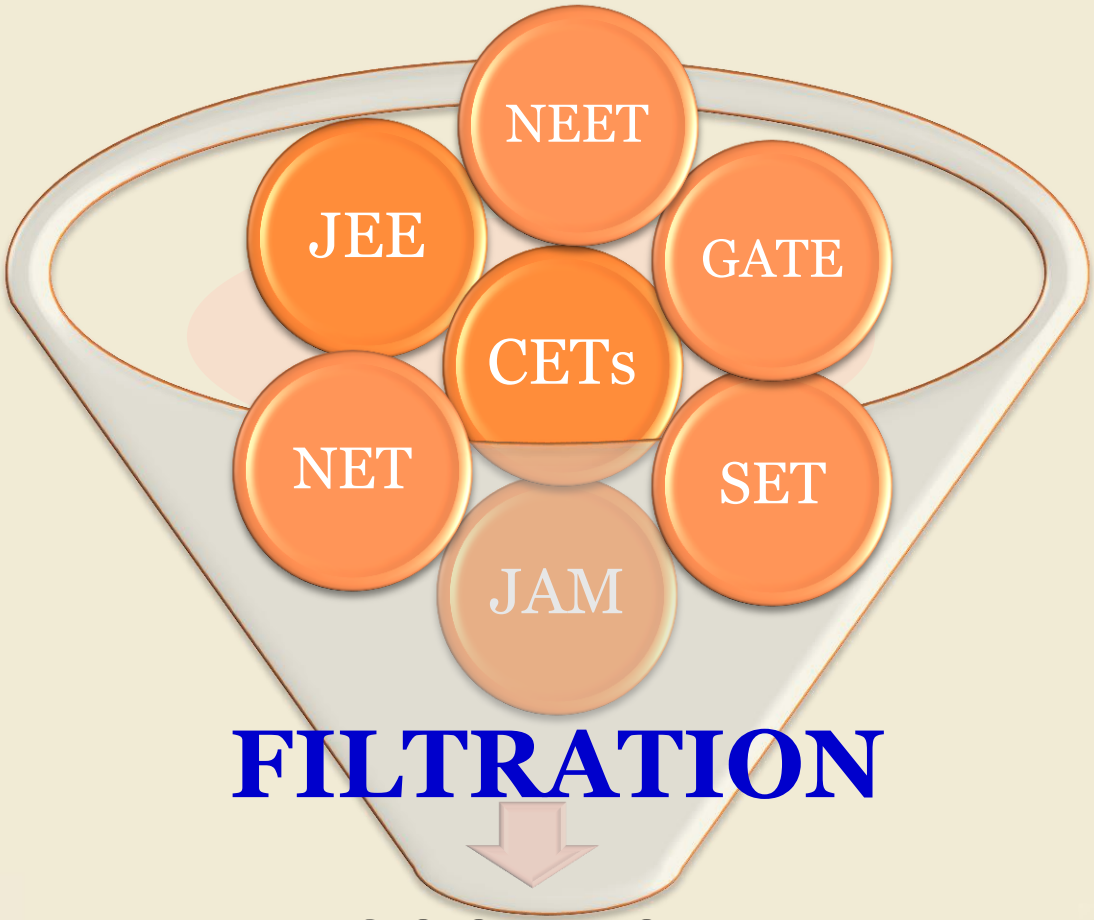
- **The duration of each theory paper : 2 hours**
- **Combine passing : (35/100)**

**Practical Examination : Marks: 50**
**: Duration: 1 day (6.5 hours)**

1. **Physical Section : 15 marks**
2. **Inorganic Section : 15 marks**
3. **Organic Section : 15 marks**
4. **Journal : 05 marks**

# Filtration: Common Way to Get Good Job






# Chemistry



**The branch of science concerned with the substances of which matter is composed, the investigation of their properties and reactions, and the use of such reactions to form new substances.**

**Study of properties (physical & chemical) of substances**

**Analytical:** Instruments and methods used to separate, identify, and quantify matter

**Inorganic: Chemistry that studies the structure, properties and reactions of inorganic compounds**

**Physical: Chemistry dealing with the relations between the physical properties of substances and their chemical composition and transformations.**

