PRIMARY STANDARD

A few volumetric reagents are obtainable in such a high state of purity that they can be used for the direct preparation of standard solutions by the use of accurately weighed quantities. Many others, including some of the most useful, cannot be so used, either because they are **hydrated** and subject to **small variations in content of water of crystallization**, or because for some other reason they cannot be guaranteed to have the degree of purity necessary. A reagent of this kind is made upto approximately the correct concentration, the solution so obtained is standardized against a pure compound, and a factor is calculated.

Primary standards are defined as the substances of known high purity (99.95 – 100.05%) with respect to the active component which should be stable at over temperatures for drying used to standardize the volumetric reagents, or Primary standards are the substances which are available in pure form with definite chemical composition are called as primary standards.

Several primary standards are available from the National Bureau of Standards and other chemical suppliers. Several substances of analytical reagent grade are sufficiently pure to serve as primary standards for ordinary work, or they may be made so by recrystallization.

Requirements for Primary Standards:-

One of the requirement needed for volumetric analysis is a substance having a known purity. The solution of this substance can be employed as a titrant. There are few known substances which can be used as a primary standard. The requirements for primary standard substances are as follows:

A Primary Standard should satisfy the following requirements

1. It must be easy to obtain, to purify, to dry (preferably at 110 – 120˚c), and to preserve in a pure state. (This requirement is not usually met by hydrated substances, since it is difficult to remove surface moisture completely without effecting partial decomposition).
2. The Substance should be unaltered in air during weighing: this condition implies that it should not be hygroscopic, oxidised by air, or affected by carbon dioxide. The standard should maintain an unchanged composition **during storage.**
3. The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general exceed 0.01-0.02 per cent).
4. It should have a high relative molecular mass so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0.1-0.2 mg; for an accuracy of 1 part in 1000. it is necessary to employ samples weighing at least about 0.2gm).
5. The substance should be readily soluble under the conditions in which it is employed.
6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below.

only substance which satisfy these requirements can be used as primary standards and their solution may be prepared by accurate weighing of the required quantity of the substance and dissolving in water to produce the required volume of the solution accurately.

Examples of Primary Standards

These are materials which, after drying under the specified conditions, are recommended for use as primary standards in the Standardization of volumetric solutions. The following are recommended for use as primary standards, as per the Indian-Pharmacopoeial committee for various titrations.

I. Acid - Base Titrations		**Primary Standard**
1. Alkalimetry (Sodium Hydroxide)	:	Potassium Hydrogen Phthalate*
2. Acidimetry (Hydrochloric Acid, Sulphuric Acid)	:	Anhydrous Sodium Carbonate*
II. Oxidation-Reduction titrations (Redox titrations)		
1. Permanganometry (Potassium Permanganate)	:	Arsenic Trioxide, Sodium Oxalate, Potassium dichromate
2. Iodometry Sodium Thiosulphate)	:	Potassium bromate* Potassium dichromate Potassium iodate
3. Iodimetry (Iodine)	:	Arsenic trioxide*
4. Ceriometry (Cerric Ammonium Sulphate)	:	Arsenic trioxide*
III. Precipitation titrations		
1. Mohr's method (Silver nitrate)	:	Sodium Chloride*
IV. Complexometric titration		
Disodium Edetate	:	Granulated zinc* Calcium carbonate Magnesium sulphate
V. Non-Aqueous titration (N.A.T)		
1. Perchloric acid	-	Potassium Hydrogen Phthalate
2. Sodium methoxide	-	Benzoic Acid*
3. Lithium methoxide	-	Benzoic Acid*
4. Tetrabutyl Ammonium Hydroxide	-	Benzoic Acid*

**used as Ideal Primary Standard for standardising the volumetric reagents given in Indian Pharmacopoeia.*

Normally hydrated salts are not used as primary standard s as they loose varying amounts of water on dying. Because of the difficulty of efficient drying. Primary standard substance are generally dried between 105 and 110^0c before use.

SECONDARY STANDARD

A secondary standard is a substance which may be used for standardizations, and whose content of the active substance has been found by comparison against a primary standard.

A secondary standard is a solution which contain exactly known amount of the substance in unit volume of the solution and which is expressed as normality or molarity and can be determined by titrating against a primary standard. It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of a primary standard solution.

Thus a solution of sodium hydroxide may be standardised by titrating against a standard solution of Potassium Hydrogen Phthalate or against a standard solution of Hydrochloric Acid (Secondary standard).

A secondary standard is a substance which for one or more of the reasons cannot be used as a primary standard.

e.g., sodium hydroxide cannot be used as a primary standard for the reason that it absorbs water and carbon dioxide from the atmosphere and the composition of its solution is subject to wide variations at different periods. Similarly Sodium thiosulphate absorbs CO2 from the atmosphere and gets decomposed. A deposit of sulphur settles at the bottom. Similarly the compositions of solution of various other substances like mineral acids, Potassium permanganate, Iodine etc , are also variable at different times. Therefore these cannot be used as primary standards. The normality or molarity of solution of such a substance can be found by titrating against a standard solution of a primary standard or in other words the solution may be standardized by titrating against the standard solution of a primary standard.

Volumetric solution also known as **Standard Solution** are solutions of reagents of known concentration intended primarily for use in quantitative determinations.

Concentrations are usually expressed in terms of molarity (M).

It is not always possible or is it essential, to prepare volumetric solutions of a desired theoretical molarity. A solution of approximately the desired molarity is prepared and standardized by titration against a solution of a primary standard. The molarity factors so obtained is used in all calculations, Where such standardised solutions are employed.

As the strength of a standard solution may change upon standing, the molarity factor should be redetermined frequently. Volumetric solutions should not differ from the prescribed strength by more than 10% and the molarity should be determined with a precision of 0.2%

When solutions of a reagent are used in several molarities, the details of the preparation and standardization are usually given for the most commonly used strength. Stronger or weaker solutions are prepared and standardised using proportionate amount of the reagent or by making an exact dilution of a stronger solution. Volumetric solutions prepared by dilution should be restandardised either or directed for the stronger solution or by comparison with another volumetric solution having a known ratio to the stronger solution.

The Water used in preparing volumetric solutions complies with the requirements of the monograph on **purified water** , unless otherwise specified. When used for the preparation of **unstable solutions such as potassium permanganate or sodium thiosulphate,** it should be freshly boiled and cooled. When a solution is to be used in an **assay** in which the end-point is determined by an electrochemical process (e.g., **potentiometrically**), the solution must be standardised in the same way.