CHAPTER 1

Definition and Scope

Pharmaceutical manufacturing industries are supposed to conduct both qualitative and quantitative analysis to assure that the raw materials used meet the desired specifications and to ensure the quality of the final product.

Analysis plays a very important role during the development and manufacturing of a pharmaceutical product. The market, as well as regulatory authority, demands evidence-based data regarding qualitative as well as quantitative measurement of a drug. This is required to make a formulation of definite strength to ensure the desired dose and safe therapeutic activity. Analysis conducted in pharmaceutical industries or laboratory on drugs or on their products is named Pharmaceutical analysis.

Various types of solutions are used in the analysis. For example; test solution, reagent solution, stock solution, dilute solution, volumetric or standard solution, etc. Each type of solution has got separate applications and importance.

LEARNING OBJECTIVES

After studying the chapter the students familiarize themselves with the following concepts:

- ✓ Different Techniques of Analysis
- ✓ Methods of Expressing Concentration
- ✓ Primary and Secondary Standards
- ✓ Preparation and standardization of various molar and normal solutions- Oxalic acid, sodium hydroxide, hydrochloric acid, sodium thiosulphate, sulphuric acid, potassium permanganate, and ceric ammonium sulphate

1.1 DIFFERENT TECHNIQUES OF ANALYSIS

A sample is analyzed primarily for two purposes – identification and determination of content. Accordingly, the techniques of analysis are classified into two categories – qualitative and quantitative.

Qualitative tests are generally conducted to detect whether the desired compound or substance is present

in the sample or not. Hence, this type of tests is for identification of the compound in the sample or for the limit test.

Quantitative tests are done to quantify or determine the amount of a particular compound or substance present in a sample. These techniques are based on (1) the quantitative measurement of the amount of the reagent added to complete the reaction or measurement of the amount of the reaction product, (2) measuring the characteristic movement of a substance in a specific medium under controlled conditions, (3) measurement of electrical properties of the compound, (4) measurement of some spectroscopic properties of the compound.

Therefore, the techniques used in the pharmaceutical analysis can be classified into four types;

1. Chemical methods:
   - Volumetric or titrimetric method
   - Gravimetric method
   - Gasometric method
2. Electrical methods:
   - Potentiometry
   - Conductometry
   - Polarography
   - Voltammetry
   - Amperometry
3. Instrumental method
4. Biological or microbiological method

(i)   Chemical methods

Volumetric or titrimetric method: In this method, a definite amount of sample is dissolved in water or in a suitable solvent and titrated with a titrant of known concentration using a suitable indicator till the end point is reached. The volume of titrant required is used to calculate the amount of the active substance present in the sample is calculated. This may be neutralization, complexometric, precipitation, oxidation-reduction, or nonaqueous titration.

Gravimetric methods: In this method, the substance to be determined is converted into an insoluble compound (precipitate) in the purest form. The precipitate is separated, washed, dried, and then weighed. The method is a time consuming one. In the electro-gravimetric method, the sample is electrolyzed over the electrode and the compound deposited is weighed after drying.

In thermogravimetry (TG) the changein weight is recorded, in differential thermal analysis (DTA) the difference in temperature between the sample and an inert reference substance is observed. While in differential scanning calorimetry (DSC) the energy required to establish a zero-temperature difference between the sample and reference substances measured.

Gasometric analysis: It refers to the measurement of the volume of gas evolved or absorbed in a chemical reaction. The gases analyzed in this method are CO_2, N_2O, N_2, cyclopropane, amyl nitrate, ethylene, helium, etc.

(ii) Electrical methods

In these methods, the electric current, voltage or resistance is measured with respect to the concentration of the same species present in the solution. This type of methods includes

Potentiometry: In this method, the electrical potential of an electrode in equilibrium with an ion is measured.

Conductometry: This method involves the measurement of electrical conductivity of an electrode with reference to a reference electrode.

Polarography, Voltammetry, and Amperometry: In these methods, electrical current at a microelectrode is measured.

(iii) Instrumental methods

In these methods, some physical properties of the compound or a substance are measured. When a very small quantity of the compound or substance is present in a sample, these methods are used. These methods are very selective, sensitive, accurate and simple. Any change in the properties such as absorbance, specific rotation, refractive index, migration difference, and charge to mass ratio of the compound or substance can be measured very quickly.

Spectroscopic methods include ultraviolet, visible, infrared, atomic absorption, x-ray, and nuclear magnetic resonance spectroscopy. These methods of analysis measure the amount of radiant energy of a particular wavelength either absorbed, scattered or emitted by the sample.

Emission spectroscopic method involves heating or electrical treatment of the sample to excite the atoms in the sample so that these emit the energy and measure the intensity of this energy. This method includes flame photometry, fluorometry, etc. While in absorption spectroscopy the amount of radiation absorbed by the sample being studied. For example, UV and visible spectroscopy, IR, NMR, AAS, etc. can be used for this purpose.

Chromatographic technique and Electrophoretic methods are based on the separation of the compounds in a mixture. The methods are used to identify the compounds of mixtures. The chromatographic techniques involve TLC, HPTLC, HPLC, GC, etc.

In Mass spectrometry, the material is vaporized using a high vacuum and the vapor is bombarded by a high energy electron beam. The molecules in vapor state fragment and produce ions of varying sizes. These ions are differentiated by accelerating them in the electrical field and then these are deflected in a magnetic field. Each type of ion produces a peak in the mass spectrum.

(iv)   Biological and microbiological methods

Biological methods are used to determine or measure the potency of a drug or its derivative when there is no suitable physical or chemical method. Such methods of analysis are called bio-assays.

Microbiological methods are used to determine the potency of antibiotics or anti-microbial agents. The inhibition of growth of bacteria by the sample is compared with that by a standard antibiotic. These methods include cup and disc, or turbidimetric.

1.2 METHODS OF EXPRESSING CONCENTRATION

The concentration of a solution means how much solute is present in a definite amount (mass or volume) of solvent or solution. It can be expressed in various ways. For example, percentage, normality, molarity, molality, mole fraction. Since a liquid can be measured by volume or mass, the percentage concentration may be weight/weight, weight/volume, volume/ volume or volume/weight.

Percentage concentration (w/w)

It refers to a number of grams of solute present in 100g of the solution according to the metric system.

That is,

$$\% \, (w/w) = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Sometimes, the quantity of the solute or solution is expressed in volume along with the density of the solute or solution. In such a case, the mass of the solute/solution is calculated prior to the calculation of percent (w/w). This is illustrated through an example below.

Example 1: A solution of sodium chloride contains 5g of sodium chloride in 250g of solution. Find out the concentration (w/w) of the solution.

Solution: Percent concentration (w/w) $= \frac{5g}{250g} \times 100 =$ **2**

Example 2: 125g of a solution contains 25mL of glycerin. The density of glycerin is 1.285g/mL. Calculate the concentration of the solution in %w/w.

Solution: Density of glycerin = 1.285g/mL, Volume of glycerin present in 125g of solution = 25mL

Mass of glycerin present in 125g of solution = density × volume = 1.285g/mL × 25mL = 32.125g

So, the percent concentration (w/w) of glycerin = $\frac{32.125g}{125g} \times 100 =$ **25.7**

Example 3: 400mL of a solution contains 320.5g of sucrose. Density of the solution is 1.255g/mL. Calculate the concentration of the solution in %w/w.

Solution: Density of the solution = 1.255g/mL,

Volume of the solution = 400mL

Mass of the solution = density × volume = 1.255g/mL × 400mL = 502.0g

Mass of the sucrose present in 502g of solution = 320.5g

So, the percent concentration (w/w) of the solution = $\frac{320.5g}{502g} \times 100 =$ **63.84**

Percentage concentration (w/v)

According to metric system it refers to number of grams of solute present in 100mL of solution.

That is,

$$\% \text{ (w/v)} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

Sometimes, the quantity of the solute or solution is expressed in grams along with the density of the solute or solution. In such a case, the volume of the solute/solution is calculated prior to the calculation of percent (w/v). This is illustrated through an example below.

Example 4: 500g of sucrose is dissolved in water to prepare 600mL of syrup. Find out the concentration of the syrup.

Solution: Volume of the syrup = 600mL,

Mass of the solute = 500g

Concentration of the syrup, $\% \text{ (w/v)} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100 = \frac{500g}{600mL} \times 100 =$ **83.33**

Example 5: To prepare 150 mL of 10%w/v solution of hydrochloric acid how many milliliters of HCl of 98.5%w/v would be required?

Solution: Concentration of HCl = 98.5%w/v;

Required amount of HCl = 10g

Volume of HCl $\equiv$ 10g $= \frac{100mL}{98.5g} \times 10g =$ **10.15mL**

Percentage concentration (v/v)

According to the metric system, it refers to a number of milliliters of solute present in 100mL of solution.

That is,

$$\% \text{ (v/v)} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

Sometimes, the quantity of the solute or solution is expressed in grams along with the density of the solute or solution. In such a case, the mass of the solute/solution is

converted into volume prior to the calculation of percent (v/v). This is illustrated through an example below.

Example 6: The concentration of a solution of sorbitol liquid is expressed as 15%w/v. If the density of the sorbitol liquid is 1.287g/mL; calculate the volume of sorbitol liquid required to make 900mL of the solution.

Solution: Density of sorbitol liquid = 1.287g/mL;

  Volume of solution = 900mL

  Concentration of the solution = 15%w/v = 15g in 100mL

  For 900mL solution the amount of sorbitol liquid would be required = $\frac{15g}{100mL}$ × 900mL = 135g

  Volume of 135g of sorbitol liquid = $\frac{\text{Mass}}{\text{Density}} = \frac{135g}{1.287g/mL}$ = **104.9mL**

Normality

Normality of a solution is defined as the number of gram-equivalents of a solute present in one litre of the solution. In other words, number of milli gram-equivalents in one mL.

  Thus,

$$\text{Normality} = \frac{\text{Number of gramequivalents}}{\text{Number of litres}} = \frac{\text{Number of milligramequivalents}}{\text{Number of millilitres(mL)}}$$

  To define normality the term *equivalent weight* is used. However, the value of equivalent weight varies with the type of chemical reaction, and it is difficult to give a clear and universal definition of the term. It is found that the same compound can have different equivalent weights in different chemical reactions.

  The definition of the term, equivalent weight, with respect to the type of chemical reaction is being explained below.

Equivalent weight

Neutralization reactions:

The equivalent weight of an acid refers to the amount of the acid containing a one-gram atom of replaceable hydrogen, i.e., 1.0078g (1.008g) *of hydrogen.* The replaceable hydrogen in an acid is alternatively called as basicity of an acid. The number of replaceable hydrogens in monobasic acid such as hydrochloric acid, acetic acid, Hydrobromic acid, hydroiodic acid is one. Dibasic acid such as sulphuric acid contains two and tribasic acid such as phosphoric acid contains three replaceable hydrogens. Thus, the equivalent weight of monobasic acid is its molecular weight, that of a dibasic acid is ½ of its molecular weight and that of a tribasic acid is 1/3 of its molecular weight.