**Organic: The studies of the structure, properties and reactions of organic compounds**

# Syllabus not to be considered for examination



| | | |
|---|---|---|
| | Chemistry | |
| B Sc. I Sem II | **DSC-3B- Paper III** Physical | **Unit II Chemical Equlibria** (whole unit) |
| B Sc. I Sem II | **DSC-4B- Paper II** Analytical Chemistry | Unit V **Analysis of Fertilizers**(whole unit) |

# B.Sc. I Semester II
# DSC-4B-Chemistry Paper IV (Analytical Chemistry)
# (Theory Credits:02, Lectures-30)

**1. Introduction to analytical Chemistry** **(06)**

1.1 Introduction
1.2 Importance of analysis
1.3 Analytical processes (Qualitative and Quantitative)
1.4 Methods of analysis (Only classification)
1.5 Sampling of solids, liquids and gases
1.6 Errors, types of errors (determinate and indeterminate), methods of expressing accuracy (Absolute and relative error)
1.7 Significant figures, mean, median, standard deviation (Numerical problems expected)

**2. Chromatography (06)**

2.1 Introduction, Basic Principle of Chromatography, Basic terms, Classification of Chromatography

2.2 Paper Chromatography- Principle, Methodology-types of papers and treatment, sample loading, choice of solvent, development-ascending, descending, circular, location of spots, determination of $R_f$ value, Applications, advantages and disadvantages

2.3 Thin layer chromatography; Principle, Solvent system, stationary phases, preparation of TLC plate, Detecting reagents, methodology-sample loading, development, detection of spot, $R_f$ value, Applications, advantages and disadvantages

2.4 Comparison of paper chromatography and TLC

**3. Theory of titrimetric Analysis (06)**

3.1 Introduction

3.2 Acid-base indicators

3.3 Theory of indicators w.r.t. Ostwald's ionization theory and quinoid theory

3.4 Neutralization curves and choice of indicators for

a. Strong acid-strong base
b. Strong acid-weak base
c. Strong base-weak acid

3.5 Complexometric titrations

a. Introduction
b. Types EDTA titrations
c. Metallochromic indicators-Eriochrome black- T
d. Indicator Action of Eriochrome black- T

**4. Water Analysis (06 )**

4.1 Physical analysis of water – pH, Conductance, Colour, odour, Turbidity and taste

4.2 Chemical Analysis – Total Dissolved solids , Hardness, Salinity, Alkalinity, Acidity, Sulphates, Nitrates, Dissolved Oxygen, Chemical Oxygen Demand, Biological Oxygen Demand

## CHEMISTRY-DSC 3B: Chemistry Paper-III (Physical Chemistry)

## (Credits :02 , Lectures-30)

**Unit -I Chemical Energetics** **(06)**

**A)Thermodynamics**

Introduction, Basic concepts of thermodynamics, First law of thermodynamics Spontaneous and non-spontaneous process with examples, Statements of second law of thermodynamics, Carnot's cycle and its efficiency. Entropy, Physical Significance of entropy, Statement of Third Law of thermodynamics and calculation of absolute entropies of substances

**B) Thermochemistry** **(04)**

Important principles and definitions of thermochemistry. Concept of standard state and standard enthalpies of formations, integral and differential enthalpies of solution and dilution. Calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data. Variation of enthalpy of a reaction with temperature – Kirchhoff's equation.

**Unit- III. Kinetic Theory of Gases** **(07)**

Postulates of Kinetic Theory of Gases and derivation of the kinetic gas equation. Ideal and Non ideal gases, Deviation of real gases from ideal behaviour, compressibility factor, causes of deviation. Van der Waals equation of state for real gases. Explanation of real gas behaviour by Van der Waal's equation, Boyle temperature (derivation not required). Critical Phenomena: PV-isotherms of real gases (Andrew's isotherms), Continuity of state, Critical constants and their calculation from vander Waals equation. Maxwell Boltzmann distribution laws of molecular velocities and molecular energies (graphic representation – derivation not required) and their importance. Temperature dependence of these distributions. Most probable, average and root mean square velocities (no derivation). Numerical Problems.

