

**Natubhai V. Patel College of Pure & Applied Sciences**

**T. Y. B.Sc. (Industrial chemistry)**

**IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals**

**UNIT – 4**

**Syllabus**

Application of synthetic dyes of various fabrics and Fastness properties. Analysis of dyes and dye intermediates: nitrite value, coupling value, Titanous chloride reduction, Halogen content determination and estimation of Cu, Ni and Cr.

**INTRODUCTION**

**Dyeing**

The **process** which is used to **transfer the color to the substrate using dyes** is generally known as **dyeing**. A colored substance is useful as a dye only if it can be attached to a fiber. The **method of applying a dye depends** upon the following **three** important factors.

- Type of the dye
- Nature of the dye
- Type of the fiber

**Wool** and **silk** may be regarded as **amphoteric proteins** and they have a **natural affinity** for substances containing **acidic or basic groups** with which they react as a result of salt formation. In other words, dyeing properties of wool and silk are similar and both of them can be **dyed directly** by introducing into a solution of either an acidic or a basic dye.

**Cotton, linen** and **rayon's**, on the other hands are composed of natural cellulose molecules. They **do not show** any **affinity** for many dyes direct to wool and silk. They may however, **react with substances** known as **substantive dyes**. Cellulose fibers, such as cotton, linen etc. can also be dyed by making use of processes of vatting, mordanting and formation of dye on the fiber.

**TYPES OF FORCES INVOLVES DURING DYING OF FIBER**

The dyeing of fiber involves one or more of the following types of forces

**Ionic Interactions**

These interactions are **due to ionic sites of opposite charge** in the fiber and the dye molecules, **E.g.** Dyeing of wool with acid dyes having fairly simple structures involves the formation of salt type chemical links between dye anions and cationic groups in the fiber. The resulting dyeing; however, had poor fastness to wet treatment, because the salt type chemical links formed between dye anion and cationic fibers can be broken easily. **Basic dyes** are **attached to** silk, wood, or acrylic fibers containing anionic sites through the salt type linkages. **Fastness to washing** on wool as well as silk is rather **poor in majority of cases**, but **good** in cases of **poly acrylonitrile fibers**. This probably due to partly in differences in the strength of salt bonds and partly to the hydrophobic nature.

**Hydrogen Bonds**

The hydrogen bonds are involved in dyeing of wool, silk and manmade fibers. **Several hydrogen bonds formed** between the dye molecule and the structure of fiber at a time are responsible for strong holding of the dye molecule to the fiber structure. The dyeing of cellulose cannot be explained on the basis of hydrogen bonding, because water has more affinity for cellulose than dye molecule.

**Vander Waal's Interaction**

In dyeing, Vander Waal's interactions take place **because of interactions** between  **$\pi$  orbital's** of the **dye** and the **fabric molecules** in linear fashion. These interactions become stronger between similar groups, **e.g.**, alkyl, aryl in polyester dyes. The dye will attach to the

fiber only when the total effect of Vander Waal's interaction becomes greater than a critical requirement. Moreover, Vander Waal's forces are **effective only** when the dye and fiber are brought in contact by salt type link or by some other means.

### **Covalent Bonds**

Such **bonds are formed** between **dye** and **fiber molecules** because of the reactions between a reactive dye and a group such as -OH. These dyes are fast to washing. For example, when a reactive dye having dichloroazine reactive system is brought in contact with a cellulose structure, possessing alcoholic hydroxyl groups, one of the chlorine atoms undergoes reaction with the -OH groups of the fiber and dye is attached to the fiber through covalent bonding.

If **dyeing** is done in **aqueous medium**, one Cl atom is replaced by the oxygen atom of -OH groups present originally in the cellulose, while other Cl atom is replaced by -OH groups by reaction with water.

On the **basis of various types of interactions** taking place between fiber and dye, it may be **concluded that**

- **Cotton** may be dyed by direct dyes, vat dyes, sulphur dyes, ingrain dyes, reactive dyes, solubilized vat dyes and pigment emulsions.
- **Silk** may be dyed with direct dyes, mordant dyes, acid dyes, and basic dyes.
- **Wool** may be dyed with acid dyes basic dyes, reactive dyes and acid mordant dyes.
- **Polyae fibers**-such as nylons may be dyed with acid dyes, disperse dyes and disperse reactive dyes.
- **Polyester fibers** may be dyes only with disperse dyes.
- Modified polypropylene fibers are dyed with only specially-selected dispersed dyes.
- **Polyacrylonitrile** fibers may be dyed by cationic dyes or disperse dyes with some limitations.

### **CROSS DYEING**

The **versatility** of the **new fibers** has now been **increased by incorporating dye sites** of varying nature in order to achieve dyability with a predetermined class of dyes. Polyesters, acrylics, polyamide fibers etc. have now been manufacturing in such a manner that they can be dyes with basic, cationic, acid, anionic or disperse dye. Textile fabrics and carpets etc are now fabricated in such patterns that they can be dyed with **three different colours** from **one dye bath** having **three different types of dyes**. The process is **known as cross-dyeing** and has become popular as a low cost or cheap method or coloration.

### **BASIC OPERATIONS IN DYEING**

The basic operation of the dyeing process involves the following important steps:

#### **1. Preparation of the Fiber**

The **raw fibers** are generally **associated** with **foreign materials** such as oils, waxes, lubricants etc used during spinning. The fibers are also associated with **sizing materials** and **dirt possessing**. The fibers are **thus scoured with soap** and **detergents** before they are subjected to dyeing. This step **helps** the dye liquor **to penetrate** through the fibrous material and hence gives **uniform** and **level dyeing**. There are various important factors such as nature of fibers, depth of the shade and the processing material to which the dyed material is subjected to, on which this treatment depends.

#### **2. Preparation of the Dye bath**

The dye bath can be **prepared by** adding **requisite amount of chemicals** and other necessary **ingredients** to the solution of **water soluble** acidic, basic, and direct dyes. The **insoluble vat dyes** in the dyeing bath are necessary to be reduced with alkaline hyposulfite in order to convert them into soluble leuco compounds. The fibers are air oxidized after dyeing as a result of which original colour is developed on the fibers.

In addition to dye, some **other ingredients** such as wetting agents, carriers, salts, etc have also been added to the dye bath to improve certain properties. **E.g.** Carriers improve the rate of dyeing of hydrophobic fibers like polyester fibers, because they act as swelling

agents. The colourless retarders slow down the dyeing process to the desired level by competing with dye for the reactive sites on the fiber. When wool is dyed with acid dyes, acetic acid is used as a retarder.

### 3. Application of the Dye

The **fiber** is dyed by **immersing** in the **dye bath** for a **special period** and at **optimum temperature**. In case of level dyeing, **stirring** is also necessary because **level dyeing** shows uniformity of the dye on the fiber and generally **depends upon three** following factors.

- Nature of dye.
- Absorptive power of fiber.
- Condition of the dyeing.

**Dyeing** can be carried out either by **hand operation** or on a **machine**. In **hand operation**, the fibrous material is moved in an open vat containing the dye colour. The **process on a machine** is continuous and **two types** of dyeing **machine** are generally used. In **one type** of continuous dyeing process, the dyeing bath is maintained stationary and the fabric is moved in it. This agitates the liquor placed, in the dyeing bath. The excess dye is squeezed out by passing the yarn or fabric through a pair of rollers. In **second type** of continuous dyeing process, the fabric is properly supported and dye liquor is allowed to pass through it under pressure in one direction. The direction of flow of dye liquor is reversed at regular intervals. As the dyeing continues, there is a gradual decrease in the concentration of dye but there is a gradual increase in concentration of dye on the fiber. A stage is reached when dyeing bath contains almost no dye and then it is said to be exhausted.