  The equivalent weight of a base is the weight of it containing one replaceable hydroxyl group, 17.008g of an ionizable hydroxyl group (17.008g of hydroxyl are equivalent to 1.008g of hydrogen).

In other words, the equivalent weight of monoacidic base sodium hydroxide, potassium hydroxide is their molecular weight. The equivalent weight of diacidic base such as calcium hydroxide, barium hydroxide, strontium hydroxide is ½ of their molecular weight.

Salts of strong bases and weak acids such as sodium carbonate or sodium acetate hydrolyzes in water and the resulting solution is alkaline. Each molecule of such salt reacts with two molecules of hydrochloric acid; hence, the equivalent weight of such salt is ½ of the molecular weight.

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Acidity}} \quad \text{(for base)}$$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Basicity}} \quad \text{(for acid)}$$

Example 7: The molecular weights of sulphuric acid, hydrochloric acid, acetic acid, and oxalic acid dihydrate are 98, 36.5, 60, and 106 respectively. Calculate their equivalent weights.

Solution: For acid, the equivalent weight $= \dfrac{\text{Molecular weight}}{\text{Basicity}}$

Basicity of sulphuric acid, hydrochloric acid, acetic acid, and oxalic acid dihydrate are 2, 1, 1, 2 respectively.

Hence, equivalent weight of sulphuric acid $= \dfrac{98}{2} = $ **49**

Equivalent weight of hydrochloric acid $= \dfrac{36.5}{1} = $ **36.5**

Equivalent weight of acetic acid $= \dfrac{60}{1} = $ **60**

Similarly, equivalent weight of oxalic acid dihydrate $= \dfrac{106}{2} = $ **53**

Note: Since oxalic acid is stable with two molecules of water of crystallization its equivalent weight should be calculated including its water of crystallization [$(COOH)_2, 2H_2O$].

Normality can also be defined as;

$$\text{Normality} = \frac{\text{Number of gram}-\text{equivalents}}{\text{Number of litres}}$$

$$= \frac{\text{Number of milligram}-\text{equivalents}}{\text{Number of millilitres (mL)}}$$

So, number of milligram-equivalents = Normality × Number of milliliters (mL)

Say, two substances X and Y are dissolved in sufficient water to make standard solutions having strength Sx and Sy respectively. If two solutions are reacted and Vx mL of X is found exactly equivalent to Vy mL of Y (that is Vx mL neutralizes completely Vy mL);

Then, Vx mL × Sx (Normality of the solution of X) = Vy mL × Sy (Normality of the solution of Y)

Example 8: Calculate the volume of 0.5N hydrochloric acid to be required to precipitate 0.45g of silver nitrate completely.

Solution: The reaction is $AgNO_3 + HCl = AgCl + HNO_3$

Equivalent weight of $AgNO_3$ being 169.89g; 1N solution of it contains 169.89g per lt.

In other words, 169.89g of $AgNO_3$ per litre makes 1N solution

Then, 0.45g of $AgNO_3$ per litre makes $\dfrac{0.45g}{169.89g}$ = 0.002648N

Say, the volume of $AgNO_3$ solution required = 1000 mL

Given that, the strength of hydrochloric acid solution = 0.5N

Volume of hydrochloric acid solution consumed = V mL

Then, V mL × 0.5N = 0.002648N × 1000mL

$$V = \frac{0.002648N \times 1000mL}{0.5N} = \textbf{5.296mL}$$

Example 9: How many milliliters of 0.125N solution A need to be diluted to prepare 500mL of 0.1N of solution?

Solution: Say, V mL of 0.125N solution A would be diluted.

Given that, the strength of solution A = 0.125N

The strength of the required solution = 0.1N

Volume of required solution = 500mL

Then, V mL × 0.125N = 500mL × 0.1N

So, $V = \dfrac{500mL \times 0.1N}{0.125N} = \textbf{400mL}$

Complex formation and precipitation reaction

The equivalent weight of the substances take part in these reactions is the amount which contains or reacts with 1gm atom of a universal cation, M^+. In other words, *the equivalent of a substance in these reactions is the amount equivalent to* 1.008g *of hydrogen*. Thus, in case of a cation, the equivalent weight would be its atomic weight divided by its valency and the equivalent weight of the substance is its weight that reacts with one equivalent of the cation.

In a precipitation reaction, the equivalent weight of salt is its gm molecular weight divided by total valency of the reacting ion. Hence, the equivalent weight of silver nitrate in the titration of chloride ion would be the molecular weight of it (silver nitrate).

In case of complex formation reaction, the equivalent weight is calculated with the help of the ionic equation of the reaction. For example, the equivalent weight of potassium cyanide in the titration with silver ions would be 2 moles (2 × 65.118).

$$2CN^- + Ag^+ \leftrightarrow [Ag(CN)_2]^-$$

Similarly, zinc is titrated with potassium ferrocyanide. According to the ionic equation as shown below the equivalent weight of potassium ferrocyanide is one-third of its formula weight.

$$3Zn^{2+} + 2K_4Fe(CN)_6 \rightarrow 6K^+ + K_2Zn_3[Fe(CN)_6]_2$$
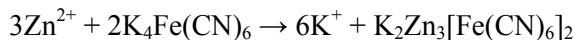
Oxidation-reduction reaction

The equivalent weight of an oxidizing or reducing substance (reagent) is commonly defined as the weight of the substance which contains or reacts with 1.008g of available hydrogen or 8.000g of available oxygen.

The term 'available' means 'the amount actually being utilized in the oxidation or reduction'. By writing the hypothetical equation for the reaction the amount of available oxygen can be known. An example is given below,

$$2KMnO_4 => K_2O + 2MnO + 5O \quad \text{(in acidic medium)}$$
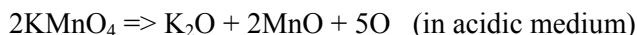
The equation shows that in acidic medium two molecules of $KMnO_4$ release 5 atoms of available oxygen.

In an actual oxidation-reduction reaction (redox reaction) electrons are transferred from the reducing agent to the oxidizing agent. Thus, oxidation is a process in which loss of one or more electrons by atoms or ions takes place while reduction is a process in which gain of one or more electrons by a reducing atom or ion takes place.

Method of calculating the equivalent weight on the basis of oxidation number has been described in Chapter 7 (Red-ox titration).

Molality

The molality of a solution is defined as the number of moles of a substance present in one kg of solvent.

$$\text{Molality or molal concentration } (m) = \frac{\text{No of moles of solute}}{\text{kg of solvent}}$$

Molarity

Molarity of a solution is defined as the number of moles of a substance present in one litre of solution. One mole is the amount of a substance that contains one gram molecular weight of that substance. In case of an element, it refers to its atomic/molecular weight, in case of a molecule it refers to the sum of the atomic weights of constituting elements, in case of a radical the same is true. For example;

One mole of hydrogen = 2 × its atomic weight = 2 × 1 = 2g, (hydrogen is diatomic; its molecular formula is H_2).

One mole of carbon = 1 × 12.01 = 12.01g ≈ 12g

One mole of SO_4^{2+} = 1 × S + 4 × O = 1 × 32.06 + 4 × 16 = 32.06 + 64 = 96.06g

One mole of Na_2CO_3 = 2 × 23 + 1 × 12 + 3 × 16 = 46 + 12 + 48 = 106g

One molar solution means one gram molecular weight of a substance is present in 1000mL of solution. Thus,

$$\text{Molarity or molar concentration M} = \frac{\text{No of moles of solute}}{\text{Liter of solutions}}$$

For example, 2g of Na_2CO_3 is dissolved in sufficient water to produce 50mL of solution. molecular weight of Na_2CO_3 and valency is 2; 50 mL $= \frac{50\text{mL}}{1000} = 0.05$lt.

The molarity of the solution $= \frac{2\text{g}}{50\text{mL}} = \frac{2\text{g}}{0.05\text{lt}} = 40$M

1.3 PRIMARY AND SECONDARY STANDARDS

Primary standards

If a substance is available in a pure and stable state, a solution of definite concentration (normality/molarity) can be prepared. This is done by accurate weighing the calculated amount of the substance, dissolving in a solvent to prepare a definite volume of the solution. Such a substance is called a *primary standard.*

The standard solution is a solution of known concentration used for titrating another solution to find out the concentration of the solution titrated.

Thus, the concentration of such standard solution, used in various titrations, is called the *strength* of the solution. This is illustrated through an example below.

Example 10: In a titration 24.65mL of 1.0053M solution of potassium dihydrogen phthalate was consumed by 25mL of sodium hydroxide solution. Find out the strength of the sodium hydroxide solution.

Solution: Volume of potassium dihydrogen phthalate solution consumed (V) = 24.65mL

Volume of sodium hydroxide solution (V_1) = 25.00mL

Strength of potassium dihydrogen phthalate solution (S) = 1.0052M

Strength of sodium hydroxide solution (S_1) = ?

According to the rule of neutralization, $V \times S = V_1 \times S_1$

So, the strength of the sodium hydroxide solution, $S_1 = \frac{V \times S}{V_1} = \frac{24.65 \times 1.0052 \text{ M}}{25} =$

0.9911M

Example 11: 20.00mL of ferrous sulphate solution reacts completely with 25.50mL of 0.15N potassium permanganate solution. Calculate the strength of ferrous sulphate solution in terms of molarity.

Solution: In this reaction, ferrous sulphate acts as reducing agent and its normal solution contain 1 mol per lt or 151.90g per lt.

Say, the strength of ferrous sulphate solution is S

Given that the volume of ferrous sulphate solution consumed = 20.00mL

The volume of potassium permanganate solution = 25.50mL

The strength of potassium permanganate solution = 0.15N

Then, S × 20.00 = 25.50mL × 0.15N

So, $$S = \frac{25.50\text{mL} \times 0.15\text{N}}{20.00\text{mL}} = 0.191\text{N}$$

Since the concentration of ferrous sulphate in its normal and moral solution is the same, the strength of ferrous sulphate solution would be **0.191M**.

Properties of a primary standard:

To become a primary standard, a substance should possess the following properties;

1. It should be easily obtained, purified, dried (preferably at around 105°C), and preserve in a pure state for a reasonable period of time. (Hydrated substances cannot fulfill this criterion because without partial decomposition their surface moisture cannot be removed completely.)

2. During weighing a substance is exposed to air. So, it must be stable in the presence of air. That is, it should not oxidize or absorb moisture (hygroscopic). It should not be affected by carbon dioxide too. The composition of the substance must remain unchanged during storage.

3. The substance should not contain impurities more than 0.02%. The impurities should be qualitatively and quantitatively measurable by using a sensitive method.

4. It should have a high equivalent weight; so that it can be weighed accurately. The precision in weighing is usually 0.1 – 0.2 mg. However, for an accuracy of 1 in 1000, at least 200 mg should be weighed.

5. The substance should be readily soluble in water or in another solvent under the normal conditions.

6. The reaction between the standard solution and the substance being titrated should be stoichiometric and instantaneous. There should be a negligible error in titration and should be easily determined.