(08)

**Unit- IV. Chemical Kinetics** **(07)**

Introduction, Rate of reaction, Definition and units of rate constant, Factors affecting rate of reaction. (Nature of reactant, Concentration, pressure, temperature and catalyst.) Order and Molecularity of reaction, Zero order reaction, First order reaction, Characteristics of first order reaction.examples, Pseudo-unimolecular reactions,examples. Second order reaction: Derivation of rate constant for equal and unequal concentration of the reactants. Characteristics of Second order reaction., Determination of order of reaction by i) integration method ii) graphical method iii) Half life method, Effect of temperature on rate of reaction, Arrhenius equation, Concept of energy of activation.

Theories of Reaction Rates: Collision theory and Activated Complex theory of bimolecular reactions. Comparison of the two theories (qualitative treatment only). Numerical problems.

# CHROMATOGRAPHY

## 2.1 INTRODUCTION

Are all organic compounds, pure? The answer of this question is No. The most organic compounds obtained from natural sources and synthesized in laboratories are not pure. Various methods are used for the purification of organic compounds that are based on the nature of the compound and the impurity present in it. Among the various separation techniques, chromatography is one of the most important separation techniques extensively used to separate mixtures into their components and the purification of compounds.

**Chromatography :** The word chromatography is originated from two Greek words : 'chroma' meaning 'colour' and 'graphy' meaning 'to write'. Thus, chromatography means colour writing. It was first employed by a Russian scientist Mikhail Tsvet for the separation of coloured substances in plants. This analytical technique has a wide range of applications in the real world, since many substances are mixtures of chemical compounds.

## 2.1.1 General Principle

Chromatography is a separation technique based on the partitioning or distribution of a sample (solute) between a moving (mobile) phase and a fixed (stationary) phase. When the mobile phase is moved over the mixture on the stationary phase, the components of the mixture gradually separate from one another.

## 2.1.2 Terms Used in Chromatography:

1. **Analyte :** It is the substance to be separated during chromatography.
2. **Chromatogram :** Visual output of the chromatograph.
3. **Detector :** It is the part of chromatographic instrument used for detection of analyte.
4. **Phases :** In the chromatographic technique two phases are used.

(i) **Stationary phase :** The mixture of substances is applied onto a phase called the stationary phase. The stationary phase may be solid or liquid.

(ii) **Mobile phase :** A moving phase that can be a pure solvent or a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. This moving phase is called the mobile phase.

## 2.1.3 Classification of Chromatography

There are various types of chromatography; these can be classified into following types;

**I. Based on mechanism of separation**:

1. Adsorption chromatography
2. Partition chromatography
3. Ion-exchange chromatography
4. Gel-permeation (molecular sieve) chromatography

**II. Based on phases**:

1. Solid phase chromatography :
   (a) Solid-liquid chromatography
   (b) Solid-gas chromatography
2. Liquid phase chromatography :
   (a) Liquid-liquid chromatography,
   (b) Liquid-gas chromatography

## III. Based on shape of chromatographic bed:

1. Planar chromatography :

   (a) Paper chromatography,

   (b) Thin Layer chromatography

2. Column chromatography :

   (a) Packed column chromatography,

   (b) Open tubular column chromatography

**I. Based on mechanism of separation :** Depending on the basic principle (mechanism) involved in chromatography, it is mainly classified into two types viz. adsorption and partition chromatography.

**II. Adsorption chromatography :** It is based on the differential adsorption of components on the adsorbent (stationary phase). This means that different compounds are adsorbed on an adsorbent at different degrees viz. column chromatography and thin layer chromatography.

**III. Partition chromatography :** The basic principle of partition chromatography is the continuous differential partitioning of the components of a mixture between the stationary phase and the mobile phase viz. paper chromatography, gas chromatography, HPLC.

**IV. Ion-exchange chromatography :** Ion-exchange chromatography is based on electrostatic interactions between charged protein groups, and solid support material (matrix). Positively charged ion-exchange matrices are called anion-exchange matrices, and adsorb negatively charged ions. While matrices bound with negatively charged groups are known as cation-exchange matrices, and adsorb positively charged ions.

**V. Gel-permeation (molecular sieve) chromatography :** The basic principle of this method is to use dextran containing materials to separate macromolecules based on their differences in molecular sizes. The molecules smaller than the pores are diffused into pores.