### 4. Finishing

**Dyed fibers** are finally finished by making use of a **number of finishing process**. These processes are **used to produce** luster, resistance to shrinkage, crease, and other desirable qualities of feel and appearance.

It should be noted that **dyeing processes** are generally performed **using water** as the medium, hence **water should** be very pure as well as soft. The sequence of operations may also be different for different fibers. **E.g.** in the dyeing of wool, finishing treatment is carried out first and then dyeing operations are performed. In dyeing of cotton, dyeing process is performed between two preparatory treatments.

## GENERAL METHODS OF APPLICATION OF DYES ON FIBRE

A **coloured substance** may be **used as a dye only** if it can be **attached to a fiber**. The method of applying a dye depends upon:

- Nature and type of dye
- Type of fiber.

**For wool and silk** are amphoteric proteins and have affinity for substance containing acidic or basic groups with which they combine by salt formation. Wool and silk have similar dyeing properties and can therefore, be dyed directly by introduction into a solution of an acidic or a basic dye. Example of direct dyes for wool and silk are Meldolas Blue, methylene blue, Martius yellow, Alizarin etc.

**Cotton, nylon and rayon** are composed of natural cellulose molecules and show no affinity for many dyes direct to wool and silk. **Cellulosic fabrics** can be dyed by vatting, mordanting and formation of dye on the fiber itself. They are also expected to combine with substantive dyes by adsorption or hydrogen bonding.

The **vat process** and one process for **indirect application** of **azo dyes** are conducted in **alkaline solution** and cannot be used for dyeing **wool** and **silk** because these are very sensitive to alkali.

**Cellulose acetate** and **nylon** are almost neutral solution and differ from cellulose because they have no hydroxyl groups available for hydrogen bonding. Hence cellulose acetate and nylon are hydrophobic fiber which are resistant to the usual cotton dyes.

Cellulose acetate and nylon are best dyes from an aqueous dispersion of a water insoluble azo or anthraquinone dye in presence of soap acting as dispersing agent. The dye enters the fiber in the form of a solid solution. Dyes containing free amino and hydroxyl groups have affinity for hydrophobic fibers under these conditions.

## METHODS OF DYEING

### Direct dyeing

Direct dyeing mainly **depends upon** the following important factors.

- Absorptive power of the fiber
- Nature of the fiber
- Dyeing condition

Moreover, the **dye** applied should be **fast to** light, washing, bleaching and other treatments. We have seen that wool and silk can be dyed directly either by acidic or basic dyes. In order to get faster and brighter shades, mordant dyeing is usually preferred. The dye **bath** can be **prepared** by **dissolving** the **dye** in **cold water** and then **adding** small amounts of  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  or  $\text{CH}_3\text{COOH}$ . The fabric to be dyed is then introduced into the dyeing bath and temperature of the bath is gradually increased to  $60^\circ\text{C}$ . Now some exhausting agents such as  $\text{NaCl}$  or Glauber's salt is added and temperature is further raised to boiling. After the dyeing is complete, the fabric is rinsed cold and dried. The **washing fastness** is **improved** by **after treatments** of the dyed fiber in a separate bath. These **treatments include**

- Development with diazonium salts.
- Diazotization and development.
- Treatment with  $\text{HCHO}$ .
- Treatment with copper salts.
- Treatment with chromic fluoride or sulphate etc.

There are **various fibers** such as cotton, linen and rayon which **do not show** much **affinity** for many dyes which are used for dyeing wool and silk. **These fibers** can however be **dyed** with **substantive dyes** by direct dyeing process. The dye is first dissolved in hot water, 5-20%  $\text{Na}_2\text{SO}_4$  and 0.5-2%  $\text{Na}_2\text{CO}_3$  are added to the dye bath. Fibers are now introduced in the dyeing bath and temperature of the bath is raised first to  $60^\circ\text{C}$  and then to  $80-85^\circ\text{C}$ . Complete dyeing takes place in about an hour.

**Synthetic fibers**, being hydrophobic are resistant to cotton dyes. These synthetic fibers can however be dyed efficiently from an aqueous dispersion of water insoluble anthraquinone or azo dye in presence of soap or a dispersing agents. As a result the dye enters the fibers in the form of a solid solution.

### Vat dyeing

Vat dyeing is one of the good methods of **dyeing cotton** with **very insoluble natural dye** indigo. The process depends upon the fact that indigo is **reduced to** a colorless di-hydro or **leuco derivative**, which is soluble in alkali. When fabric is immersed in the alkaline solution of a reduced dye (vat), the leuco compound is adsorbed and on withdrawal and exposure to the air is **oxidized to** the dye. The latter gets fixed to the cotton-fiber or cloth. Satisfactory results are obtained when leuco compounds or anion had affinity for the filler through hydrogen bonding. The reducing agent used for reduction of dye is  $\text{Na}_2\text{S}_2\text{O}_4$  (sodium hydrosulphite).

For vat dyeing, the **dye bath** is generally **prepared by adding** the **paste of dye** in **water** and a **dispersing agent** to **water** which **contains** caustic soda and hydrosulphite. Such dyes are called vat dyes. There are at present several hundred such dyes other than indigo. Vat dyes are quinonoid substances that can easily reduce to hydro-quinoid compounds re-oxidisable by air. **Vat dyeing** is now carried out by a **continuous process**. The cotton cloth from a roll is conveyed over a system of rollers into a solution of reduced dye, where the cloth is impregnated with vat liquor. It is then led into a chamber where a leuco compound is properly fixed to impregnated fabric by steaming and acetic acid or per-borate. The fabric is finally passed into soaping, rinsing and drying baths.

Thus vat dyeing is carried out **partly by a continuous process** in which cotton cloth is impregnated with vat liquor. It is then steamed for proper fixation of leuco compound to the fabric and then passed through a bath containing oxidizing agents such as chromate, and acetic acid or per-chlorate. As a result, colour is generated; finally it is soaped, rinsed and dried.

**Mordant dyeing**

In this method cotton is dyed in such a manner that acidic or basic groups capable of combining with a basic or an acidic dye are fixed on it. The **processing agent between cloth and dye** is called **mordant** and hence the **process** is called **mordant dyeing**.

**Alizarin** is a principal coloring material of this class. For **production of colour** known as **Turkey red, cotton** was **impregnated first** with rancid oil, olive oil containing lime and **then with** a solution of aluminum sulphate and **finally steamed**. The **mordanted cloth** was then treated with aqueous suspension of the dye. The colloidal metal hydroxide adheres to the fiber and dye molecule reacts with metallic mordant to form a **complex salt or lake**. This **process** is however very much **time consuming** and takes about **4 months** for completion.

In **modern methods, sulfonated castor oil** is used **instead of olive oil**. The colour can be varied by using other metals. For example chromium mordant gives brownish red colour and iron mordants give violet colour.

**Wool and silk** can also be dyed by the same method. Dyes of a number of chemical types can be applied to cloth mordanted with metal oxides which provide basic groups to the fiber. Acidic groups suitable for binding basic dyes can be affixed to cotton by impregnating cotton cloth with tannic acid which is fixed on the fiber with potassium antimonyl tartrate, tannic acid contains a number of acidic groups some of these are bound as antimonyl groups in fixation, while other are free to bind basic dyes (tri-phenyl methane).

**Substantive dyeing**

**Congo red** is a substantive dye capable of dyeing cotton directly. It is fugitive and so sensitive to acid.

**Disperse dyeing**

Disperse dyeing which was **originally developed** for **cellulose acetate** and **polyae fibers**, has **now** been **used** for **polyester fibers**. In this type of dyeing the **dye is pasted into the fiber** with **water** at about **35-40°C** and then **suitable dispersing agent** and **carrier** such as biphenyl, o-phenyl phenol or trichlorobenzene are added to the dye bath and temperature of the dyeing bath is raised to **80°C**.