Practically it is very difficult to get a substance which can be used as an ideal primary standard. It is necessary to compromise between the ideal properties. Different substances are used as the primary standard in specific titration. For example, sodium carbonate, borax, potassium hydrogen phthalate, succinic acid, etc., are used as the primary standard in acid-base titrations. The primary standards used with respect to the type of titration are mentioned in Table 1.1 below.

Table 1.1: List of substances used as the primary standard

Type of titration	Substances used as Primary standards
Acid-base	Potassium hydrogen phthalate $KH(C_8H_4O_4)$ Sodium carbonate $[Na_2CO_3]$ Borax $[Na_2B_4O_7]$ Thallous carbonate $[Tl_2CO_3]$ (poisonous) Potassium bi-iodate $[KH(IO_3)_2]$

	Succinic acid [$H_2(C_4H_4O_4)$]
	Benzoic acid [$H(C_7H_5O_2$]
	Adipic acid [$H_2(C_6H_8O_4)$]
	Furoic acid [$H(C_5H_3O_3)$]
	Hydrochloric acid [HCl] (constant boiling)
Complexometric	Silver nitrate [$AgNO_3$]
	Sodium chloride [NaCl]
	Potassium chloride [KCl]
	Disodium ethyl enediaminetetra-acetate dihydrate and anhydrous
	Soluble salts of various metals such as Zinc, Magnesium, Copper, and spectroscopically pure manganese depending on the reaction
Precipitation	Silver [Ag]
	Silver nitrate [$AgNO_3$]
	Sodium chloride [NaCl]
	Potassium chloride [KCl]
	Potassium bromide (obtained from potassium bromate)
Oxidation-reduction	Potassium dichromate [$K_2Cr_2O_7$]
	Potassium bromate [$KBrO_3$]
	Potassium iodate [KIO_3]
	Potassium bi-iodate [$KH(IO_3)_2$]
	Iodine [I_2]
	Sodium oxalate [$Na_2C_2O_4$]
	Arsenious oxide [As_2O_3]
	Electrolytic or pure iron

Usually, hydrated salts are not used as primary standard; because these cannot be dried efficiently. The salts such as borax [$Na_2B_4O_7$, $10H_2O$], oxalic acid [$H_2C_2O_4$, $2H_2O$], copper sulphate [$CuSO_4$, $5H_2O$] do not effloresce. Experimentally, these have been found satisfactory as a secondary standard.

In general, the standard solution (*titrant*) is added from a burette. Addition of standard solution or titrant is continued till the reaction is complete. The substance being titrated is called *titrate* and the process is called *titration*. The point at which the reaction becomes complete is called *endpoint* or *equivalencepoint*. The completion of the titration is detected by the change of color of a substance added in the form of solution to the titration mixture. Such a substance is called an *indicator*.

Secondary standards

The name itself tells that this is a standard which comes second. That's why the name is secondary. In laboratories,the secondary standard is used to prepare reagents, kits or to produce quality control material for other labs. The primary standard is used as the primary calibrator or primary reference material. A secondary standard is used for the purpose of calibration of control material for analysis of the unknown concentration of a substance. So principally, secondary standard serves the purpose of external quality

control. This makes it essential that the secondary standard must first be standardized against the primary standard. There are other points to remember. For preparing the standard solutions distilled water must be used.

Similarly, before using the chemicals it is necessary to check the date of manufacture, expiry date, date of receipt of chemical, whether the conditions for its transport was followed or not, whether the seal tampers, etc. Solutions of these substances are routinely used in laboratories of institutes and industries also. The secondary standard substances possess many of the properties of primary standards, but not all. These substances are not available as purest and stable form. For example, sodium hydroxide and potassium hydroxide are commonly used as standards. These are extremely hygroscopic, are not obtained as purest form, contain some amount of carbonates. Exact results cannot be obtained in the presence of carbonate. Hence, these substances are used as a secondary standard. Certain important properties of secondary standards are given below;

- It has less purity than the primary standard
- Less stable and more reactive
- Their solutions remain stable for a long time
- Standardized against a primary standard

The best and common example is anhydrous sodium hydroxide (NaOH) and potassium hydroxide (KOH). It is extremely hygroscopic. As soon as the bottle is opened, sodium hydroxide starts absorbing moisture from the atmosphere and within a short time it becomes moist.

Another example is potassium permanganate ($KMnO_4$) very often used as a secondary standard. It is a good oxidizing agent or in other words, it is reactive hence, less stable. Due to its reactivity, it is oxidized to manganese oxide (MnO_2) which contaminates the $KMnO_4$. For this reason, it is unsuitable for being a primary standard. But it can be used very well as a secondary standard.

1.4 PREPARATION AND STANDARDIZATION OF VARIOUS MOLAR AND NORMAL SOLUTIONS

Preparation of various molar and normal solutions

These are primarily standard solutions because their concentrations in terms of normality or molarity have to be measured and maintained. The solution may be of a primary standard or secondary standard substance.

A solution of definite strength can be prepared by accurately weighing the substance, dissolving in an appropriate solvent, usually water to make up a definite volume. This is done when the substance is available in a pure and stable state, and if it neither absorbs nor releases moisture. The solution is prepared in a volumetric flask.

When a solution of exact strength such as 0.1 N or 0.1 M is required, the solution can be prepared as follows;

Initially, a slightly concentrated solution is prepared. After determining the actual strength of the solution, a measured volume of the solvent is added to the standardized solution and mixed thoroughly. The solution thus prepared possesses the exact strength. This is explained through the following example. Say, 500mL of the 0.1M solution of NaOH is to be prepared. According to the molecular weight, 2g is to be dissolved in water to make 500mL. Now, 2.2g of NaOH is taken and 500mL of its solution is prepared, standardized against potassium hydrogen phthalate. Say, the actual strength is 1.127(0.1)M or 0.1127M and during titration 53.00mL of alkali solution is consumed. Then the balance amount of alkali solution becomes 500 – 53 = 447 mL.

So, $0.1M \times V\ mL = 0.1127M \times 447\ mL$

Or, $V = \dfrac{0.1M \times 447mL}{0.1127M} = 503.769mL \approx 503.80\ mL$

Thus, 503.80 mL – 447.00 mL = 56.8 mL of water should be added to 447mL of alkali solution and mixed thoroughly to obtain the exact strength of 0.1M.

Note that the extra volume of water must be accurately measured.

When substances such as most alkali hydroxides, some inorganic acids, etc. are not available in a pure and stable state, their solutions nearest to the required strength are prepared. These solutions are standardized with appropriate primary standard solutions to find out their actual strength. This type of substance is called a secondary standard.

Preparation of molar solutions

The one molar solution is prepared by dissolving one gram molecular weight of a substance in sufficient solvent, usually water, to make 1000mL of the solution.

Preparation of normal solutions

Normal solution

Normal solutions solutionthat contains 1 g. the equivalent weight of a substance per litre of solution. It is expressed as N. The strength of a solution can be N, N/2 (0.5N), N/5 (0.2N), N/10 (0.1N), N/50 (0.02N), N/100 (0.01N), etc.

For example, equivalent weight of NaOH = $\dfrac{40}{1}$ = 40; similarly, equivalent weight of $Na_2CO_3 = \dfrac{106}{2} = 53$

Thus, when 40g of NaOH present in one litre it makes 1N solution and 1N solution of Na_2CO_3 means 53g of Na_2CO_3 is present in one litre of solution.

If the substance is available in pure form, a solution of particular strength (normality/molarity) can be easily prepared by weighing the required amount accurately and dissolving in the solvent, usually distilled water to make the required volume.

If the substance can absorb some moisture (unbound moisture), the substance should be dried in a hot air oven or under vacuum drier and cooled in a desiccator, thereafter it is used.

1. Preparation and standardization of 0.1M Oxalic acid

The molecular formula of oxalic acid is $(COOH)_2, 2H_2O$ and its molecular weight is 126.068. Hence, 1M solution of oxalic acid shall contain 126.068g per litre. A.R. oxalic acid has been widely used as standard. Since the water content of oxalic acid is uncertain, it is not really recommended to use as a primary standard. Only it is used by elementary students. It should be stored or preserved in well-closed container in a desiccator over an appropriate deliquescent such as sodium bromide.

Preparation of 0.1M Oxalic acid

To prepare 250mL of the 0.1M solution of oxalic acid $\frac{126.068}{4}$ g = 31.517g would be required.

- ➢ Weigh accurately 31.517of oxalic acid, transfer into a clean 250mL volumetric flask.
- ➢ Dissolve in freshly prepared distilled water and make up the volume.

Standardization of 0.1M Oxalic acid against 0.1M potassium permanganate

- ➢ Pipette out accurately 25.00mL of oxalic acid solution in a 250mL clean conical flask, add 100mL of freshly prepared distilled water.
- ➢ Add 6mL of concentrated sulphuric acid slowly, mix; if necessary heat the solution to 70°C.
- ➢ Rinse a 50mL clean burette with 0.1M potassium permanganate solution, fill the burette with 0.1M potassium permanganate solution, open the stopcock and drain the solution to remove air bubble from the jet completely.
- ➢ Refill the burette with 0.1M potassium permanganate solution; adjust the meniscus at zero marks of the burette.
- ➢ Titrate the hot solution (temperature should be within $65^{\circ} - 70^{\circ}$C) of oxalic acid slowly with 0.1M potassium permanganate solution until a pale pink color appears which persists for at least 30 seconds. Note the volume of 0.1M potassium permanganate solution consumed (titer value).
- ➢ Repeat the determination twice and take the average of the titer values for calculation.

Calculation

Say, the volumes of 0.1M potassium permanganate solution consumed are 24.90mL, 24.90mL and 24.95mL. The average volume, $V = \frac{24.90+24.90+24.95}{3}$mL = 24.92mL

Strength of 0.1M potassium permanganate solution, $S = 1.0006$

The volume of oxalic acid solution titrated, $V_1 = 25.00$mL

The strength of 0.1M oxalic acid solution, $S_1 = \frac{24.92 \times 1.0006}{25.00} = 0.9974$

Or, the strength of oxalic acid solution is 0.09974M

2. Preparation and standardization of 0.1M Sodium hydroxide

The molecular formula of sodium hydroxide is NaOH; it is most commonly used as a standard alkali because it is very cheap. However, potassium hydroxide and barium hydroxides are also used as standard alkali. All these alkalis are the strong base. But, none of these is available in the purest form. Sodium and potassium hydroxides are very hygroscopic and mostly contain a certain amount of carbonate along with water. Hence, none of these can be used as a primary standard, because the exact result would not be obtained with due to the presence of carbonate. A.R. Sodium hydroxide contains 1 - 2% sodium carbonate and commercially available sodium hydroxide which is prepared from metallic sodium contain less than 1% of sodium carbonate. Due to extreme hygroscopicity, it is not chosen as the primary standard.

The molecular weight of sodium hydroxide, NaOH is 40. Thus, one-liter solution of 1M NaOH will contain 40g of it. Since it is a monoacidic base, its equivalent weight is also 40. Hence, one-liter solution of 1N NaOH will contain 40g of it. It is available in the form of sticks, flakes, or pellets.