## 2.2 PAPER CHROMATOGRAPHY

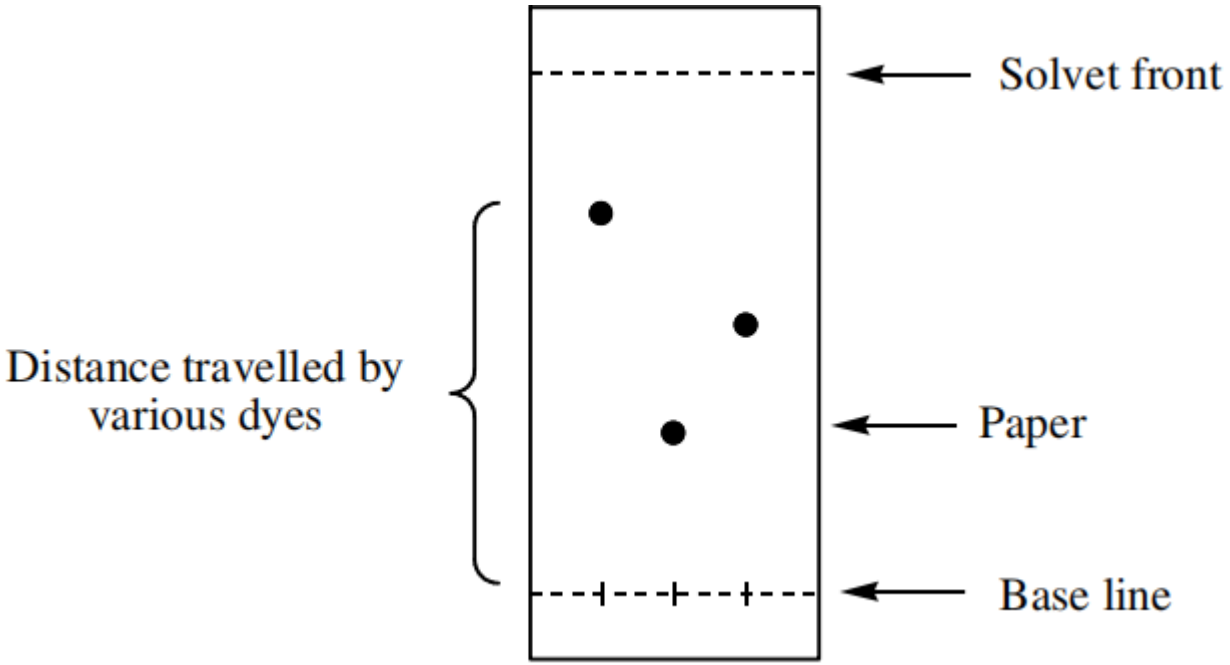
Paper chromatography is one of the types of chromatography procedures, which run on a piece of specialized paper. It is a planar chromatography system wherein a cellulose filter paper acts as a stationary phase on which the separation of compounds occurs.

**(i) Stationary phase :** It is a special quality paper called chromatography paper *viz*. Whatmann paper 1.

**(ii) Mobile phase :** It is a solvent or a mixture of solvents.

## 2.2.1 Principle

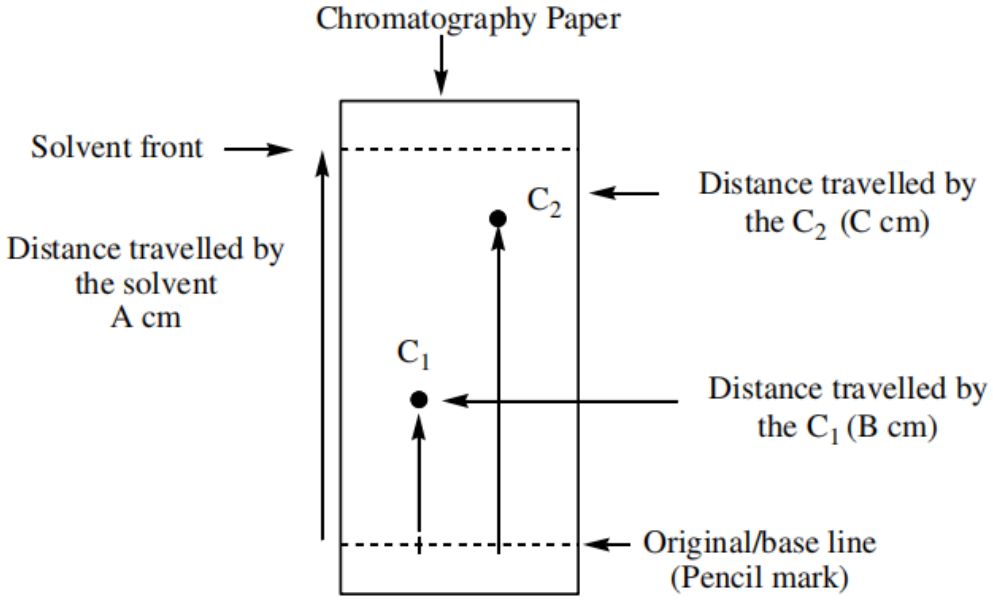
A solution of the mixture is spotted on a line about 2 cm above from the bottom of the paper, called original line or base line and then suspended in a chromatography chamber containing suitable solvent. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is called chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of the initial spot on the chromatogram. The spots of the separated colourless components may be observed either under ultraviolet light or by the use of an appropriate spraying reagent.