Disperse dyes have also been applied by a dry heat or thermosol process to the polyester fiber.

**Formation of dye on the fiber**

**Azoic dyes** are produced **inside textile fiber** by **azo coupling**. The process consists in impregnating the fiber with an alkaline solution of the coupling agent and then treating the coupling component simultaneously from aqueous dispersion. Finally the product is treated with nitrous acid to develop with colour.

**Dyeing with reactive dye**

**Impregnation by padding** and **dyeing in dye bath** are the two important methods which are used for **dyeing fiber** with **reactive dye**.

In **impregnation method**, the dye is dissolved in one vessel and wetting agent,  $\text{Na}_2\text{SO}_4$  and sodium bicarbonate are dissolved in another vessel. Before dyeing bath solutions are mixed and cotton fabric is padded through the mixed solution and then dyed above  $100^\circ\text{C}$  the  $\text{NaHCO}_3$  liberated the alkali which is capable of fixing the reactive dye on the cotton fabric.  $\text{Na}_2\text{SO}_4$  prevents the movement of dye during drying.

**Dyeing in dye bath** with certain reactive dyes can be performed in cold, using 2-3% of the dye in presence of relatively high concentration of  $\text{NaCl}$ .

**Formation of dye on the fiber**

**Azo dyes** can be applied to **cotton fibers** by **soaking cotton** in an **alkaline solution** of phenol and then in an **ice cold solution** of a **diazonium salt**. The **azo dye** is developed **directly** on the **fiber** and azo dyes **applied in this manner** are **called ice colours**.

In **ingrain dyeing**, the cotton impregnated with an amine is diazotized and then developed by immersion in a solution of phenol. The **first ingrain dye** was **Primulin Red**.

**Dyes** on fiber are also **produced** by **oxidation of aromatic amines**. **E.g.** aniline black is made by impregnating cotton with aniline hydrochloride solution, an oxidizing agent, an oxygen carrier and hygroscopic salt. The cloth is dried at  $35^\circ\text{C}$ . The dark bottle green coloured fabric is then immersed in a bath containing aniline, dichromate, diluted  $\text{H}_2\text{SO}_4$  and finally dried at about  $80^\circ\text{C}$ . Jet black coloured aniline black dye is produced on the fiber.

**Dyeing of wool with acid dye**

Dyeing of **wool** with **acid dyes** can be carried out by preparing dyeing bath in which dye is dissolved in cold water and small quantities of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  or  $\text{CH}_3\text{COOH}$  are added. The fiber is now introduced in to the bath and temperature of the bath is gradually raised. The complete dyeing takes place in about 90 minutes at the boiling temperature. The dyed fiber is rinsed and finally dried.

**FASTNESS PROPERTIES**

The **ability** of the **dye** in **association with** a given substrate **to withstand** various **agencies** (like sunlight, washing, dry cleaning, water, perspiration etc.) **in processing or in use** is called **Fastness Properties**.

The various kinds of fastness have been given **quantitative expression** by carefully standardized comparative tests.

In **1934** the **Fastness test committee** of the **society of dyes & colourists published methods** for the **determination** of light, perspiration and washing fastness.

Methods were described for preparing the standards, **carrying out** the **tests** and **assigning numbers** to indicate the **degree of fastness**. **Fastness to light** is graded from **1 to 8** and **all other fastness** properties from **1 to 4 or 5**, the **fastness increasing with increasing numbers**.

The alteration in depth and tone of a dyeing are only examined visually, an absolute assignment of grades is not possible and it is necessary to make a comparison with a set of standard dyeing on which the same tests are simultaneously carried out.

**Colour fastness**

These measure the resistance of the textiles when they are exposed to various agencies. The usually practice is to apply the dye on the fabric in specified strength and subjected to the various agencies. For this, a **scale** of **1 to 5** is employed. In this scale, **1** means **Poor** and **5** means **Excellent**.

**Sublimation fastness**

A dyed fabric is kept in contact with undyed piece and subjected to heat. Alternation in colour and degree are noted. This fastness is **graded** from **1 to 5** where **1** denotes lowest rate in sublimation while **5** denotes highest rate in sublimation.

**Burnt gas fumes fastness**

A dyed piece is exposed to oxides of nitrogen. Alternation in colour is assessed. This test is largely used for synthetic fibers.

**Rubbing (dry and wet) fastness**

**Transfer of color** from **textile material** is **undesirable** and causes much trouble to both textiles finishing and processing as well as during wear of garments. This test is applicable to textiles made up of all fibers in the form of yarn and fabrics. The specimens are fastened. Crock meter, which causes a **piece of standard white cloths** (starch free 96x100 cotton fabric long type) **to rub against** the **colour specimen** under **controlled conditions** of pressure and speed. The rubbing fingers are covered with white cloths both for dry and wet test and slide back and forth for twenty rubbing stocks. The colour transfer to white cloth is compared with grey scale. The grey scale for alteration in colour consists of **grades** as **1 to 5**.

Observation	Grade	Qualitative assessment
No dye stain on un-dyed fabric	5	Excellent
Slight dye stain on un-dyed fabric	4	Very good
Moderate stain on un-dyed fabric	3	Good
Distinct stain on un-dyed fabric	2	Fair
Very much dyed stain on un-dyed fabric	1	Poor

**Fastness to perspiration**

This test is applicable to all fibers. Since **human perspiration** can be **acidic** or **alkaline**, so both acid and alkaline solutions have to be used for the test. Each solution contains 10gm of NaCl and 1gm di-sodium hydrogen phosphate per liter, the acid solution contains in addition 1gm lactic acid and the alkaline solution 4gm ammonium carbonate. The tests are carried out in glass tubes which are placed in a drying oven. The test specimen is made up

by taking a piece of the dyed or printed fabric its length and width similar to test piece. The 4 tests corresponds to **grades 1 to 4** differ only in the **time of treatments** 40 min, 2, 6, & 18 hours.

Test specimen and test cloths are thoroughly wetted with the acid solution so that the weight of the two is about trebled. The two pieces are then rolled together and place in oven or desiccators. A similar test is performed with alkaline solution. On removal, the specimens are dried without rinsing, and the fastness graded according to the maximum numbers of the test in which the staining of the multi-fiber test cloth is no greater than Munsell Neutral Value Scale No-8 and there is no appreciable migration and change in colour.

#### Light fastness

The dyed textiles are often exposed to light and hence it is essential that the **color** should **not fade** on **exposure** to **light** so the study of light fastness of dye becomes essential. The dyed patterns are exposed to light along with standard dyed patterns of specific rating, such standard samples are blue wool standard developed produced in Europe and are identified by numerical designations **1 to 8**. Higher the rating better the lighting fastness.

Rating	Qualitative assessment	Rating	Qualitative assessment
8	Outstanding	4	Fairly good
7	Excellent	3	Fair
6	Very good	2	Poor
5	Good	1	Very poor

#### Wash fastness

The wash fastness of dyed pattern is another important property desired of a dye. The dye textile materials are often washed with soap detergents thus it becomes very necessary that the colour should not fade on washing. For wash fastness study **five test methods** are developed by **Indian Standard 58%**. The dyed pattern tested with another piece made of the fiber indicated in the following table.

Test pieces	Second pieces
Cotton	Viscous
Viscous	Cotton
Acetate	Viscous
Polyamide	Viscous or Cotton
Polyester	Viscous or Cotton
Linen	Viscous
Acrylic	Viscous or Cotton

The **study carried out** by **IS test method** in the **following manner**

The test piece was placed in container with 12 S.S. balls. To it 50 ml soap soda solution (5 gm soap and 2 gm anhydrous sodium carbonate in 1000 ml distilled water) at 50 °C was added. The test pattern was treated for 30 minutes then the pattern was removed from the container, rinsed twice with cold water for 10 minutes and squeezed. The stitches were removed and test specimen was opened out and dried in air. The change in color was evaluated on grey scale. Scales for alteration of color consisting of 1 to 5 grades are as follows.

