

## 6 ANALYTICAL CHEMISTRY

### 1'3'4. Major, Minor and Trace Constituents

A *major constituent* is one whose amount is 1 per cent or more of the sample material. A *minor constituent* is 0'01 to 1 per cent of the sample and a constituent present in quantities smaller than 0'01 per cent is called a *trace constituent*.

### 1'3'5. Complete and Partial Analysis

Chemical analysis is said to be *complete* when it involves the determination of all the components detected qualitatively in the sample. The analysis is *partial* when it aims at determining only one or a few of the components of the sample such as, determination of copper in a copper ore.

### 1'3'6. Major Steps of Quantitative Analysis

Quantitative chemical analysis consists of the following four main steps :

(a) Sampling, that is, selecting a representative sample of the material to be analysed ;

(b) Conversion of the desired constituent into a form suitable for measurement ;

(c) Measurement of some property on which the determination is based, such as measurement of weight as in gravimetric analysis or measurement of volume as in volumetric analysis, or measurement of potential as in potentiometric titrations ; and

(d) Calculation and interpretation of the result.

Analytical methods are sometimes classified on the basis of the property whose measurement underlie the method of determination.

### 1'3'7. Classical Chemical Analysis

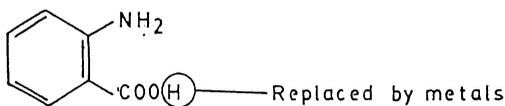
Quantitative chemical analysis started with the application of techniques of *gravimetric procedures*. In a gravimetric determination, a known volume of sample solution is treated with an excess of a suitable reagent which quantitatively precipitates the desired constituent present in the sample solution. The precipitate which is of known composition is filtered, washed, dried and weighed. Knowing the weight of the precipitate, the amount of the desired constituent in the test solution is calculated. For example, an excess of dilute sulphuric acid is added to a given solution containing barium ions. The precipitate of barium sulphate formed is filtered, washed, dried and weighed. From the weight of barium sulphate, the quantity of barium in the given solution is calculated. Because such determinations are based on the measurement of weight, these are referred to as gravimetric determinations.

medium as compared to the copper quinaldinate. By properly controlling the pH of the solution copper can be precipitated while cadmium and zinc will remain in solution. Thus, copper can be separated from cadmium and zinc. Many other separations can be achieved by making proper use of complexing reagents.

Copper quinaldinate after drying at 110–115°C has a composition represented by  $(\text{Cu}(\text{C}_{10}\text{H}_8\text{NO}_2)_2 \cdot \text{H}_2\text{O})$ .

(vii) **Anthranilic acid**

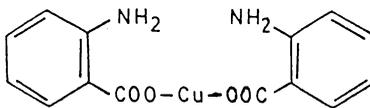
A 3 per cent aqueous soln of sodium salt of the acid is used as reagent. In neutral or weakly acidic soln, this reagent precipitates Zn, Cd, Co, Ni, Cu, Pb, Ag and Hg. The precipitation is done at controlled pH. Copper, cadmium, zinc and cobalt are quantitatively precipitated; these have a general formula  $\text{M}(\text{C}_7\text{H}_6\text{ON})_2$ . The ppt. is dried at 105–110°C.



Anthranilic acid

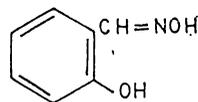
(viii) **Salicylaldoxime**

It is a white crystalline solid which is not much soluble in water. Hence, the reagent soln is prepared in water-alcohol mixture. This reagent reacts with Cu, Pb, Bi, Zn, Ni and Pd.



Copper quinaldinate

Salicylaldoxime is mainly used for the determination of copper. In presence of acetic acid (pH of soln 2.6) copper is precipitated in the form of a greenish yellow ppt of formula  $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ . The ppt is dried at 100–105°C and then weighed. Iron interferes with the determination but Ag, Cd, Hg, As and Zn have no effect in acetic acid medium. By proper control of pH copper can be separated from nickel.



Salicylaldoxime

**6.9.1. Gravimetric Determination of Nickel as Nickel Dimethylglyoxime**

An accurately weighed sample containing nickel is transferred into a 800 ml beaker having a stirring glass rod and a watch-glass cover (if sample is in the form of soln, its known volume is taken in the beaker). The sample material is dissolved in water, about 5 ml of dilute HCl (1 : 1) is added and soln diluted to 200 ml. The soln is heated to 70 to 80°C and about 30 to 40 ml of 1 per cent soln of dimethylglyoxime (DMG) in rectified spirit is added (note that the reagent is insoluble in water hence its alcoholic soln is used). Immediately after this, a soln of ammonia in water is dropwise added with stirring until a red ppt appears (Ni-DMG is soluble in acid hence, its ppt did not appear in acidic medium) and then ammonia soln is added in slight excess. The beaker containing the ppt is kept over a steam bath for about 30 minutes so that

The appearance of red colour thus indicates the end point of the titration.