Since sodium hydroxide contains extra moisture 10 – 15% more of the calculated quantity should be taken. That is in place of 40g one should take 48 – 50g for making 1lt of 1N/1M solution.

Preparation of 0.1M Sodium hydroxide solution

Take a clean and dry weighing bottle of 15mL capacity, weigh it. Transfer about 2.2g of A.R. NaOH as quickly as possible, close the bottle with lid and weigh the weighing bottle accurately and transfer the content into a clean 500mL volumetric flask. Weigh the empty bottle. The difference in two weights provides the amount of sodium hydroxide taken. Dissolve in freshly distilled water. Shake well and make up the volume up to the mark.

Sodium hydroxide solution can be standardized against various substances such as standard hydrochloric acid, potassium hydrogen phthalate, benzoic acid, succinic acid, adipic acid, potassium bi-iodate, oxalic acid, potassium bi-tartrate, etc. Among these substances, potassium hydrogen phthalate is widely used.

Preparation of 0.1M potassium hydrogen phthalate

A.R. potassium hydrogen phthalate, $HK(C_8H_4O_4)$, is available with a purity of 99.9%. As such it is not hygroscopic. If it is not properly stored, it may contain some moisture. It is to be dried at $120^{\circ}C$ for 2 hrs and cooled in a desiccator before use. The molecular weight of potassium hydrogen phthalate is 204.22. Since it has one replaceable hydrogen atom, its equivalent weight would be 204.22. Thus, one litre of the 1M solution will contain 204.22g of potassium hydrogen phthalate and the 0.1M solution will contain 20.422g of potassium hydrogen phthalate per litre.

Standardization of 0.1M Sodium hydroxide against potassium hydrogen phthalate

➢ Take about 2.05g of potassium hydrogen phthalate in a clean and dry weighing bottle, weigh accurately (*x*)g.

➢ Transfer the content of the bottle into a clean 100mL volumetric flask, weigh the empty bottle accurately (*y)*g. The difference between the two weights (i.e., [*x* – *y*]) would be the amount of potassium hydrogen phthalate taken.

➢ Rinse the inner walls and add 60 – 70mL of freshly prepared hot water to the flask, dissolve potassium hydrogen phthalate.

➢ After complete dissolution adds freshly distilled up to the mark, shake well.

➢ Pipette out 25.00mL of the potassium hydrogen phthalate solution into a 250mL clean conical flask, add few drops of phenolphthalein solution.

➢ Rinse a 50mL clean burette thrice with sodium hydroxide solution, fill the burette with sodium hydroxide solution, open the stopcock and drain some solution to remove air bubble completely and to fill the jet with an alkali solution.

➢ Refill the burette with alkali solution up to the zero marks, titrate potassium hydrogen phthalate solution till a pink color is noticed. Note the titer value.

➢ Repeat the titration twice more and note the titer values, take the average of the three values for calculation of the strength of the sodium hydroxide solution.

Calculation

Say, the volume of potassium hydrogen phthalate solution $(V_1) = 25.00$mL

Say, the amount of potassium hydrogen phthalate taken, $x – y = 2.0498$g

Strength of 0.1M solution of potassium hydrogen phthalate $(S_1) = \dfrac{\text{Practical weight}}{\text{Theoretical weight}}$

$= \dfrac{2.0498\text{g}}{2.0422\text{g}} = 1.0037$

Volume of sodium hydroxide solution consumed $(V) = \dfrac{24.95 + 24.95 + 25.00}{3} = 24.97$mL

$$V \times S = V_1 \times S_1$$

The strength of 0.1Msolution of sodium hydroxide $(S) = \dfrac{25.00\text{mL} \times 1.0037}{24.97\text{mL}} = \mathbf{1.0049}$

Preparation and Standardization of 0.1N Sodium hydroxide against potassium hydrogen phthalate Same procedure as described above for preparation and standardization of 0.1N Sodium hydroxide against potassium hydrogen phthalate shall be followed.

3. Preparation and standardization of 0.1N hydrochloric acid

Concentrated hydrochloric acid is about 10.5 – 12 N if it is stored properly and not opened frequently. If this concentrated acid is diluted appropriately with freshly distilled water, a standard solution of desired strength can be prepared. Usually concentrated hydrochloric acid contains vapor of hydrogen chloride. When the bottle is opened the vapor goes out and the acid loses its concentration with time. To avoid this volatility and hygroscopicity, and to maintain the concentration constant, constant-boiling-point HCl can be used. In fact, the constant-boiling-point HCl can be prepared with regular concentrated HCl.

In practice, normal or molar solution of HCl is prepared by diluting regular concentrated HCl. The strength of concentrated HCl available is 10.5 N – 12N. To prepare 1N HCl 90.00mL of concentrated HCl is diluted with freshly prepared distilled water to make 1000mL.

Preparation of 0.1N HCl: The solution of 0.1N HCl is prepared by diluting 9.00mL of concentrated HCl to 1000mL with freshly distilled water.

Standardization

(A) Standardization against anhydrous sodium carbonate

For this purpose, A.R. sodium carbonate having 99.9% purity is used. This may contain little moisture. So, it needs to be dried at $260 - 270^{\circ}$C for 30 min and cooled in a desiccator before use. If it is dried at a temperature above 270°C, sodium carbonate may lose carbon dioxide. The equivalent weight of Na_2CO_3 is $106/2 = 53$. Hence, to make a 1N solution of Na_2CO_3 53g of it should be contained in 1 L of solution.

To prepare 0.1N solution 5.3 g of Na_2CO_3 should be present in one litre of solution. Here only 100mL of 0.1N solution shall be prepared; so, 0.53g of Na_2CO_3 shall be dissolved in water to make 100mL.

Preparation of 0.1N solution of sodium carbonate

Weigh accurately about 0.53g of A.R. sodium carbonate (dried) taken in a weighing bottle and transfer into a 100mL volumetric flask, weigh the empty bottle.

The difference in two weights provides the exact amount of sodium carbonate transferred. Dissolve the sodium carbonate in sufficient freshly prepared distilled water, make up the volume with water, and shake well.

Procedure

➢ Pipette out 25.00mL of sodium carbonate solution and take it in a clean 250mL conical flask, add 2 - 3 drops of methyl orange indicator solution to the alkali solution.

➢ Take a clean 50mL burette; rinse it thrice with an acid solution; then fill the burette with alkali solution above the zero marks.

➢ Open the stopcock of the burette, drain the acid to ensure complete removal of air bubble from the jet and filling of the jet with the acid, close the stopcock.

➢ Refill the burette with the acid slightly above the zero marks; adjust the meniscus of the acid at zero marks.

➢ Titrate the alkali solution with the acid and rotate the flask so that reaction is completed; continue the titration till the color of the solution becomes faint yellow.

➢ Wash the walls of the conical flask with fresh water, mix and add the acid dropwise with constant swirling.

➢ Continue the addition of acid dropwise till the color of the solution changes to orange or light pink.

➢ Note the volume of acid required for titration (titer value).

➢ Repeat the process twice more and take the average titer value for calculation.

Calculation of strength of 0.1N HCl solution

Say, the average titer value is 24.75mL (V_1, volume of acid required),

Amount of Na_2CO_3 to be taken (theoretical weight) = 0.53g for 100mL of 0.1N solution

Weight of Na_2CO_3 taken =0.5297g

Strength of 0.1N solution of Na_2CO_3 (S) = $\dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{0.5297\text{g}}{0.53\text{g}} = 0.9994$

Volume of Na_2CO_3 solution = V mL

Say, strength of acid solution = S_1

According to law of mass action, $V_1 \times S_1 = V \times S$

$$24.75\text{mL} \times S_1 = 25\text{mL} \times 0.9994$$

So, the strength of 0.1N HCl solution, $S_1 = \dfrac{25\text{mL} \times 0.9994}{24.75\text{mL}} = 1.009$

In other words, the strength of acid = **0.1009N**

Standardization against borax

Borax is tetraborate decahydrate ($Na_2B_4O_7$, $10H_2O$) is a primary standard. The advantages of borax are;

- Its equivalent weight (190.72) is more than that of Na_2CO_3 (53), the extent of error will be less since more amount of borax is to be weighed.
- It can be easily and economically purified by recrystallization from water,
- Drying for making anhydrous is not required,
- It is practically non-hygroscopic, and
- By using methyl red indicator, a sharp endpoint can be observed. Methyl red is not affected by boric acid, a very weak acid.

$$B_4O_7{}^{2-} + 2H^+ + 5H_2O \leftrightarrow 4H_3BO_4$$
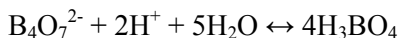
Procedure

The equivalent weight of borax is 190.72; hence to prepare a 1N solution of it 190.72g should be dissolved in water to make 1000mL.

Hence, to make 1000mL of 0.1N solution 19.072g of borax would be required and $\dfrac{19.072 \times 25}{1000}$ g = 0.4768g would be required for 25mL of 0.1N solution.

➢ Weigh accurately 0.48g of A.R. borax and transfer into a clean 250mL conical flask, dissolve in 50 – 60mL of freshly prepared distilled water, add few drops of methyl red solution.

➢ Take a clean 50mL burette; rinse it thrice with an acid solution; then fill the burette with alkali solution above the zero marks.

➢ Open the stopcock of the burette, drain the acid to ensure complete removal of air bubble from the jet and filling of the jet with the acid, close the stopcock.
➢ Refill the burette with the acid slightly above the zero marks; adjust the meniscus of the acid at zero marks.
➢ Titrate the borax solution with the acid and rotate the flask so that reaction is completed; continue the titration till about 24mL of the acid is consumed.
➢ Wash the walls of the conical flask with fresh water, mix and add the acid dropwise with constant swirling.
➢ Continue the addition of acid dropwise until the pink color is observed.
➢ Note the volume of acid required for titration (titer value).
➢ Repeat the process twice more and take the average titer value for calculation.

Calculation of strength of 0.1N HCl solution

Strength of borax solution: Amount of borax to be taken = 0.4768g (Theoretical weight)

Say, the amount of borax taken (1) 0.4729g, (2) 0.4770g, and (3) 0.4765g

Strength of borax solution,

$$S = \quad 1. \quad \frac{\text{Practical weight}}{\text{Theoretical weight}} = \frac{0.4729g}{0.4768g} = 0.9918$$

$$2. \quad \frac{\text{Practical weight}}{\text{Theoretical weight}} = \frac{0.4770g}{0.4768g} = 1.0004$$

$$3. \quad \frac{\text{Practical weight}}{\text{Theoretical weight}} = \frac{0.4765g}{0.4768g} = 0.9994$$

Volume of borax solution, V = 25.00mL

Say, the Volume of HCl solution consumed, V_1 in three titrations are 25.00mL, 24.95mL, and 25.00mL

If the strength of HCl solution is S; then $SV = S_1 V_1$

$$1. \quad S_1 = \frac{S \times V}{V_1} = \frac{25.00mL \times 0.9918}{25.00mL} = 0.9918$$

$$2. \quad S_1 = \frac{S \times V}{V_1} = \frac{25.00mL \times 1.0004}{24.95mL} = 1.0024$$

$$3. \quad S_1 = \frac{S \times V}{V_1} = \frac{25.00mL \times 0.9994}{25.00mL} = 0.9994$$

The average strength of 0.1N HCl solution is $\frac{0.9918+1.0024+0.9994}{3} = \mathbf{0.9978}$

In other words, the strength of HCl solution is 0.09978N

Preparation and standardization of 0.1M hydrochloric acid

The molarity and normality of hydrochloric acid are same, since basicity of it is unity (one). Hence, for preparation of 0.1M HCl solution 9.00mL is diluted to 1000mL with freshly distilled water (free from dissolved CO_2).