Observation	Grade	Qualitative assessment
Shade unaltered	5	Excellent
Very slight loss in depth	4	Very good
Appreciable loss or alteration	3	Good
Distinct loss or alteration	2	Poor
Great loss or much alter	1	Fair

## ANALYSIS OF DYES AND INTERMEDIATES

### Introduction

**Accurate analytical determination** of starting materials is **essential** in the dye industry. The methods which are used are partly physical, partly chemical. With many products, only physical data, such as melting point, freezing point, and boiling point, are determined. Thus, aniline, toluidine, nitro compounds, and many others, are characterized solely by these

measurements; in some cases, the specific gravity (density) and even the refractive index to monochromatic light are determined.

Test samples of materials which are purchased should be investigated without delay in the analytical laboratory. The sampling is frequently specified in the purchase contract, as are the methods of heating to be used in melting point and freezing point determinations. Materials prepared in the plant are frequently used in technical solutions whose content of active material is determined by analysis. The large firms are going over more and more to the practice of weighing out their solutions directly into the reaction vessels, using balances with a total capacity of up to 40,000 kilograms and a sensitivity of 100 grams.

The molecular weight, calculated from the chemical formula is given as a characteristic for each product in the dye industry. Now, **many substances are used in different forms, e.g.**, benzidine as the sulfate and as the free base, and Cleve acids as the free acids and as the sodium salts. It is agreed, therefore, always to take the same value for molecular weight, whereby of course a salt comes out with a lower purity than the free acid. The molecular weight of any material purchased is always specified along with the price per kilogram of pure material. For example, if 1 kilogram of benzidine (mol. wt. 184gms) costs 3/-Rs and 1 kilogram of benzidine sulfate costs 2/-Rs then the pure base in benzidine sulfate costs  $2 \times 282/184$  or 3.02/-Rs. The cost of the base is therefore identical in the two products. In the above example, the sulfate would be 65.2 per cent pure (mol. wt. 184) and to obtain 184 kilograms of benzidine base, 282 kilograms of the sulfate would have to be used.

### **PREPARATION OF STANDARD TITRIMETRIC SUBSTANCES**

The determination of sodium nitrite is done by the well-known oxidation method with potassium permanganate. This procedure however, always gives too high values for the plant chemist since the permanganate oxidizes any other oxidizable material which may be present in the nitrite. Despite this disadvantage, the method is used in nitrite plants. Only one other method is available to the dye chemist namely, the sulfanilic acid method which with practice can be made to give accurate results.

#### **Preparation of Pure Sulfanilic Acid**

A **strongly alkaline** solution of **250 grams** of technical **sulfanilic acid** in about **1 liter soda solution** is **boiled** until all of the aniline has been driven off. The solution is then **filtered** and made **strongly acidic** with hydrochloric acid. The **precipitated** material is **filtered off** after **12 hours**, **washed** with a small amount of water, **re-dissolved** in 400c.c. water containing enough soda ash (about 60 grams) to make the solution neutral. The hot solution is **cooled** to 0°C. With stirring and the precipitate of sodium sulfanilate is filtered off. If the apparatus is available the mother liquor is removed by centrifuging. The **crystals** are **dissolved** in 500 cc. distilled water, the solution is filtered and acidified with pure hydrochloric acid (concentrated). The solution is stirred so that only small crystals are formed. The precipitate is filtered off after a day washed carefully with distilled water to wash out all of the sodium chloride. The **material** is then **recrystallized** once from hot distilled water and **dried at 120°C** to constant weight. The purified material is stored in a tight glass bottle with ground glass stopper. It is almost white contains less than 0.01 per cent of impurities. A **solution** of the reagent is **prepared** by dissolving **173 grams** in **100 cc** of **ammonia** (20% NH<sub>3</sub>) **diluting to 1 liter** at **17.5°C**. This solution is stable in the dark for many months but should be checked at intervals of 3 months. This standard solution is used in the preparation of 1 N nitrite solution (NaNO<sub>2</sub>).

#### **Preparation of 1.0N Sodium Nitrite Solution**

A **solution** of **75gms** of technical **sodium nitrite** in a small volume of water is filtered and **made up to 1 liter** at 17.5°C. This solution is used to titrate 50 cc. 1 N sulfanilic acid solutions as follows

The sulfanilic acid solution is pipette into a 500cc. beaker, diluted with 200cc. ice water and acidified with 25cc. HCl. The nitrite solution is added from a burette whose tip extends beneath the surface of the liquid. After 45 cc. has been added, the addition is continued drop wise until a **drop** of the mixture **on starch-iodide paper produces** an immediate, very weak, but permanent **blue coloration**. This test must be made by spotting

(not rubbing) on starch-iodide paper. The whole diazotization takes about 10 minutes. From the volume of nitrite solution used, it can be calculated how much water must be added to make the solution exactly 1 N. The solution should always be diluted to 1N strength instead of using it as it comes out, since the use of a factor in all subsequent calculations involves too much work.

After the sulfanilic acid and nitrite solutions have been standardized, 1 N aniline solution is prepared. Pure aniline (200cc.) is distilled from a small distillation flask at such a rate that the distillation is complete in 45 minutes. The aniline, which comes over within a range of one-half degree between 184 and 185°C is used for preparing the solution. The specific gravity should be 1.0260 to 1.0265 at 17.5°.

**93 grams** of the **pure aniline** is **dissolved** in **150cc.** pure **30% HCl** the solution is **made up to 1 liter** at 17.5°C.

If the nitrite and sulfanilic acid solutions have been prepared correctly 100cc. of either the sulfanilic acid or the aniline solution should require exactly 100cc. of the nitrite solution.

#### **Preparation of 0.1N Phenyl Diazonium Solution**

**50cc** of the **aniline** solution is measured out and mixed with **50cc conc. HCl**. The mixture is cooled by placing the measuring flask in ice water, **50cc. 1 N nitrite** solution is added while the mixture is swirled to provide agitation. The solution is kept in ice water for 20 minutes after which it should show only the slightest reaction for nitrous acid. Ice water is added to make the volume up to 500cc. and the solution is ready for use. Under no circumstances must the diazotization be carried out in less than 20 minutes since the reaction takes this long under the conditions employed. The diazo solution can be held unchanged for about 4 hours at 0°C in dark, so it must be freshly prepared.

### **DETERMINATION OF AMINES**

#### **(a) Direct Determination**

The amine is titrated with hydrochloric acid sodium nitrite in very dilute solution and the resulting diazonium salt is coupled with an accurately known amount of a phenol, usually Schaeffer salt. With other compounds, such as H acid, amino R acid, etc., one sample is diazotized and another is coupled with diazotized aniline or other amine. Under some circumstances it is possible to determine two substances in mixture if one of them reacts much more rapidly than the other. Thus with a little practice one can determine quite accurately both G salt and R salt in mixtures of the two R salt couples very rapidly with diazotized aniline producing a red dye, while G salt couples more slowly and gives a yellow dye. A large number of other special methods are available which permit the determination of the individual constituents in mixtures.

Diazonium compounds other than phenyldiazonium chloride are also used, but to a smaller extent. Thus, in some plants, diazotized m-xylidine is used but this appears to have no advantage since the diazonium solution is less stable. Diazotized p-amino acetanilide, on the other hand, is used in certain cases because it couples more vigorously and gives a very stable solution; o- and p-Nitro aniline are used less frequently as highly reactive.

For each gram of nitrite, 5 grams of soda ash or if coupling is carried out in acetic acid solution at least 15 grams of sodium acetate is used. Nitro aniline requires double these amounts and still more is required if the substance contains a sulfo group. Coupling should be carried out below 5°C. and the solution must be very dilute (about 1 per cent).