Solvet front
Distance travelled by various dyes
Paper
Base line

## $R_f$ Value (Rate of flow or Retardation factor or Retention factor):

It is defined *as the distance moved up or travelled by the component from the original line (base line) to the distance travelled by the solvent front from the original line (base line).*

$$R_f = \frac{\text{Distance travelled by the component from the base line}}{\text{Distance travelled by the solvent front from the base line}}$$




$R_f$ value of compound 1 = $\frac{B}{A}$

$R_f$ value of compound 2 = $\frac{C}{A}$

In the few cases to achieve the required separation the solvent front needs to be run off the end of filter paper. In such cases, $R_x$ value is used.

$$R_x = \frac{\text{Distance travelled by a substance}}{\text{Distance travelled by the standard (solvent)}}$$

**Example :** If the red dye travelled 1.7 cm from the baseline, while the solvent had travelled 5.0 cm, then the $R_f$ value for the red dye is : 1.7/5.0 = 0.34

**Factors affecting on $R_f$ value :** The following factors determine the $R_f$ value of any component.

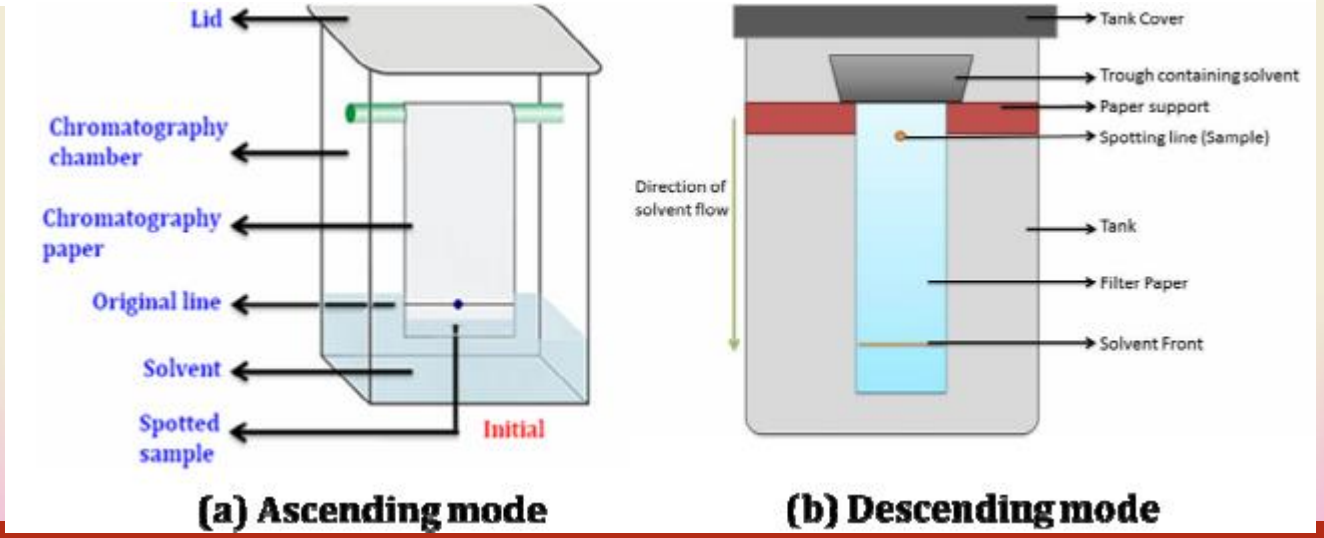
1. The quality and dimensions of paper used.
2. The solvent system used.
3. The nature of the sample to be analyzed.
4. Temperature of the environment.
5. Size of chamber used for development.