Preparation of 0.1M Sodium carbonate

The molecular weight of sodium carbonate (Na_2CO_3) being 106, 1M solution of it contains106g of Na_2CO_3. For 0.1M solution, 10.6g of Na_2CO_3 should be dissolved in sufficient water to make 1000mL or 1.06g of Na_2CO_3 in 100mL of solution.

The method of preparation and standardization would remain the same as mentioned for preparation and standardization of 0.1N HCl solution.

Calculation of strength of 0.1M HCl solution

Say, the average titer value is 24.95mL (V_1, volume of acid required),

Amount of Na_2CO_3 to be taken (theoretical weight) = 1.06g for 100mL of 0.1N solution

Weight of Na_2CO_3 taken =1.0608g

Strength of 0.1N solution of Na_2CO_3 (S) $= \dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{1.0608g}{1.06g} = 1.0007$

Volume of Na_2CO_3 solution, V = 25.00mL

Say, strength of acid solution = S_1

According to law of mass action, $V_1 \times S_1 = V \times S$

$$24.95mL \times S_1 = 25.00mL \times 1.0007$$

So, strength of 0.1N HCl, $S_1 = \dfrac{25mL \times 1.0007}{24.95mL} = 1.0027$

In other words, the strength of acid = **0.1003N**

Preparation of 0.1M Borax

The molecular weight of borax is 381.44; hence, 1M solution of borax 381.44g shall be present in 1000mL of solution. To prepare 1000mL of 0.1M solution 38.144g of borax should be dissolved in sufficient water to make 1000mL and 100mL of the 0.1M solution will contain 3.8144g of borax. 25mL of 0.1M solution shall contain 0.9536g of borax.

Standardization

The method of titration shall be the same as followed in case of standardization of 0.1N solution of HCl.

Calculation of strength of 0.1M HCl solution

Strength of borax solution: Amount of borax to be taken = 0.9536g (Theoretical weight)

Say, the amount of borax taken (1) 0.9565g, (2) 0.9537g, and (3) 0.9542g

Strength of borax solution,

$S = $ 1. $\dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{0.9565g}{0.9536g} = 1.003$

2. $\dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{0.9537g}{0.9536g} = 1.0001$

3. $\dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{0.9542g}{0.9536g} = 1.0006$

Volume of borax solution, V = 25.00mL

Say, the Volume of HCl solution consumed, V_1 in three titrations are 25.00mL, 24.95mL, and 25.00mL

If the strength of HCl solution is S; then $SV = S_1V_1$

1. $S_1 = \dfrac{S \times V}{V_1} = \dfrac{25.00mL \times 1.003}{25.00mL} = 1.003$

2. $S_1 = \dfrac{S \times V}{V_1} = \dfrac{25.00mL \times 1.0001}{24.95mL} = 1.0001$

3. $S_1 = \dfrac{S \times V}{V_1} = \dfrac{25.00mL \times 1.0006}{25.00mL} = 1.0006$

The average strength of 0.1M HCl solution is $\dfrac{1.003 + 1.0001 + 1.0006}{3} = 1.0012$

4. Preparation and standardization of 0.1M Sodium thiosulphate

Preparation of 0.1M Sodium thiosulphate

Sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) is readily available as a pure state. It is a reducing agent. But, it is efflorescent in nature. Due to this, its water content may vary. As a result, it is not used as a primary standard. The half-cell reaction is

$$2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2e$$
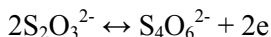
The molecular weight of $Na_2S_2O_3$ is 158.11 and that of $Na_2S_2O_3$, $5H_2O$ is 248.18 and its valency is 2. Hence, 1M solution of $Na_2S_2O_3$, $5H_2O$ contains 248.18g per litre. The valency of $Na_2S_2O_3$, $5H_2O$ being 2; its equivalent weight would be $\dfrac{248.18}{2} = 124.09$. Thus, 1N solution of sodium thiosulphate contains 124.09g per litre.

Sodium thiosulphate solution has certain stability problems, such as

- The water used to prepare the solution should be freshly prepared or conductivity water, because dissolved carbon dioxide accelerates the decomposition of sodium thiosulphate.
  $S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S$
- Microbial contamination (e.g., Thiobacillusthioparas) can facilitate the decomposition of sodium thiosulphate if the solution is kept for some time.
- Sodium thiosulphate is photosensitive. Light accelerates the decomposition of sodium thiosulphate.

Thus, sodium thiosulphate solution should be prepared with freshly prepared distilled water and per one litre of the solution either 3 drops of chloroform or 10mg of mercuric iodide should be added.

- ➢ If the pH of the solution is kept within 9 to 10, the decomposition activity of the bacteria is negligible.
- ➢ If 0.1g of sodium carbonate is added to each litre of solution, the pH of the solution becomes alkaline (9 – 10).
- ➢ Borax should not be added, because it can accelerate the decomposition.
  - $S_2O_3^{2-} + 2O_2 + H_2O \leftrightarrow 2SO_4^{2-} + 2H^+$

➢ Sodium thiosulphate solution should be stored in an amber color bottle to protect it from sunlight.

Procedure

For making 1 L of 0.1M solution weigh 25g of sodium thiosulphate, A.R. ($Na_2S_2O_3$, $5H_2O$) and transfer it into a 1 L volumetric flask. Dissolve the sodium thiosulphate insufficient amount of freshly distilled water. Once it goes into solution, make up the volume with freshly distilled water. If the solution is stored for more than a few days, add 0.1g of sodium carbonate, A.R. Shake well to dissolve the sodium carbonate. Store the solution in an amber color bottle.

Standardization of 0.1M Sodium thiosulphate

(a) With the 0.1M solution of potassium iodate

The purity of A.R. potassium iodate is 99.9%, it is dried at 120^oC. Potassium iodate reacts with potassium iodide and molecular iodine is formed;

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

Sodium thiosulphate solution can be standardized with various substances such as potassium iodate, potassium bromate, potassium dichromate, pure copper, pure iodine, a standard solution of iodine, potassium permanganate, and with ceric sulphate. Here, few shall be described.

Preparation and standardization of 0.1N Sodium thiosulphate

Preparation of 0.1N Sodium thiosulphate

Dissolve about 26g of sodium thiosulphate and 0.2g of sodium carbonate in 1000mL of freshly prepared distilled water. Shake well.

Standardization of 0.1N Sodium thiosulphate

As mentioned above standardization of sodium thiosulphate solution with potassium iodate solution, potassium dichromate solution and with standard iodine solution are discussed below.

With 0.1N potassium iodate (KIO_3) solution

The purity of potassium iodate A.R. grade is not less than 99.9%, it can be dried at 120^oC without any stability problem. The molecular weight of KIO_3 is 214.001g/mol and equivalent weight is $1/6^{th}$ of its molecular weight as an oxidizing agent. That is, its 1N solution contains 35.67g per litre of solution and 0.1N solution should contain 3.567g per litre of solution.

Dry about 0.5g of KIO_3 at 110^oC for 2 hrs and then put in a desiccator to cool to room temperature.

➢ Weigh accurately about 0.145g of dried KIO_3 transfer carefully into a 250mL iodine flask.
➢ Add 25mL of freshly boiled and cooled distilled water and dissolve the potassium iodate.
➢ Add 2g of pure potassium iodide (iodate free) and dissolve.
➢ Add 5mL of 2N H_2SO_4 solution.

> ➤ Stopper the flask.
> ➤ Rinse thrice a clean 50mL burette with 0.1N sodium thiosulphate solution.
> ➤ Fill the burette with 0.1N sodium thiosulphate solution up to the zero marks.
> ➤ Titrate the liberated iodine with 0.1N sodium thiosulphate solution with constant stirring until a pale-yellow color is produced.
> ➤ Wash the inner walls of the flask with about 150mL of freshly boiled and cooled distilled water.
> ➤ Add 2mL of starch solution, the blue color is produced.
> ➤ Continue the titration with 0.1N sodium thiosulphate solution until the solution becomes colorless. The endpoint is sharp. Note the volume of 0.1N sodium thiosulphate solution consumed (titer value).
> ➤ Repeat the titration twice more and take the average titer value (V) for calculation.

Calculation

Theoretical weight of KIO_3 = 0.14268g

Say, the amount of KIO_3 taken (average) = 0.1427g

Strength of 0.1N KIO_3 solution (S_1) = $\dfrac{\text{Practical weight}}{\text{Theoretical weight}}$ = $\dfrac{0.1427g}{0.14268g}$ = 1.0001

Volume of 0.1N KIO_3 solution (V_1) = 40mL

Say, average volume of 0.1N sodium thiosulphate solution consumed (V) = 39.83mL

Strength of 0.1N sodium thiosulphate solution, S = $\dfrac{40mL \times 1.0001}{39.83mL}$ = 1.00436 ≈ **1.0044**

With 0.1N potassium dichromate solution

The molecular weight of potassium dichromate, $K_2Cr_2O_7$ is 294.22g/mol. In acidic medium potassium dichromate is reduced by the acid. According to the equation given below, its equivalent weight would be 1/6th of the molecular weight; that is, 49.037g.

$$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$$
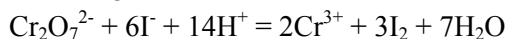
There are certain errors related to this reaction;

- The HI (from excess of iodide and acid) is readily oxidized by air, particularly in the presence of chromic salt.
- The reaction is not instantaneous. Thus, a current of carbon dioxide should be passed through the reaction flask before and during titration. However, there is an alternative and simple way to pass carbon dioxide. To the acid solution, some amount of sodium bicarbonate is added and the flask is kept closed as much as possible; so that the reaction between $NaHCO_3$ and acid can produce CO_2 which can pass through the reaction.

Preparation of 0.1N potassium dichromate solution

A.R. grade potassium dichromate has a purity of 99.9%. Take 5 – 6g of potassium dichromate crystals, crush it in glass mortar to make powder, transfer the powders into a weighing bottle, dry at about 145°C for 60min, close the weighing bottle and keep it in a desiccator to cool to room temperature.