The excess of diazonium salt is determined by spot-testing on filter paper after first salting out any easily soluble dyes. Easily coupling amines or phenols, such as resorcinol, R salt or H acid are used as coupling reagents. Some laboratories use a fresh hydrocyanic acid solution which gives a yellow colour. An excess of phenol or amine is determined simply by spot testing on filter paper with the diazonium solution this procedure involving only negligible losses.

#### **(b) Indirect Determination**

Many amines cannot be analyzed directly by diazotization either because they form diazoamino (-N=N-NH-) compounds or because they give diazonium compounds which

colour starch-iodide paper just as free nitrous acid does. These amines exemplified by the nitro-anilines, dichloro aniline etc. must be determined indirectly.

The amine (0.01 moles) for example is dissolved in concentrated or partially diluted acid, and the solution, after dilution with water and ice is diazotized with an appreciable excess of sodium nitrite. The clear diazonium solution is made up to a known volume in a calibrated flask and is then added from a burette or a graduated cylinder to a carbonate solution of  $\beta$ -naphthol or accurately determined strength. The end point is taken as the point where a spot test with diazonium solution on filter paper shows the absence of  $\beta$ -naphthol. Usually, the proportions of the reactants are so chosen that the number of cubic centimeters used divided into 100 gives the percent of amine present in the original sample.

For example, 3.45 grams of p-Nitroaniline (2.5/100 mole) is dissolved in 10cc 30% HCl and 10cc water. The clear solution is poured into 50 grams of water and 50 grams of ice and treated with 20% solution containing 2 grams of pure sodium nitrite. The clear solution containing about 0.2 gram of excess  $\text{NaNO}_2$  is made up to 250cc.

100cc of this solution is measured out in a graduate and added portion wise with thorough stirring to a solution containing 1.44 grams of 100 percent  $\beta$ -naphthol, 2cc 30% NaOH, and 20 grams of soda ash in 300cc ice water. Spot tests are made on filter paper to determine the point where the reaction mixture no longer gives a reaction for  $\beta$ -naphthol with diazonium solution. The number of cubic centimeters of Nitroaniline solution divided into 100 gives the per cent purity. If the Nitroaniline is 100% pure, exactly 100cc is required. Usually, 101 to 102cc will be used.

## **DETERMINATION OF NAPHTHOLS**

### **$\beta$ -Naphthol**

A solution of 0.01 moles (1.44 grams) of  $\beta$ -naphthol in 2 cc 30% NaOH is diluted to 400cc. and 25cc 10% soda ash is added. Ice-cold 0.1N phenyldiazonium solutions is added from a graduated cylinder or a cooled burette until a drop of the reaction mixture on filter paper forms no more orange red dye with the diazo solution. Impurities may cause the formation of a coloured streak after a few seconds but this is always cloudy and is easily distinguished with a little practice from the pure naphthol dye. The number of cubic centimeters of the diazonium solution used gives the percent purity of the  $\beta$ -naphthol directly. A good product should be at least 99.5% pure.

### **$\alpha$ -Naphthol**

$\alpha$ -Naphthol couples much more easily than  $\beta$ -naphthol and would give too high values in alkaline solution. Hence, the coupling is carried out in acetic acid solution in the following manner.

The  $\alpha$ -naphthol is dissolved as described for  $\beta$ -naphthol and the solution is diluted and then precipitated with dilute acetic acid in the presence of 25cc 25% sodium acetate solution. The coupling is carried out as with  $\beta$ -naphthol except that when the reaction for  $\alpha$ -naphthol disappears the solution is made alkaline with sodium hydroxide reprecipitated with acetic acid and the titration continued until the  $\alpha$ -naphthol reaction again disappears. Frequently, as much as 90 percent of the total volume of the diazonium solution is added in the second part of the titration since so much of the naphthol is carried down by the dye.

Only  $\alpha$ -naphthol can be determined in this way since  $\beta$ -naphthol does not couple in acetic acid solution. If it is desired to determine the  $\beta$ -naphthol subsequently, 0.1N p-nitrophenyldiazonium solution is added until all of the  $\beta$ -naphthol is reacted. Thus, it is easy to determine both  $\alpha$ - and  $\beta$ -naphthol in impure  $\alpha$ -naphthol samples.

### **Dihydroxy naphthalene**

These compounds are determined in exactly the same way as  $\alpha$ -naphthol. They couple very readily and the "after-coupling" is usually strong and very impure, so the endpoint is easily determined.

### **Determination of amino sulfonic acids**

A solution of 0.01 mole of the acid in the required amount of soda solution is diluted to about 250cc, acidified with 25cc conc. HCl and titrated with 1N  $\text{NaNO}_2$  solution. The

percent purity is given by number of "cc x 10". The endpoint must be determined by spotting on starch-iodide paper since accurate results cannot be obtained by streaking.

It should be noted that many highly reactive diazonium salts (especially when in strong mineral acid solution) rapidly turn starch-iodide paper blue therefore it is essential to know the sensitivity of the paper. Sulfanilic acid, Metanilic acid, and Naphthylaminesulfonic acids are diazotized at 15°C.

Cleve acids cannot be determined so easily because they couple with themselves immediately. In this case it is best to add the bulk of the nitrite to the neutral solution and acidify the mixture with good stirring. The diazotization can also be carried out directly at 0°C adding nitrite until the original violet color gives way to a pure brown. The indirect method is preferred however, because it is more rapid.

#### **Determination of aminonaphtholsulfonic acids**

Two determinations are always made. In the first, the amount of nitrite which is used is measured to give the "nitrite value." Then, the compound is titrated with diazonium solution to give the "coupling value." If the two values agree then it is known that the aminonaphtholsulfonic acid has been correctly made.

If the nitrite value is too high it may be concluded that the fusion was too short. If the nitrite value is smaller than the coupling value, the fusion was carried too far. A correctly prepared aminonaphtholsulfonic acid should give nitrite and coupling values agreeing to within 1 %.

It is perhaps unnecessary to point out that all such determinations, like all analyses should be run in duplicate.

#### **1-amino-8-naphthol-3, 6-disulfonic acid (H-acid)**

##### **(a) Nitrite Value :( Calculated in terms of the acid sodium salt, mol. wt. 341)**

A solution of 3.41 grams of H-acid in 5cc 10% soda ash solution is diluted to 250cc, precipitated with 25cc conc. HCl and diazotized at 5°C with 1 N nitrite solution. H-acid should give a yellow diazo compound which can be salted out as beautiful crystals. The number of cubic centimeters of nitrite multiplied by 10 gives the per cent purity.

##### **(b) Coupling Value**

To a solution of 3.41 grams of H-acid in 50cc 10% soda solution, diluted to 300cc, is added at 0°C enough phenyldiazonium solution to give a minimum excess of diazo compound. The endpoint is determined by placing a few drops of the red mixture on a small heap of salt on filter paper. After 5 minutes the colorless outflow is tested with diazotized aniline solution if H-acid is present, a red ring is formed immediately. If the diazo solution is in excess, a red ring is formed with H-acid solution. The last traces of H-acid often react very slowly and hence the last test should be delayed for 15 minutes. The nitrite value of a good sample of H-acid is about 0.3% higher than the coupling value. The number of cubic centimeters is equal to the per cent purity.

All aminonaphtholdisulfonic acids as well as the mono-sulfonic acids are determined in this way. The diazonium solution is added from 100cc graduate and the per cent purity is read off directly. Many laboratories use elegant but complicated, ice-cooled burettes. The solution is stirred with a glass rod bent at the end to form a large loop. Coupling is conducted in a clean porcelain dish.