## 2.2.2 Types of Paper Chromatography

Based on the way of development of chromatogram on paper, these are of following types.

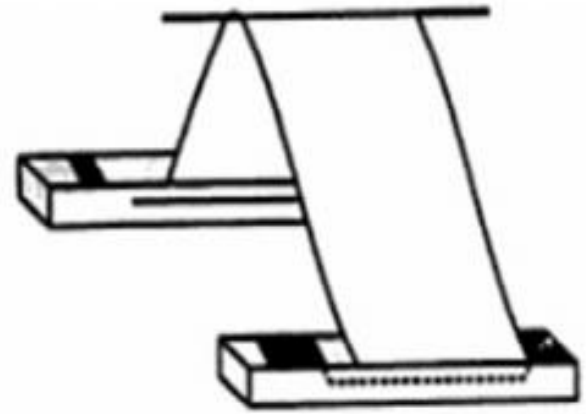
1. **Ascending paper chromatography :** As the name indicates, the chromatogram ascends. Here, the development of the paper occurs due the upward movement of solvent. The solvent reservoir is at the bottom of the beaker. The paper tip with sample spot just dips into the solvent at the bottom so that spot remains well above the solvent. [Refer Fig. 2.3 (a)].

2. **Descending chromatography :** Here the development of the paper occurs due to solvent travel downwards on the paper. The solvent reservoir is at the top. The movement of solvent is assisted by gravity, besides the capillary action [Refer Fig. 2.3 (b)].

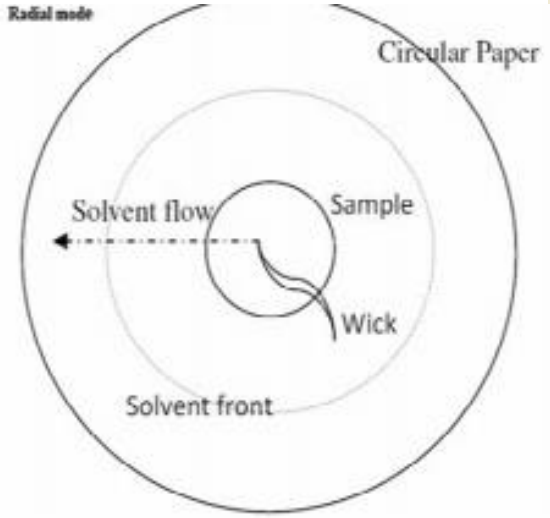


**3. Ascending-Descending mode :** Here the solvent first travels upwards and then downwards on the paper. Only length of separation increases. First ascending takes place, followed by descending [Refer Fig. 2.3 (c)].

**4. Radial mode :** Here the solvent travels from centre (mid-point) towards the periphery of the circular chromatography paper. The entire system is kept in a covered petridish for the development of the chromatogram. The wick at the centre of paper dips into the mobile phase in a petri dish, by which the solvent drains on to the paper and moves the sample radially to form the sample spots of different compounds as concentric rings [Refer Fig. 2.3 (d)].



(c) Ascending-descending mode




(d) Radial mode

## 2.2.3 Experimental Methodology

In paper chromatography, the sample mixture is applied to a piece of filter paper, the edge of the paper is immersed in a solvent, and the solvent moves up the paper by capillary action.

**General Requirements :** The apparatus required for paper chromatography are as follows.

1. **Filter paper :** Filter paper is selected based on pore size, the quality of the sample to be separated, and also mode of development. The paper commonly used consists of highly purified cellulose. Most commonly used paper is Whatmann filter paper number 1.

2. **Suitable type of development/solvent system :** The use of solvent system depends on the complexity of the mixture, solvent, paper, etc. (Table 2.1).

3. **Preparation of the sample :** Preparation of the sample involves dissolution of sample in suitable solvent used in making mobile phase. The *solvent used should be inert with the sample* under analysis.