- Weigh accurately about 2.45g of dried potassium dichromate.
- Transfer the material carefully into a 500mL clean volumetric flask, to avoid loss during transfer using a glass funnel.
- Rinse the funnel and inner walls of the flask with freshly prepared distilled water, remove the funnel, and close the flask tightly.
- Shake the flask to dissolve the material.
- Add sufficient water to make up the volume.
- Mix thoroughly.

Take 500mL clean glass-stoppered flask (iodine flask), pour 100mL of freshly boiled and cooled distilled water.

- Add 3g of pure potassium iodide (iodate free) and 2g of pure sodium bicarbonate; rotate the flask to dissolve the solids.
- Add slowly 6mL of concentrated HCl, rotate the flask to mix the contents thoroughly.
- Measure 25.00mL of 0.1N potassium dichromate solution accurately and transfer into the flask, stopper the flask tightly and keep it in the dark for 5min to complete the reaction.
- Rinse the flask with the distilled water.
- Rinse a 50mL clean burette with the 0.1N sodium thiosulphate solution thrice.
- Fill the burette with 0.1N sodium thiosulphate solution up to the zero marks.
- Titrate the 0.1N potassium dichromate solution with 0.1N sodium thiosulphate solution until a yellowish green color is produced.
- Add 2mL of starch solution to the content in the flask, blue color is produced.
- Note the volume of 0.1N sodium thiosulphate solution consumed (titer value, V').
- Continue titration till the blue color turns to light green color. The endpoint is sharp.
- Carryout a blank determination with 25mL of distilled water in place of 0.1N potassium dichromate solution.
- Note the volume of 0.1N sodium thiosulphate solution consumed (v).
- Subtract the v from V', this gives the volume of 0.1N sodium thiosulphate solution consumed by 25.00mL of 0.1N potassium dichromate solution (V)
- Repeat the determination twice more using 25.00mL of 0.1N potassium dichromate solution at each time. Take the average of three titer values for calculation.

Calculation

Theoretical weight of potassium dichromate = 2.4517g

Say, the amount of potassium dichromate taken = 2.4525g

Strength of 0.1N potassium dichromate solution $= \dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{2.4525\text{g}}{2.4517\text{g}}$

= 1.0003

The volume of 0.1N potassium dichromate solution taken, $V_1 = 25.00$mL

Say, the average volume of 0.1N sodium thiosulphate solution consumed (V) = 24.93mL

The strength of 0.1N sodium thiosulphate solution $= \dfrac{25.00\text{mL} \times 1.0003}{24.93\text{mL}} = \mathbf{1.0031}$

With 0.1N iodine solution

Preparation of 0.1N iodine solution

Solubilization of iodine in water has two problems:

- Iodine is almost insoluble in water. Its solubility in water is 0.0335g in 100mL of water.
- Despite this poor solubility, iodine volatilizes, and the vapor of iodine exists over the solution.

Both of these problems can be solved by dissolving iodine in a solution of potassium iodide. The solubility of iodine increases with increase in the concentration of potassium iodide. This is due to the formation of the tri-iodide ion as shown below;

$$I_2 + I^- \leftrightarrow I_3^-$$
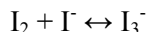
The solution thus produced allows much less iodine to vaporize and remain in the vapor state. Hence, the loss of iodine is much less. Maybe in a very lesser amount, some amount of iodine is lost from its solution if the solution is kept open or in lightly sealed condition. Following precautions should be taken while storing an iodine solution;

- The solution of iodine should be stored in amber colored, airtight bottle.
- Iodine interacts with rubber. So, iodine solution should never be kept in contact with a rubber material.
- Potassium iodide used to prepare the iodine solution should be free from iodate.
- The solution of iodine should be kept away from light.

Iodine solution can be standardized against pure arsenious oxide, pure barium thiosulphate monohydrate, or with sodium thiosulphate solution.

Procedure

- ➢ Transfer about 14g of iodine into a 1000mL volumetric flask.
- ➢ Add a solution of 36g of potassium iodide in 100mL of freshly prepared distilled water.
- ➢ Dissolve the iodine in potassium iodide solution.
- ➢ Add 3 drops of concentrated hydrochloric acid and mix thoroughly.
- ➢ Dilute the solution to 1000mL with freshly prepared distilled water.
- ➢ Stopper the flask and mix thoroughly.

Standardization of 0.1N iodine solution

The purity of A.R. arsenious oxide or arsenic trioxide (As_2O_3) may be not less than 99.9%. Its molecular weight is 197.84g/mol. Arsenious oxide has been used as a favored primary standard for iodine solutions since long. Because of its poisonous effect, even the use of small amounts of arsenic-containing compounds is avoided. Barium thiosulfate monohydrate and anhydrous sodium thiosulfate have been favored as alternative

standards. Perhaps the most convenient method of determining the concentration of an iodine solution is the titration of aliquots with a sodium thiosulfate solution that has been standardized against pure potassium iodate. Instructions for this method follow. The reaction between arsenious oxide and iodine is,

$$H_3AsO_3 + I_2 + H_2O \leftrightarrow H_3AsO_4 + 2H^+ + 2I^-$$
$$H_3AsO_3 + I_3^- + H_2O \leftrightarrow H_3AsO_4 + 2H^+ + 3I^-$$
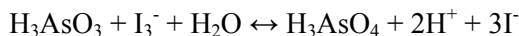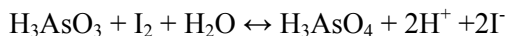
The reaction proceeds towards right quantitatively if the HI produced in the reaction is removed immediately after formation. For this reason, sodium bicarbonate ($NaHCO_3$) not sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) is added to the reaction mixture. Sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) reacts with iodine and forms iodide, hypo-iodide, and iodate.

- Weigh accurately about 130mg of pure arsenious oxide (arsenic trioxide).
- Transfer it into a 250mL iodine flask, add 20mL of 1N NaOH solution,
- Dissolve by warming, if necessary.
- Dilute the solution with 40mL of water.
- Add 2 drops of methyl orange T.S.
- Add diluted HCl dropwise until the yellow color is changed to pink.
- Add 2g of sodium bicarbonate and 50mL of water.
- Add 3mL of starch T.S.
- Titrate the solution with an iodine solution from a burette until a permanent blue color is produced.
- Note the volume of iodine solution consumed.
- Repeat the process twice more and take the average titer value for calculation.

Calculation

Say, the weight of arsenious oxide taken (practical weight) = 0.1303g

The weight of arsenious oxide to be taken (theoretical weight) = 0.12365g for 25mL

The strength of arsenious oxide solution = $\frac{\text{practical weight}}{\text{theoretical weight}} = \frac{0.1303g}{0.12365g} = 1.054$

Say, the strength of iodine solution = S and volume of iodine solution required = 25.05mL

Now, S × 25.05mL = 1.054 × 25mL

$$S = \frac{1.054 \times 25mL}{25.05mL} = \textbf{1.052N}$$

5. Preparation and standardization of 0.1N Sulphuric acid

Preparation

The molecular weight of sulphuric acid is 98.08 and its basicity is 2. Hence, the equivalent weight of sulphuric acid is $\frac{98.08}{2}$ = 49.04g. The 1N solution of sulphuric acid contains 49g in 1000mL. Say, the density of sulphuric acid used is 1.834g/mL.

Then, the volume of 49.04g of sulphuric acid $= \dfrac{49.04\text{g}}{1.834\text{g/mL}} = 26.74\text{mL}.$ $[\rho = \dfrac{m}{v}]$

- Measure 27.00mL of concentrated sulphuric acid.
- Take a clean and washed 1000mL volumetric flask.
- Pour 800mL of distilled water, cool it in an ice bath.
- Transfer the acid gradually into the volumetric flask with constant swirling.
- Once the acid is transferred completely, allow the solution to cool to room temperature.
- Make up the volume with water and stopper the flask, mix thoroughly.

Standardization

As mentioned earlier anhydrous sodium carbonate is used for standardization of hydrochloric acid or sulphuric acid. The process of standardization is given below.

- ➤ Take about 2g of anhydrous sodium carbonate A.R. into a clean dry weighing bottle, dry it in a hot air oven at about 105°C for 2 hrs.
- ➤ Close the bottle with its lid, transfer the bottle into a desiccator.
- ➤ Weigh accurately about 1.10g of anhydrous sodium carbonate.
- ➤ Transfer the weighed anhydrous sodium carbonate into a 250mL of the conical flask.
- ➤ Add 50mL of distilled water and dissolve.
- ➤ Add 2 drops of methyl red T.S.
- ➤ Titrate the solution with sulphuric solution from a burette until pink color is produced.
- ➤ Boil the solution and titrate with the sulphuric acid solution until the faint pink color produced does not fade away.
- ➤ Note the volume of sulphuric acid solution consumed.
- ➤ Repeat the process twice more and take the average titer value for calculation.

Calculation

Say, the weight of sodium carbonate taken (average practical weight) = 1.0655g

The weight of sodium carbonate to be taken (theoretical weight) = 1.0599g for 20mL

Strength of sodium carbonate solution $= \dfrac{1.0655\text{g}}{1.0599\text{g}} = 1.0053\text{N}$

Say, the average volume of sulphuric acid solution consumed = 20.03mL and the strength of sulphuric acid solution = S

Then, S × 20.03mL = 1.0053N × 20.00mL

So, S $= \dfrac{1.0053\text{N} \times 20.00\text{mL}}{20.03\text{m}} = \mathbf{1.0038N}$

Preparation and standardization of 0.1M Sulphuric acid

Preparation

The molecular weight of sulphuric acid is 98.08. One molar solution contains 98.08g of sulphuric acid.

Its density should be 1.84g/mL. since the purity of concentrated sulphuric acid varies from 95 - 98%, its density is less than the theoretical value. To prepare one litre of 1M solution of sulphuric acid 57mL of concentrated sulphuric acid is diluted to 1000mL with distilled water. The method is similar to that described above. Thus, to prepare one litre of 0.1M solution of sulphuric acid 5.7mL of concentrated sulphuric acid is diluted to 1000mL with distilled water.

Standardization

Follow the method described earlier for 0.1N Sulphuric acid.

6. Preparation and standardization of 0.1M Potassium permanganate

The molecular weight of potassium permanganate is 158.034. The 1M solution contains 158.034g of potassium permanganate per liter. So, the 0.1M solution contains 15.8034g of potassium permanganate per litre. Potassium permanganate, $KMnO_4$ is not a primary standard. It is very difficult to obtain Potassium permanganate in the purest form.

- It contains free manganese dioxide as a common impurity that catalyzes auto-decomposition of potassium permanganate on standing. The decomposition reaction is

    $4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^-$
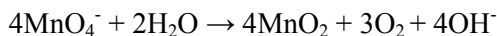
- Potassium permanganate is inherently unstable in the presence of manganese ion, Mn^{2+}

    $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$
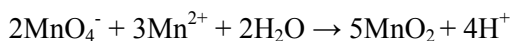
- Potassium permanganate is reduced on contact with organic material such as rubber; hence its solution should not be kept in contact with such materials.

- In acidic medium, the decomposition reaction is slow; while in the neutral medium the reaction is relatively faster.

- When exposed to bright sunlight it and even its pure solution decompose slowly.