#### **Determination of Naphthol mono and disulfonic acids and Dihydroxynaphthalene mono and disulfonic acids**

##### **Nevile-Winther acid (1-Naphthol-4-sulfonic acid, Molecular Weight 224)**

Coupling is carried out with 0.1 N diazotized aniline solution (just as prescribed for H-acid) and at the end the dye is salted out in the reaction dish so that the remainder of the naphtholsulfonic acid is easily determined.

Starting out with 2.24 gram sample, the volume of diazotized aniline in cubic centimeters gives the per cent purity directly. Coupling should be carried out at 0°C.

Schaeffer salt, R-salt, and other naphtholsulfonic acids are analyzed in exactly the same manner.

Dihydroxy Naphthalene mono and disulfonic acids couple so rapidly, even the second time that the coupling is carried out in acetic acid solution containing sodium acetate, using diazotized p-amino acetanilide. With many of the acids, the-coupling requires

several hours, e.g. with chromotropic acid. In this case also, the dye is highly soluble and separates slowly from the unreacted chromotropic acid so that considerable care must be exercised.

The determination of the individual sulfonic acids in a mixture can be accomplished in some cases although the results are rarely accurate. For example, mixtures containing Schaeffer salt (Na-2-naphthol-6-sulfonate) and R salt (Na-2-naphthol-3,6-disulfonic acid) can be analyzed in the following way.

The total content of coupling substance is determined by titration with diazotized aniline solution. Another sample is dissolved in the minimum amount of water and treated with 20 parts of 96% alcohol to precipitate the R salt. The mixture is shaken for about 30 minutes to free the Schaeffer salt enclosed in the precipitate and then the precipitate and the filtrate are analyzed separately to determine R salt and Schaeffer salt respectively.

A second method consists of first titrating the whole mixture with diazotized aniline, and then eliminating the Schaeffer salt in a second sample by means of formaldehyde. For example, 5 grams of the mixture is dissolved in 100 cc water and to the solution are added 5cc pure 30% HCl and 2.5cc 40% formaldehyde. The mixture is heated for 1 hour on a water bath and then reanalyzed the difference between the two values representing the content of Schaeffer salt.

A third method utilizes iodine titration. Both R salt and Schaeffer salt are iodinated by iodine, preferably in the presence of sodium bicarbonate. A sample is titrated with 0.1 N iodine solution, adding an excess and back-titrating. A second sample is then separated into its constituents by alcohol as described above and a second determination is made. Some dye chemists believe that this is the best method since the coupling methods give values which are too high; this belief is probably correct.

#### **Determination of 2-Naphthylamine-5, 7-di-sulfonic acid in the presence of 2-Naphthylamine-6, 8-disulfonic acid**

The analysis of mixtures of these two acids is very simple. The mixture is first titrated with nitrite to determine the total of the two acids and then the 2,5,7 acid is titrated with sodium hypobromite. The 2,5,7 acid reacts smoothly in hydrochloric acid solution with sodium hypobromite, taking up two atoms of bromine, while the 2,6,8 acid is entirely un-reactive. This behavior is surprisingly similar to that of Schaeffer salt and R salt.

To carry out the Second titration, a measured amount of the sulfonic acid sample is dissolved in 300 parts of water and 20cc conc. HCl is added for each 2 grams of the sulfonic acid. The temperature is lowered to 0°C by addition of ice and the solution is titrated with 0.2N NaOBr solution to a definite blue coloration with starch-iodide paper. The 0.2N hypobromite solution is prepared in the following way

To a solution of 14 grams of pure NaOH in 500cc water containing about 200 grams of pure ice is added, with thorough stirring, 16 grams of bromine. The solution is diluted to 1 liter and standardized by known methods (e.g., with arsenious acid).

A dilute solution of the pure 2,6,8 acid containing hydrochloric acid gives an immediate test for free bromine with only one drop of the hypobromite solution.

#### **VOLUMETRIC DETERMINATION OF DYES BY THE EDMUND KNECHT REDUCTION METHOD**

In many cases, testing a dye for color strength and tint by means of a dyeing test is replaced by a simple analysis by reduction with titanium trichloride ( $TiCl_3$ ) to determine the content of reducible substance present. This elegant method is usable for homogeneous products, but it fails if the dye being tested is a mixture of isomers, or if it contains impurities which also consume the reducing agent.

For these reasons, this method of analysis is not widely used in the older dye plants which are equipped with proper dyeing standards. It has however, attained certain popularity in smaller plants in England and America because it is much easier to carry out a simple titration than to conduct the delicate but conclusive dyeing test. The evaluation of a dyeing test is always dependent on individual factors and can only be done by trained, absolutely reliable persons.

#### **Principle of the Knecht Method**

Titanium trichloride is an extremely easily oxidized material which dissolves in water to form a violet solution. On oxidation, it is converted to the colorless titanous acid,  $Ti(OH)_4$ . Using a titanium trichloride solution of known strength, it is possible to reduce quantitatively dyes of various classes the endpoint being taken as the point where the color of the dye disappears.

All azo dyes, as well as Thiazine, Safranin, Tri-phenyl methane, Indigo, and many other dyes, can be analyzed with great accuracy by means of Titanium trichloride.

#### Preparation of the Titanium trichloride Solution

In principle, a known amount of ferrous iron is oxidized to ferric iron and this is reduced with titanium trichloride using potassium thiocyanate as an indicator.

As the ferrous salt, Knecht used Iron ammonium sulfate (Mohr salt) and oxidized this to ferric sulfate with 0.02N potassium permanganate in sulfuric acid solution. The resulting ferric salt was then back-titrated with titanium trichloride solution.

The other, equally simple method consists in dissolving pure iron wire in pure hydrochloric acid and oxidizing the ferrous chloride solution with a few drops of bromine. The excess bromine is removed by boiling and the solution is titrated with the titanium trichloride solution.

The commercial titanium trichloride solution (about 15%) is diluted by mixing 100cc with 100cc pure 30% HCl. The mixture is heated to boiling and then made up to 1 liter at 18°C. This solution can be held unchanged by storing under carbon dioxide or hydrogen but it should be restandardized at regular intervals.

To standardize the solution with iron an iron solution containing exactly 2 grams of iron per liter is used. This solution should contain 5% HCl or  $H_2SO_4$ . As an example, it is found that 6.85cc of a titanium trichloride solution corresponds to 25cc of the iron chloride solution, using potassium thiocyanate as the indicator (spot test). Since the iron solution contains 2 grams of iron per liter, 1cc  $TiCl_3$  solution corresponds to 0.05/6.85 or 0.007299 grams of iron.

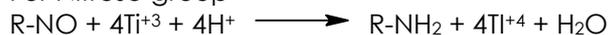
#### Estimation of Nitro (-NO<sub>2</sub>), Nitroso (-NO) and Azo (-N=N-) Groups

The compound containing nitro, nitroso or azo group is dissolved in water / alcohol / acetic acid and excess of titanous salt solution. Boiled the reaction mixture under the current of  $CO_2$  or  $N_2$  gas (inert atmosphere). Finally excess titanous salt is titrated with standard ferric ammonium sulphate solution using ammonium thiocyanate solution as an indicator.

a) For determination of nitro groups, standard equation comes from following equation.



b) For Nitroso group



c) For Azo group



#### Titration of Methylene Blue

One mole of methylene blue (MW 319.6) requires two equivalents of iron (112 grams) for reduction and therefore 1cc titanium trichloride solution corresponds to  $(0.007299 \times 319.6 / 112) = 0.02083$  gram of methylene blue ( $C_{16}H_{18}N_3SCl$ )

For example, exactly 0.2 gram of methylene blue (zinc-free) is dissolved in about 100cc water in a 250cc round-bottomed flask. A stream of carbon dioxide is passed into the flask and the solution is heated to boiling. Titanium trichloride solution is added from a burette to the boiling solution until the solution is just decolorized. Standard methylene blue (zinc-free) required 7.86cc  $TiCl_3$  solution for 0.2 grams of the dye (average of three titrations). The dye content is,

$$0.02083 \times 7.86 = 0.1637 \text{ gram of pure dye OR}$$

$$0.1637 \times 100 / 0.2 = 81.8 \% \text{ purity.}$$

#### Methylene Green (MW 364.6 grams)

Methylene Green is a nitro methylene blue and its reduction requires 6 equivalents of iron. Therefore, 1 cc titanium trichloride solution is equivalent to:  $0.007299 \times 364.6 / 336$  or 0.00809 grams of dye.

