

Natubhai V. Patel College of Pure & Applied Sciences  
B.Sc. Semester VI  
Industrial chemistry/Industrial chemistry (Vocational)  
US06ICH01/US06CICV01: Dyes and intermediates  
UNIT – 4

**SYLLABUS**

Analysis and application of dyes and dye intermediates: Analysis of intermediates different methods used in the analysis. Nitrite value determination, coupling value, titanous chloride reduction, halogen content determination, etc

**4.0 ANALYSIS OF DYES AND INTERMEDIATES**

**4.0.1 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.

**4.1 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.

**4.1.1 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>).

#### 4.1.2 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.

#### 4.1.3 Preparation of 0.1N phenyldiazonium 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.

## 4.2 DETERMINATION OF AMINES

### 4.2.1 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.

#### 4.2.2 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.

### 4.3 DETERMINATION OF NAPHTHOLS

#### 4.3.1 $\beta$ -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.

#### 4.3.2 $\alpha$ -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.

#### 4.3.3 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.

#### 4.3.4 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 1 N NaNO<sub>2</sub> 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.

#### 4.3.5 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.

#### 4.3.6 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.

#### **4.3.7 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 to 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.

#### **4.3.8 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.

#### 4.4 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 ( $\text{TiCl}_3$ ) 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.

##### 4.4.1 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,  $\text{Ti}(\text{OH})_4$ . 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.

##### 4.4.2 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  $18^\circ\text{C}$ . 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  $\text{H}_2\text{SO}_4$ . 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  $\text{TiCl}_3$  solution corresponds to  $0.05/6.85$  or 0.007299 grams of iron.

##### 4.4.3 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  $\text{CO}_2$  or  $\text{N}_2$  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



##### 4.4.4 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 ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ )

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<sub>3</sub> solution for 0.2 grams of the dye (average of three titrations). The dye content is,

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

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

#### **4.4.5 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.

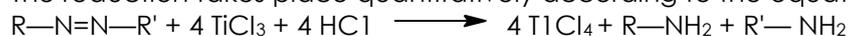
0.2 gram of methylene green used 20cc titanium trichloride solutions and contained therefore:  $0.00809 \times 20$  OR 1.618 grain of dye.

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

#### **4.4.6 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.

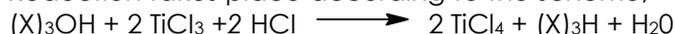
The reduction takes place quantitatively according to the equation:



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.

#### **4.4.7 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.

### **4.5 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.

#### **4.5.1 Calculation**

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

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

Then,  $(B \times 1.25 - A) \times 1.308 = \% \text{ Zinc metal.}$

### **4.6 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.

### **4.7 HALOGEN CONTENT DETERMINATION**

#### **4.7.1 Estimation of Chloride**

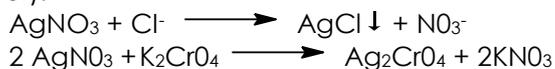
There- are two methods available for determination of Chloride.

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

#### 4.7.1.1 Silver nitrite method

##### ➤ Principle

$\text{AgNO}_3$  react with  $\text{Cl}^-$  and to form  $\text{AgCl}$ . The completion of reaction is indicating by the red colouration produced by reaction of  $\text{AgNO}_3$  with potassium chromate ( $\text{K}_2\text{CrO}_4$  as an indicator).



##### ➤ Procedure

Place 100ml of sample in conical flask. Maintain the pH in the range of 7 to 9.5 by using  $\text{H}_2\text{SO}_4$  or alkali. Now add 1 ml  $\text{K}_2\text{CrO}_4$  as an indicator. Titrate against the standard  $\text{AgNO}_3$  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

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

#### 4.7.1.2 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.

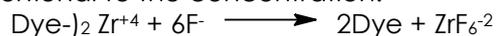
SPADNS and SCOH methods are colorimetric methods. Compare to SCOH method the SPADNS method tolerates much interference and determines fluoride in the range of 0.001 to 1.400 mg/lit. The reaction is immediate, stable colour and no waiting period is necessary whereas SCOH method require 20 minutes for 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  $\text{Cl}_2$  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 litter.

## 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

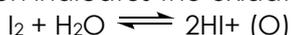
Placed the 400ml distilled water in the one litter RBF. Carefully added 200ml concentrated H<sub>2</sub>SO<sub>4</sub> and make it homogeneous. Add glass beads and connected the flask with distillation apparatus. Heat the flask slowly at first than rapidly. As the temperature reaches 180°C stop the heating 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 sulfate carry over.

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

## 4.8 ESTIMATION OF COPPER

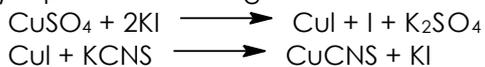
An aqueous solution of iodine is a mild oxidizing agent, it will therefore only act effectively with powerful reducing agents. One mole of iodine reacts with one mole of water and supply free oxygen for oxidation (to reducing agent). This reaction is reversible i.e. oxidation-reduction.

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. Than titrated the liberated iodine using standard solution of sodium thiosulfate.

### 4.8.1 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.

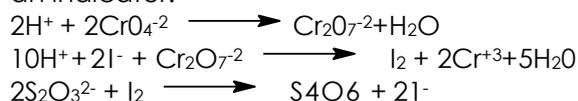
Add diluted solution of H<sub>2</sub>SO<sub>4</sub> and pinch of Urea and boil for few minutes. Now add ammonia till slight precipitate forms. Then add 2cc of 4N H<sub>2</sub>SO<sub>4</sub> and dilute up to 40ml by means of water. Add 1.25-1.5 gm of KCNS and 2.0cc of a 10% solution of potassium iodide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

## 4.9 ESTIMATION OF CHROMIUM

Chromium is generally determined by volumetric method.

### 4.9.1 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.



#### 4.9.2 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 =  $\frac{\text{B.R.} \times \text{Normality of Na}_2\text{S}_2\text{O}_3 \times 38.7 \times 10^6}{\text{ml of sample} \times 10^3}$

#### 4.10 DETERMINATION OF NICKEL (NI) BY DIRECT TITRATION

##### 4.10.1 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.

##### 4.10.2 Process

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.

1 mole EDTA = 1 mole Ni<sup>2+</sup>

#### 4.11 THE COMMON TEST PAPERS

##### 4.11.1 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.

##### 4.11.2 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.

##### 4.11.3. 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.

#### 4.11.4 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.

#### 4.11.5 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.

#### 4.11.6 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.

### 4.12 SOLUTION FOR SPOT TESTS ON FILTER PAPER

#### 4.12.1 H-acid Solution

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

#### 4.12.2. Resorcinol solution

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

#### 4.12.3. 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.

#### 4.12.4. 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.

#### 4.12.5. Alkali sulfide solution

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