- The bottle should be rinsed with dichromate-sulphuric acid and then washed thoroughly with distilled water. The bottle is then used to preserve potassium permanganate solution.

Preparation of 0.1M Potassium permanganate

- Weigh 7.9g of A.R. potassium permanganate on a watch glass, transfer it to a 1000mL beaker,
- Add 500mL of distilled water, cover the beaker with a beaker-cover,
- Boil for 15 – 30 min, allow to cool to room temperature,
- Filter the solution through a funnel plugged with purified glass wool or through a sintered glass crucible,

- Collect the filtrate in a container which has been cleaned with the chromic acid mixture and subsequently washed with distilled water,
- Store the filtered solution in clean, amber color glass bottle fitted with stopper, keep the bottle in dark or under diffuse light.

Standardization of 0.1M Potassium permanganate against arsenious oxide

- Take about 1g of arsenious oxide in a weighing bottle, dry it at 105° – 110^oC for 2hrs and keep it in a desiccator at room temperature to cool.
- Weigh accurately 0.25g of arsenious oxide accurately from the weighing bottle, transfer to a 500mL clean conical flask.
- Weigh the weighing after the transfer of arsenious oxide, the difference between the two weights shall be the weight of arsenious oxide taken.
- Add 10mL of 20% sodium hydroxide solution and mix.
- Allow standing for 8 – 10 min with occasional stirring.
- When the arsenious oxide is completely dissolved add 100mL of water, 10mL of concentrated HCl, and 1mL of 0.0025M iodine-monochloride (ICl) solution.
- Titrate the solution with potassium permanganate solution until a faint pink color appears and persists for at least 30 seconds.
- If the color disappears within 30 sec, add potassium permanganate solution dropwise; once the first drop disappears add next. Continue till the faint pink color persists for 30 secs.
- Note the volume of potassium permanganate solution consumed.
- Repeat the same for two more determinations. Take the average value for calculation of the strength of potassium permanganate solution.

Calculation

The molecular weight of arsenious oxide is 197.82. The 1M solution of arsenious oxide will contain 197.82g per litre. Or, 0.1M solution of arsenious oxide will contain 19.782g per litre (0.019782g/mL).

For 50mL of 0.1M solution $50 \times 0.019782g = 0.9891g$ of arsenious oxide should be taken (theoretical weight)

Say, the weight of arsenious oxide taken = 0.9902g (average of three weights of three determinations)

So, the strength of 0.1M solution of arsenious oxide, $S_1 = \dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{0.9901g}{0.9891g} = 1.0010$

Volume of arsenious oxide solution, $V_1 = 50.00mL$

Volume of potassium permanganate solution consumed, $V = 49.90mL$

Strength of potassium permanganate solution = S

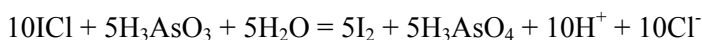$$S \times V = S_1 \times V_1$$

$$S = \frac{S_1 \times V_1}{V} = \frac{50 \times 1.001}{49.90} = 1.0030$$

Preparation of 0.1N Potassium permanganate

The molecular weight of potassium permanganate is 158.034g. The equivalent weight of potassium permanganate depends on the acidity of the medium. The valency state of Mn in $KMnO_4$ is +7 which gains 5 electrons in acidic medium. Hence, the equivalent weight of $KMnO_4 = \frac{158.034}{5}$ = 31.6068g. When the pH of the medium is alkaline or neutral $KMnO_4$ gains 3 electrons; hence, its equivalent weight in the alkaline or neutral medium is $\frac{158.034}{3}$ = 52.678g. Usually, 0.1N solution of potassium permanganate is prepared by dissolving 15.8034g in sufficient water to prepare one liter.

Standardization of 0.1N Potassium permanganate against arsenious oxide

Arsenious oxide oxidizes rapidly and stoichiometrically at room temperature in presence of trace amount of iodine. Iodine works as a catalyst. Compounds containing iodine reduce and form iodine when added to arsenious acid (H_3AsO_3). Permanganate oxidizes iodine rapidly to all. The iodine-monochloride then oxidizes arsenious acid and itself reduces to iodine (I_2).

$$5I_2 + 2MnO_4^- + 10Cl^- + 16H^+ = 10ICl + 2Mn^{2+} + 8H_2O$$

$$10ICl + 5H_3AsO_3 + 5H_2O = 5I_2 + 5H_3AsO_4 + 10H^+ + 10Cl^-$$

One molecule of arsenious oxide consumes two atoms of oxygen as indicated below;

$$As_2O_3 + 2O = As_2O_5$$

Thus, the above equation manifests that the equivalent weight of arsenious oxide is $\frac{1}{4}$ th of its molecular weight; that is the equivalent weight $= \frac{1 \times 197.82}{4} = 49.455g$. In other words, 1N solution of arsenious oxide will contain 49.455g per litre. Or, 0.1N solution of arsenious oxide will contain 4.9455g per litre or 0.0049455g/mL.

For 50mL of 0.1N solution $50 \times 0.0049455g = 0.247275g$ of arsenious oxide should be taken (theoretical weight).

Say, the weight of arsenious oxide taken = 0.2499g (average of three weights of three determinations)

So, the strength of 0.1N solution of arsenious oxide, $S_1 = \frac{\text{Practical weight}}{\text{Theoretical weight}} = \frac{0.2499g}{0.2473g} = 1.0105$

Volume of arsenious oxide solution, $V_1 = 50.00mL$

Volume of potassium permanganate solution consumed, $V = 49.90mL$

Strength of potassium permanganate solution = S

$$S \times V = S_1 \times V_1$$
$$S = \frac{S_1 \times V_1}{V} = \frac{50 \times 1.0105}{49.90} = 1.0125$$

Standardization of 0.1N Potassium permanganate against sodium oxalate

The molecular weight of sodium oxalate, $Na_2C_2O_4$ is 134 and valency is 2. So, its equivalent weight is $\frac{134}{2} = 67g$. To prepare a 1N solution of sodium oxalate, 67g should be present in one litre. Thus, a 0.1N solution contains 6.7g of sodium oxalate per litre of solution.

Take about 1g of sodium oxalate in a weighing bottle, dry it in a hot air oven at 110^oC for about 2 hrs, cool it to room temperature in a desiccator.

- Weigh accurately 0.67g of sodium oxalate from the weighing bottle, transfer it into a 100mL volumetric flask and dissolve it in freshly prepared distilled water.
- Pipette out exactly 25.00mL of sodium oxalate solution into a 250mL conical flask, add 100ml of distilled water, then add slowly 6ml of concentrated sulphuric acid, if required heat to about 70^oC.
- Rinse a 50mL clean burette with potassium permanganate solution, fill, then open the stopcock to remove some potassium permanganate solution; once the jet is completely filled with potassium permanganate solution and air is completely removed, refill the burette up to the zero mark.
- Titrate the hot sodium oxalate slowly with potassium permanganate solution with constant stirring until a pale pink color is produced and persists for at least 15 seconds. Note the volume of potassium permanganate solution consumed (titer value).
- Repeat the determinations twice more; make the average of three titer values and use for calculation.

Note that till end of the titration the temperature of the solution must remain within 60° – 65^oC.

Calculation

Say, the amount of sodium oxalate taken = 0.6704g for 250mL solution

Theoretical weight of sodium oxalate to be taken = 0.6700g for 250mL of 0.1N solution

The strength of 0.1N solution of sodium oxalate, $S_1 = \frac{Practical\ weight}{Theoretical\ weight}$

$= \frac{0.6704g}{0.6700g} = 1.0006$

The volume of sodium oxalate solution used, $V_1 = 25mL$

Say, the average volume of potassium permanganate solution consumed,

$$V = \frac{25.05 + 25.00 + 25.00}{3}$$

$$= 25.02 \text{mL}$$

$$V \times S = V_1 \times S_1$$

The strength of 0.1N potassium permanganate solution, $S = \frac{25.00 \times 1.0006}{25.02} = 0.9998$

In other words the strength of potassium permanganate solution = 0.09998N

7. Preparation and standardization of 0.1N Ceric Ammonium Sulphate solution

Preparation

The molecular weight of ceric ammonium sulphate, $(NH_4^-)_4[Ce(SO_4)_4],2H_2O$ is 632.57. Its equivalent weight is also 632.57. Hence, 1N or 1M solution of ceric ammonium sulphate contains 632.57g per lt.

➢ Weigh about 66g of ceric ammonium sulphate and transfer it into a clean 500mL conical flask, add a mixture of 30mL concentrated sulphuric acid and 500mL of distilled water and heat gently to dissolve the ceric ammonium sulphate completely.

➢ Allow the solution to cool to room temperature.

➢ Transfer the solution into a clean 1000mL volumetric flask, dilute to 1000mL with distilled water, stopper the flask tightly and shake well.

Standardization

➢ Weigh accurately about 0.1g of dried arsenic trioxide, transfer it into a 500mL conical flask.

➢ Wash thoroughly the inner walls of the flask with 100mL of distilled water.

➢ Add 300mL of dilute sulphuric acid, 0.15mL of osmic acid and 0.1mL of ferroin T.S. (indicator).

➢ Take a 50mL clean burette, rinse with ceric ammonium sulphate solution and then fill.

➢ Adjust the meniscus at zero mark of the burette.

➢ Titrate arsenic trioxide solution with ceric ammonium sulphate solution until the pink color of the solution changes to pale blue or yellowish green color.

➢ Repeat the titration twice and take the average titer value for calculation of the strength of the ceric ammonium sulphate solution.

Calculation

Each mL of 0.1N ceric ammonium sulphate solution ≈ 4.946mg ≈ 0.004946g of arsenic trioxide

Gram-equivalent wt of arsenic trioxide = 49.46g; that is 0.1N solution of it contains 4.946g/lt

Say, the amount of arsenic trioxide taken = 0.1076g for making 1000mL solution and average titer value is 20.05mL.

Say, the average titer value = 20.05mL; in other words, 20.05mL of ceric ammonium sulphate solution is consumed by 0.1076g of arsenic trioxide.

0.004946g of arsenic trioxide ≈ 1mL of 0.1N ceric ammonium sulphate solution

So, 0.1076g of arsenic trioxide $\approx \dfrac{1 \times 0.1076g}{0.004946g}$ = 21.75mL of 0.1N ceric ammonium sulphate solution

Say, the strength of ceric ammonium sulphate solution = xN

Then, x N × 20.05mL = 0.1N × 21.75mL

Or, the strength of ceric ammonium sulphate solution, $x = \dfrac{0.1N \times 21.75mL}{20.05mL}$ = **0.1085N**

Preparation and standardization of 0.1M Ceric Ammonium Sulphate solution

Since the gram-molecular weight and gram-equivalent weight of ceric ammonium sulphate are same, 632.57g, the method of preparation and standardization of 0.1M ceric ammonium sulphate solution is same.