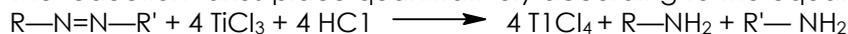
0.2 gram of methylene green used 20cc titanium trichloride solutions and contained therefore:  $0.00809 \times 20$  OR 1.618 grain of dye.

The purity is therefore 80.9%. The colour change in this titration is not very sharp.

#### Azo Dyes

Determination of azo dyes is done most satisfactorily in the presence of sodium tartrate which prevents the precipitation of the difficultly soluble dye acids (e.g., benzopurpurin, see Knecht process). Yellow dyes cannot be easily titrated because titanium tartrate is strongly yellow in color.

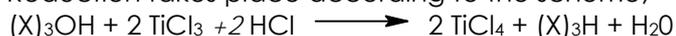
The reduction takes place quantitatively according to the equation:



It is only necessary to know the molecular weight of the dye and the number of azo groups present. The titration is carried out exactly as described above.

### **Triphenylmethane Dyes**

Reduction takes place according to the scheme;



Titration is carried out to a colorless endpoint, which is usually very sharp. Knecht has titrated Eosin, Malachite green, Acid green, Aniline blue, Rhodamine, other dyes by this method.

Safranin behaves exactly like methylene blue.

### **EVALUATION OF ZINC DUST**

1 gram of Zn dust is dissolved in a solution of 4 grams of sodium bi-chromate in 1 liter water and 20cc 20% H<sub>2</sub>SO<sub>4</sub> added with thorough stirring. A 250cc portion of this solution is diluted with 900cc water and 150cc 20% H<sub>2</sub>SO<sub>4</sub> and 100cc 0.1N KI solutions are added. The mixture is allowed to stand in the dark for 30 minutes and then the iodine is back-titrated with 0.1N thiosulfate solution. To determine the strength of the bi-chromate exactly 0.800 grams of it are treated in the same way.

#### **Calculation**

B = cc. thiosulfate for 0.800 g. bi-chromate.

A = cc. thiosulfate for 4g. bi-chromate + 1 gm zinc dust.

Then, (B X 1.25—A) X 1.308 = % Zinc metal.

### **EVALUATION OF LEAD PEROXIDE PASTE**

A good average sample of 3 to 5 grams of the paste is weighed out between two watch glasses and treated with exactly 5 grams of Mohr salt (ferric ammonium sulfate). The mixture is rinsed into 200cc flask heated for 30 minutes on a boiling water bath after which 25cc conc. HCl is added. The mixture is heated to boiling after cooling the excess of Mohr salt is back-titrated with potassium permanganate.

### **HALOGEN CONTENT DETERMINATION**

#### **A) Estimation of Chloride**

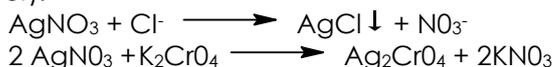
There- are two methods available for determination of Chloride.

1. Silver nitrite method,
2. Mercuric nitrite method.

#### **1. Silver nitrite method**

##### **Principle**

AgNO<sub>3</sub> react with Cl<sup>-</sup> and to form AgCl. The completion of reaction is indicating by the red colouration produced by reaction of AgNO<sub>3</sub> with potassium chromate (K<sub>2</sub>CrO<sub>4</sub> as an indicator).



##### **Procedure**

Place 100ml of sample in conical flask. Maintain the pH in the range of 7 to 9.5 by using H<sub>2</sub>SO<sub>4</sub> or alkali. Now add 1 ml K<sub>2</sub>CrO<sub>4</sub> as an indicator. Titrate against the standard AgNO<sub>3</sub> solution with constant stirring until a slight precipitation (reddish coloration). Conduct the blank experiment by taking 100 ml of water free from chlorine. A blank of 0.2 to 0.3 ml is usual for the method.

**Procedure for colored or turbid sample**

If the sample is highly coloured or turbid, add 3 ml aluminum hydrazide to a measured volume of the sample in a beaker. Stir well and allow to settle. Filter and wash the precipitate with chloride free distilled water. Combine the filtrate and washing and bring the pH in the range of 7 to 9.5. Finally titrate as above method.

**Calculation**

$$\text{Cl}^- \text{ mg/ml} = \frac{(\text{B.R. Blank} - \text{Sample}) \times \text{N of AgNO}_3 \times 35.5 \times 1000}{\text{ml of sample taken}}$$

**B) Estimation of Fluoride**

There are four methods available for determination of fluoride.

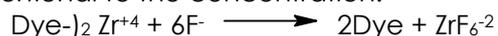
1. SPADNS method.
2. SCOH-Sanchis method.
3. Preliminary distillation.
4. Electrode method.

SPADNS and SCOH methods are colorimetric methods. Compare to SCOH method the SPADNS method tolerates much interference and determines fluoride in the range of 0.001 to 1.400 mg/lit. The reaction is immediate, stable colour and no waiting period is necessary where as SCOH method require 20 minutes for colour comparison also suffer from interference.

When the sample is highly colored and turbid than distillation method is used.

**1. SPADNS Method****Principle**

Fluoride ion changes the color of Zirconium SPADNS complex and the colour change is proportional to the concentration.

**Procedure****a) Standard plot**

- Pipette 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 ml fluoride standard solution in the 50ml Nessler tubes and makeup to the mark with distilled water.
- Add exactly 10 ml Zirconium SPADNS reagent to each tube and mix well.
- Set the spectrophotometer to zero absorbance using reference solution at 570nm and measure the absorbance of the above prepared standard solutions.
- Plot a calibration curve (Absorbance v/s Concentration).

**b) Sample preparation**

Place a 50 ml of sample (diluted if necessary) in Nessler tube. If the sample contains any residual chloride than add 1.0 drop of sodium arsenite solution for each 0.1 mg Cl<sub>2</sub> and mix well.

Add exactly 10.0 ml of the acid-Zirconium SPADNS reagent and mix well. After setting the spectrophotometer to zero absorbance with reference solution, measure the absorbance of the sample. Find out the mg of fluoride present in sample from standard plot.

Express the result as mg fluoride per liter.

**2. Preliminary distillation**

If the sample is highly coloured or turbid or known to contain excess concentration of interfering substances, distillation of the sample is necessary. Fluoride is separated from other constituents by distillation as hydrofluoric acid.

**Procedure**

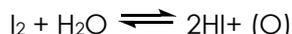
Placed the 400ml distilled water in the one litter RBF. Carefully added 200ml concentrated H<sub>2</sub>SO<sub>4</sub> and make it homogeneous. Add glass beads and connected the flask with distillation apparatus. Heat the flask slowly at first than rapidly. As the temperature reaches 180°C stop the heating and allow it to cool. Discard the distillate. This process serves to remove fluoride if any in the glass ware or in the reagents. After cooling to 120 °C add 300ml sample, mix thoroughly and distilled until the temperature exceed 180°C as it may cause sulphate carry over.

Collect the distillate in 300ml volumetric flask for fluoride determination.

**ESTIMATION OF COPPER**

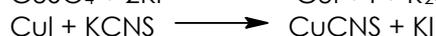
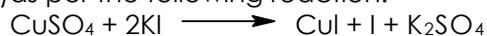
An aqueous solution of iodine is a mild oxidizing agent, it will therefore only act effectively with powerful reducing agents. One mole of iodine reacts with one mole of water and supply free oxygen for oxidation (to reducing agent). This reaction is reversible i.e. oxidation-reduction.