(vi) *Formation of a coloured ppt.* Silver ions react with  $\text{Cl}^-$  ions to form a white ppt of  $\text{AgCl}$  and with  $\text{CrO}_4^{2-}$  ions to form a red ppt of  $\text{Ag}_2\text{CrO}_4$ . If a soln of  $\text{AgNO}_3$  is gradually added to a chloride soln containing little  $\text{K}_2\text{CrO}_4$ , a red ppt of  $\text{Ag}_2\text{CrO}_4$  will appear as soon as all the  $\text{Cl}^-$  ions have been precipitated and an extra drop of  $\text{AgNO}_3$  soln is added. (The solubility of  $\text{AgCl}$  is smaller than that of  $\text{Ag}_2\text{CrO}_4$ , hence  $\text{AgCl}$  is precipitated first.)

(vii) *External indicators.* Potassium ferricyanide acts as an external indicator in the titration of iron(II) soln with  $\text{K}_2\text{Cr}_2\text{O}_7$ . Ferricyanide ion reacts with iron(II) to form a blue ppt. The titration of iron(II) is done by adding  $\text{K}_2\text{Cr}_2\text{O}_7$  soln very gradually from a burette. At different stages of the titration, a drop of the reaction mixture is taken out and added to potassium ferricyanide soln. The point at which this soln ceases to turn blue is the end point of the titration (after the completion of the reaction there are no  $\text{Fe}^{2+}$  ions left, hence the indicator soln does not turn blue).

[B] **ELECTRICAL METHODS.** There are several titrations in which end point is located by measuring the change in some electrical properties of the titration mixture during the course of the titration. Later a graph is plotted between the magnitude of the electrical property and corresponding volumes of the titrant added. A sudden change in the graph gives the end point of the titration. Such titrations are known as electrometric titrations. These generally involve the measurement of potential (potentiometric), conductance (conductometric), current strength (amperometric) or quantity of electricity (coulometric titrations). These will be dealt in some detail in Chapter 14.

## 7.6. INDIRECT TITRATIONS

In a direct titration a known volume of an analyte is titrated with a standard soln of a reagent (taken in a burette) or, a known volume of the reagent soln can be titrated with the analyte soln (taken in a burette). For example, iodine soln can be titrated with a standard soln of thiosulphate or,  $\text{HCl}$  can be titrated with standard  $\text{NaOH}$  soln. In these titrations, at the equivalence point, neither the analyte nor the reagent is present in excess.

If the reaction between the analyte and the reagent is slow, the direct titration will take too much time for completion and is, therefore, not practicable. In such cases, those conditions are used which are helpful in accelerating the reaction rate, such as adding excess of reagent or heating the reaction mixture. To a known volume of the analyte soln, a known excess (100 to 200%) of the reagent is added. The reaction mixture is heated or kept for some

(c) Ten g NaOH, *i.e.*,  $10/40=0.25$  mole of NaOH is present in 1 litre, hence the molarity will be 0.25. (Note that, wt present per litre/mol wt, gives the number of moles present per litre of soln).

(d) Two litre soln has 10 g NaOH, so 1 litre will contain 5 g. Now,

$$\text{number of moles} = \frac{\text{wt present per litre}}{\text{mol wt}} = \frac{5}{40} = 0.125.$$

Thus, 0.125 mole is present in a litre of soln, hence, the molarity of the soln will be 0.125.

(iv) *In terms of normality.* A gram-equivalent (g eq) of a substance means its eq wt expressed in g. For example, the eq wt of HCl is 36.5, hence, its one g eq will contain 36.5 g of HCl. If a soln contains 1 g eq of a substance per litre, it is called a *normal solution* or its normality is said to be 1; such a soln is denoted as 1 N soln. If we have 1 g eq of HCl (36.5 g HCl) in 1 litre of a soln, it will be called a normal soln of HCl or the normality of the soln will said to be 1; such a soln is written as 1 N HCl soln. Now :

36.5 g HCl means 1 g eq of HCl

$\therefore$  18.25 g HCl ... 1/2 or 0.5 g eq of HCl

If we have 18.25 g HCl present in a litre of a soln, it will contain 0.5 g eq of HCl and normality of the soln will be 0.5. Thus normality is defined as the number of gram-equivalents present in a, litre of the given soln.

**Table 8.1. Normalities of Different HCl Solutions**

<i>HCl (in g) present per litre</i>	<i>HCl (in g eq) present per litre</i>	<i>Normality</i>	<i>Soln denoted as</i>
73.0	$73/36.5=2$	2	2N
36.5	$36.5/36.5=1$	1	1N (Normal)
18.25	$18.25/36.5=0.5$	0.5	0.5N
3.65	$3.65/36.5=0.1$	0.1	(semi-normal) 0.1N
0.365	$0.365/36.5=0.01$	0.01	(decinormal) 0.01N
	(eq wt of HCl = 36.5)		(centinormal)