Determination of strength of a primary standard solution

The strength of a primary standard solution is not calculated through titration, it is calculated on the basis of the exact amount dissolved in the solution. Hence, proper care must be taken to achieve accurate strength. The accuracy in the strength of the solution depends on;

➢ Accuracy in weighing,
➢ Transferring the material into the flask,
➢ Dissolving, and
➢ Making up the volume.

The strength of a solution of the primary standard can be calculated as;

Strength of a solution of primary standard $= \dfrac{\text{Practical weight}}{\text{Theoretical weight}}$

Example 12: A molar solution of sodium carbonate should contain 165.012g of Na_2CO_3 in one litre of its solution. If a litre of solution contains 164.625g of Na_2CO_3, what would be the strength of the solution?

Solution: Sodium carbonate is a primary standard.

The strength of the solution $= \dfrac{\text{Practical weight}}{\text{Theoretical weight}} = \dfrac{164.625}{165.012}$ = **0.9976 M**

Example 13: A normal solution of sodium carbonate should contain 82.506g of Na_2CO_3 in one litre of its solution. If 250 mL of 1N solution is to be prepared, calculate the amount of Na_2CO_3 required.

Solution: 1 litre = 1000mL of the solution contains 82.506g of sodium carbonate

250mL of the solution should contain $\frac{82.506g}{1000mL}$ × 250mL = **20.6265g** of sodium carbonate

Example 14: In a neutralization reaction 25.00 mL of the 0.1N hydrochloric acid solution is completely neutralized by 12.50 mL of sodium hydroxide solution. Find out the strength of the sodium hydroxide solution.

Solution: Given that, V_{HCl} = 25.00 mL, V_{NaOH} = 12.50 mL

S_{HCl} = 0.1N, S_{NaOH}= ?

It is known that S × V = S_1 × V_1

Hence, V_{HCl} × S_{HCl}= V_{NaOH}× S_{NaOH}

Or, 25.00 mL × 0.1N = 12.50 mL × S_{NaOH}

Or, S_{NaOH}= $\frac{25.00mL \times 0.1N}{12.50mL}$ = **0.2N**

Determination of strength of a secondary standard solution

Depending on the chemical property a solution of the secondary standard is standardized. For example, sodium hydroxide solution is standardized using a standard solution of hydrochloric acid or potassium hydrogen phthalate solution. Potassium permanganate solution is standardized against a standard solution of sodium oxalate. A perchloric acid solution is standardized against potassium hydrogen phthalate. Iodine solution is standardized against a standard solution of sodium thiosulphate or arsenic trioxide. Few are described below.

Standardization of 0.1N solution of sodium hydroxide

Dry about 11g of potassium hydrogen phthalate in powder form at 105°C for 3 hrs, cool it in a desiccator.

Weigh accurately about 10.21g and transfer it into a 50mL clean volumetric flask. Add 40mL of freshly prepared distilled water, dissolve. If necessary, warm it to complete dissolution. Allow to cool to room temperature and make up the volume, mix thoroughly. Pipette out accurately 20mL of potassium hydrogen phthalate solution and transfer into a clean 250mL conical flask. Add 2 drops of phenolphthalein solution T.S. and titrate with sodium hydroxide filled in a burette till a permanent pink color is produced. Repeat the titration and take the average titer value for calculation of the strength of sodium hydroxide solution.

Calculation

Say, the weight of potassium hydrogen phthalate taken (practical weight) = 10.225g

The strength of potassium hydrogen phthalate solution = $\frac{practical\ weight}{theoretical\ weight}$

= $\frac{10.225g}{10.21g}$ = 1.0015N

Say, the average titer value (volume of NaOH solution consumed) = 20.05mL

Then, the strength of NaOH solution = $\frac{20\ mL \times 1.0015N}{20.05mL}$ = **0.9990N**

Standardization of 0.1N solution of potassium permanganate

Dry about 1g of sodium oxalate in powder form at $110^{o}C$ until a constant weight is obtained, cool it in a desiccator. Weigh accurately about 200mg of dried sodium oxalate and transfer it into a 500mL conical flask. Dissolve the sodium oxalate in 250mL of freshly prepared distilled water; add 7mL of sulphuric acid. Heat the mixture to about $70^{o}C$ and then titrate slowly with potassium permanganate solution from a burette with constant stirring until a pale pink color which persists for at least 15 sec, is produced. The temperature of the titration mixture should not fall below $60^{o}C$. Each mL of 0.1N potassium permanganate solution is equivalent to 6.700mg of sodium oxalate. Repeat the titration twice and take the average titer value to calculate the strength of the potassium permanganate solution.

Calculation

Say, the average titer value = 29.03mL and the amount of sodium oxalate taken = 198.98mg

Each 6.700mg of sodium oxalate ≈ 1mL of 0.1N potassium permanganate solution.

198.98mg of sodium oxalate ≈ $\dfrac{1\text{mL of }0.1\text{N} \times 198.98\text{mg}}{6.700\text{mg}}$ = 29.70mL of 0.1N potassium permanganate solution

If the strength of 0.1N potassium permanganate solution is x(N)

Then, x(N) × 29.03mL = 0.1N × 29.70mL

The strength of 0.1N potassium permanganate solution is;

$x = \dfrac{0.1\text{N} \times 29.70\text{mL}}{29.03\text{mL}} = \mathbf{0.1023(N)}$

A. MULTIPLE CHOICE QUESTIONS

1. A sample contains 10ppm of iron, this is the result of
   (a) Qualitative test
   (b) Quantitative test
   (c) General test
   (d) None of the above
2. A sample contains sulphate, this is the result of
   (a) Qualitative test
   (b) Quantitative test
   (c) General test
   (d) None of the above
3. Qualitative tests are generally conducted to
   (a) Detect whether the desired compound or substance is present in the sample
   (b) Detect whether the desired compound or substance is not present in the sample
   (c) Identify the presence of the compound
   (d) All of the above
4. Chemical methods of analysis include
   (a) Gasometric analysis
   (b) Polarographic analysis
   (c) Voltametric analysis
   (d) Amperometric analysis

5. Electrical method of analysis include
   - (a) Gasometric method
   - (b) Potentiometric method
   - (c) UV-spectrophotometric method
   - (d) All of the above

6. Conductometry is a
   - (a) Chemical method of analysis
   - (b) Electrical method of analysis
   - (c) Instrumental method of analysis
   - (d) None of the above

7. Titrimetry is a
   - (a) Chemical method of analysis
   - (b) Electrical method of analysis
   - (b) Instrumental method of analysis
   - (d) None of the above

8. A microelectrode is required for
   - (a) Polarography
   - (b) Voltametry
   - (c) Amperometry
   - (d) All of the above

9. Ingasometry method which gas is used?
   - (a) CO_2
   - (b) NO
   - (c) O_2
   - (d) H_2

10. Absorption spectroscopy include
    - (a) TLC
    - (b) IR
    - (c) HPTLC
    - (d) None of the above

11. Number of gram-equivalents of a solute present in one liter of the solution is called as
    - (a) Molality
    - (b) Molarity
    - (c) Normality
    - (d) None of the above

12. Sodium hydroxide solution should be standardized against
    - (a) Potassium dihydrogen phthalate solution
    - (b) Potassium permanganate solution
    - (c) Sodium oxalate solution
    - (d) None of the above

13. Solution whose strength is measured, is called
    - (a) Reagent solution
    - (b) Volumetric solution
    - (c) Test solution
    - (d) Indicator solution

14. Which of the following is a primary standard?
    - (a) Oxalic acid
    - (b) Sulphuric acid
    - (c) Acetic acid
    - (d) None of the above

15. Which of the following is used to express concentration?
    - (a) %w/v
    - (b) N
    - (c) M
    - (d) All of the above

16. Sulphuric acid volumetric solution can be standardized with
    - (a) Sodium sulphate
    - (b) Potassium sulphate
    - (c) Sodium hydroxide
    - (d) Potassium permanganate

17. Sodium thiosulphate volumetric solution can be standardized with
    - (a) Potassium dichromate
    - (b) Potassium permanganate
    - (c) Oxalic acid
    - (d) Hydrochloric acid
18. Silver nitrate is used as primary standard in
    - (a) Complexometric titration
    - (b) Potentiometric titration
    - (c) Acid-base titration
    - (d) None of the above
19. Number of moles present in 1lt of solution, the concentration of the solution is expressed as
    - (a) Molality
    - (b) Molarity
    - (c) Normality
    - (d) None of the above
20. Which of the following is secondary standard?
    - (a) Sodium carbonate
    - (b) Potassium dihydrogen phthalate
    - (c) Sodium hydroxide
    - (d) Silver nitrate

B. SHORT QUESTIONS

1. Name the types of solutions used in analysis.
2. Name the methods used for the analysis of various substances.
3. What are the methods used in the chemical analysis?
4. What are the electrical methods of analysis?
5. Name the instruments used in chromatographic analysis.
6. Define the term used to express the concentration of sodium hydroxide solution T.S.
7. Define the term used to express the concentration of dilute alcohol.
8. How many grams of sodium carbonate would be required to prepare 0.1M solution?
9. How can you express the concentration of a powder mix?
10. Define the term 'Equivalent weight'.
11. What is molarity?
12. Define the term 'Molality'
13. What is 'mole fraction'?
14. Define the term 'Normality'.
15. What is a 'Primary standard'?
16. What is 'Secondary standard'?
17. How can you prepare 1 L of 10%v/v solution of hydrochloric acid?
18. Calculate the equivalent weight of potassium permanganate.
19. What is a neutralization reaction?
20. Mention how precipitation reaction takes place.
21. What are the properties of secondary standards?
22. What are the factors influencing the accuracy of a primary standard solution?

C. LONG QUESTIONS

1. Explain briefly volumetric analysis using a suitable example.
2. Classify the techniques of analysis.
3. What is the utility of different types of analysis in the pharmacy?
4. Mention the desired characteristics of the primary standard.
5. Explain why sodium hydroxide is not considered as a primary standard.
6. Distinguish between molarity and molality with example.
7. Describe briefly how you can prepare decinormal solution of potassium permanganate.
8. Describe the method of preparation of 500 mL of 0.01N Sulphuric acid.
9. Explain the principle of gravimetric analysis.
10. Write down the properties of primary standards.
11. Describe the method of preparation and standardization of 0.1M solution of oxalic acid.
12. Write down the names of two substances used as primary standards with respect to various types of analysis.
13. Describe the method of preparation and standardization of 0.1N Sodium hydroxide solution.
14. Describe the method of preparation and standardization of 0.1N Hydrochloric acid using anhydrous sodium carbonate as a primary standard.
15. What do you mean by Complex formation and precipitation reaction? Mention a suitable example.
16. What do you mean by the oxidation-reduction reaction? Mention a suitable example.
17. Describe the method of preparation and standardization of 0.1M Sodium thiosulphate against KIO_3.
18. Describe the method of preparation and standardization of 0.1N potassium permanganate against sodium oxalate.
19. Describe the method of Preparation and standardization of 0.1M Ceric Ammonium Sulphate solution.
20. Describe the method of Preparation and standardization of 0.1N Ceric Ammonium Sulphate solution.