The HI is powerful reducing agent which takes up and liberated water. The following reaction indicates the oxidation-reduction reaction of I<sub>2</sub>.



The direct iodometric titration method (sometimes termed iodimetry) refers to titration with a standard solution of iodine. The indirect iodometric titration method (sometimes termed iodometry) deals with the titration of iodine liberated in chemical reactions.

The iodometric process provides the most accurate method of estimating copper, but it's expensive. On slight modification i.e. addition of KI increased the efficiency and accuracy of process in which copper is precipitated as CuI and it is react with Potassium thiocyanate (KCNS) as per the following reaction.



A reaction of KI with copper solution, a cuprous iodide (CuI) is precipitated. On addition of KCNS, solution becomes darkens due to the formation of soluble cuprous thiocyanate. No precipitate forms due to absence of CuI. Then titrated the liberated iodine using standard solution of sodium thiosulphate.

#### Procedure

If the copper in the form of metal or alloy has been brought into solution by means of HNO<sub>3</sub>. Oxides of nitrogen must be removed by evaporation.

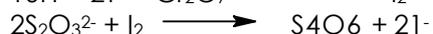
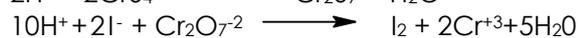
Add diluted solution of H<sub>2</sub>SO<sub>4</sub> and pinch of Urea and boil for few minutes. Now add ammonia till slight precipitate forms. Then add 2cc of 4N H<sub>2</sub>SO<sub>4</sub> and dilute up to 40ml by means of water. Add 1.25-1.5 gm of KCNS and 2.0cc of a 10% solution of potassium iodide and titrate with 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using starch as indicator.

### ESTIMATION OF CHROMIUM

Chromium is generally determined by volumetric method.

#### Principle

This method is based upon the oxidation of iodide to iodine by dichromate in acidic condition. The liberated iodine is titrated with standard solution of thiosulphate using starch as an indicator.



#### Process

Take 100ml of sample in conical flask. Add following reagents in order with mixing after each addition.

1. 5.0ml of 10N H<sub>2</sub>SO<sub>4</sub>
2. 2.0ml of 1.0N AgNO<sub>3</sub> solution.
3. 2.0gm of Potassium persulphate

Now add few glass beads and boil on a hot plate for 15 minutes. Cool the solution and dilute to 100ml with distilled water. Add 1.0gm ammonium bifluoride stir the solution. Finally add 2.0gm KI and keep the flask in dark for five minutes. After that, titrate with standard solution of 0.1N sodium thiosulphate. Where starch is use as an indicator.

Total Chromium (as a CrO<sub>4</sub><sup>2-</sup>) mg/liter =  $\frac{B.R. \times \text{Normality of Na}_2\text{S}_2\text{O}_3 \times 38.7 \times 10^6}{\text{ml of sample} \times 10^3}$

### DETERMINATION OF NICKEL (Ni) BY DIRECT TITRATION

#### Requirements

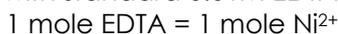
- Murexide indicator (0.1gm Murexide+ 10.0 gm potassium nitrate).
- 1.0M ammonium chloride (26.75gm dissolve in 500ml de-ionized water in RBF).

- 0.01M EDTA solution.

Pipette 25ml nickel solution into a conical flask dilute to 100ml with de-ionized water. Add the 50mg solid indicator and 10ml of 1M ammonium chloride solution and then add concentrated ammonia until the pH is about 7 as shown by the yellow colour of the solution. Titrate with standard 0.01M EDTA solution until the end point is approached then render the solution strongly alkaline by the addition of 10ml of concentrated ammonia solution and continue the titration until the colour changes from yellow to violet. The pH of the final solution must be 10.

In second process 0.05gm Bromopyrogallol red in 100ml of 50% ethanol and a buffer solution (100ml of 1M ammonium chloride and 100ml of 1M aqueous ammonia solution) are used.

In which pipette out 25ml of nickel solution in conical flask and dilute to 150ml with de-ionized water. Add about 15 drops of the indicator solution, 10ml of the buffer solution and titrate with standard 0.01M EDTA solution until the colour changes from blue to claret red.



## **THE COMMON TEST PAPERS**

### **1. Litmus Paper**

This is an indicator for all acids and bases, weak or strong. Acids turn it red, bases blue. In preparing litmus paper, only the best litmus is used. The cubes, which contain from 50 to 90% of gypsum, are broken up and extracted once with alcohol. The dye is then dissolved in water 4 to 5 grams per liter and pure filter paper is soaked in the solution. The sheet is suspended on a cord to dry and is then cut into thin strips. For red litmus paper, a few drops of acetic acid are added to the solution and for blue litmus paper, a few drops of ammonia. The less pronounced the colour of the paper, the more sensitive it is.

### **2. Congo red Paper**

This is a reagent for strong acids. It is turned to a pure blue by mineral acids and to a violet colour by strong organic acids. The paper is prepared by soaking filter paper in a warm solution of 0.5 gram of Congo red in 1 liter of water containing 5 drops of acetic acid, and drying in a clean place.

### **3. Thiazole Paper (Mimosa Paper)**

This indicator is used to test for free alkali. It is coloured a pure red by alkalis and is far better for this purpose. The paper is prepared as described for Congo red paper, except that the acetic acid is omitted. Ammonia has no effect on this paper unless it is in very concentrated solution.

### **4. Phenolphthalein Paper**

This paper is turned red by alkalis, including ammonia and sodium carbonate solutions, but not bicarbonates. It can be used to advantage for differentiating among the alkalis. The paper is prepared by soaking filter paper in a hot solution of 1 gram of phenolphthalein in 1 liter of water.

### **5. Starch iodide Paper (Nitrite Paper)**

Pure starch (10 grams) is rubbed with a small amount of water, and 1 liter of boiling water is added with thorough stirring. After the solution has cooled, 2 grams of potassium iodide is added and sheets of clean filter paper are soaked in it and allowed to dry in a clean place. This paper is very sensitive, giving a definite reaction nitrous and hypochlorous acids. Small amounts of oxidizing agents turn with 1% HCl solution containing one drop of 1N nitrite solution per liter.

### **6. Lead Paper**

This reagent for hydrogen sulfide is prepared by soaking filter paper in a solution containing 5 grams of lead nitrate per liter and drying in air free from H<sub>2</sub>S. Instead of this paper one can use paper moistened with ferrous sulfate or lead acetate solution.

## **SOLUTION FOR SPOT TESTS ON FILTER PAPER**

### **1. H-acid Solution**

1% in 5% soda is used to test for easily coupling diazo compounds in spot tests on filter paper. R salt,  $\beta$ -naphthol, hydrocyanic acid etc. can also be used for this purpose.

**2. Resorcinol Solution**

1% in 5% soda is used to test for all diazo compounds including those which do not react with H-acid.

**3. Diazotized p-Nitroaniline**

It can easily react with all phenols and amines. It must be kept in the dark and after 1 to 2 days it gives a yellow colour with soda alone so care is necessary in its use. Diazotized o-chloroaniline can be used equally satisfactorily.

**4. Sulfone Reagent**

This reagent is 10% solution of 4, 4'-diaminodiphenylmethane-2, 2'-sulfone in 2N hydrochloric acid. The solution becomes green in time and dark coloured precipitate forms, but the supernatant solution remains usable for a long time. Nitrite gives an intense but unstable blue colouration; the reaction is not prevented by strong acids or by weak oxidizing agents such as ferric salts.

**5. Alkali Sulfide Solution**

Used to test for heavy metals (Iron, Copper, Tin etc.) in solution.