4. **Spotting of sample on the paper :** Samples are to be spotted at proper position on the paper preferably using a capillary tube.

5. **Development of chromatogram :** Sample spotted paper is subjected to development by immersing it in the mobile phase. The mobile phase moves over the sample on the paper under the capillary action of paper.

6. **Drying of the paper and detection of compounds :** Once the development of chromatogram is over, the paper is held carefully at the borders so as to avoid touching the sample spots and dried using an air drier. Sometimes the detecting solution is sprayed in the developed paper and dried to identify the sample chromatogram spots by using spraying agent **(Table 2.1)**. *Thus sparing agent is a chemical agent used to locate the components on paper.*

**Table 2.1 : Commonly used solvent systems and spraying agents**

| Component | Solvent system | Spraying agent |
|---|---|---|
| Amino acids | MeOH : Pyridine : $H_2O$ (25 : 12 : 63)<br>Phenol : $H_2O$ (80 : 20) | Ninhydrine |
| Carbohydrates | *i*-PrOH : Pyridine : $H_2O$ : AcOH (8 : 8 : 4 : 1) | Ammoniacal $AgNO_3$, Alkaline $KMnO_4$, Aniline, Diphenylamine |
| Chlorophylls and carotenoids | *i*-PrOH : Pet ether | Self |
| Metal ions | EtOH : 5MHCl (90 : 10) | Rubeanic acid, $NH_3$ |

## 2.2.4 General Procedure

1. Take a Whatman filter paper strip and using a pencil draw a horizontal line 2 cm from one end of the paper.
2. Using a fine capillary tube put a drop of the mixture. Let it dry in air. Put another drop on the same spot and dry again, so that the spot is rich in the mixture.
3. Pour equal amounts of isopropyl alcohol and distilled water into a chromatographic chamber and mix it well using a glass rod. This is used as the solvent.
4. Suspend the filter paper vertically in the chromatographic chamber containing the solvent in such a way that the pencil line remains above the solvent level.
5. Close the jar with lid and keep it undisturbed.
6. Notice the rising solvent along with spots. After the solvent has risen about 15 cm you will notice different spots on the filter paper.
7. Take the filter paper out of the jar and using a pencil mark the distance that the solvent has risen on the paper. This is called the solvent front.
8. Dry the filter paper and put pencil marks at the centre of the red and blue ink spots.
9. Measure the distance of the two spots from the original line and the distance of the solvent from the original line.

## 2.2.5 Applications of Paper Chromatography

1. Paper chromatography is specially used for the separation of a mixture having polar and non-polar compounds.
2. It is used for the separation of amino acids.
3. It is used for the analysis of the reaction mixture as well as analysis of biochemical samples like urine, blood etc. It also used for the detection of drugs and dopes in animals and humans.
4. **Pharmaceutical industry :** In the pharma sector, it is used for the determination of chemical hormones, drugs, etc. It also used in the analysis of cosmetics.
5. **Food industry :** For the detection of adulterants/contaminants in foods and drinks.
6. **Inorganic chemistry :** Sometimes it is used for evaluation of inorganic compounds like salts and complexes as well as metal ions.
7. **Agriculture fields :** For the study of ripening and fermentation.

### 2.2.6 Advantages and Disadvantages of Paper Chromatography

| Advantages | Disadvantages |
|---|---|
| 1. It requires very less sample. | 1. Large quantity of sample cannot be applied on paper chromatography. |
| 2. It is cheaper as compared to other chromatography methods. | 2. In quantitative analysis paper chromatography is not effective. |
| 3. Both inorganic and organic compounds can be identified by using paper chromatography. | 3. Complex mixture cannot be separated by paper chromatography. |
| 4. It does not occupy much space as compared to other analytical methods/equipment. | 4. Less accurate as compared to other chromatography. |
| 5. It is inexpensive, easy to set up, and it is easy to look the colourful dots separating from each other. | 5. It cannot be used in separation of volatile substances such as hydrocarbons and volatile fatty acids. |
| 6. The operational time for this is less. | |
| 7. One of the major advantage of paper chromatography is the sensitivity with which compounds can be located after separation. Amounts as little as 0.1 microgram can be detected with routine reagents. | |


Thank You!