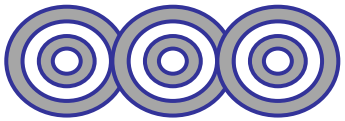
Fundamentals of Analytical Chemistry



Volumetric Analysis an overview

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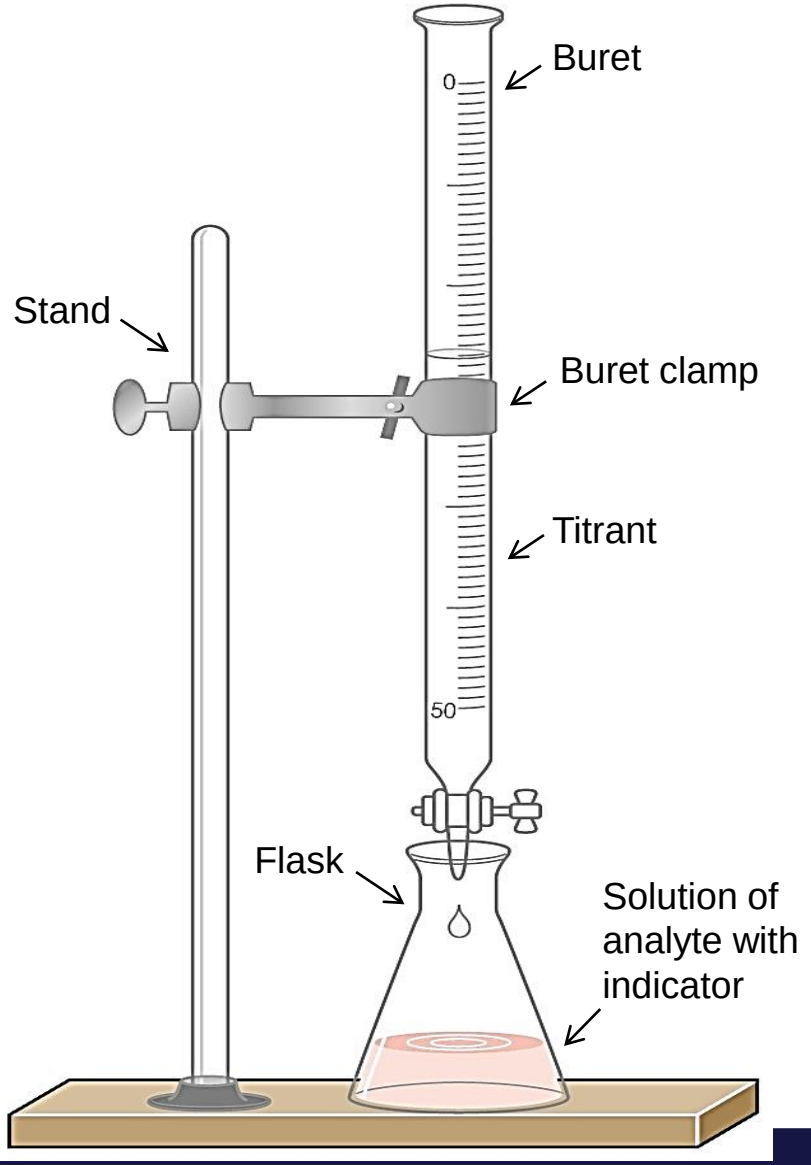
Volumetric or titrimetric analyses are among the most useful and accurate analytical techniques, especially for millimole amounts of analyte. They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, e.g., pH measurement.

Other than pedagogic purposes, manual titrations nowadays are generally used only in situations that require high accuracy for relatively small numbers of samples. They are used, e.g., to calibrate or validate more routine instrumental methods. Automated titrations are useful when large numbers of samples must be processed. A titration may be automated, for instance, by means of a color change or a pH change that activates a motor-driven buret to stop delivery. The volume delivered may be electronically registered.

General Process of Titration

In a titration, the test substance (**analyte**) reacts with an added reagent of known concentration, generally instantaneously. The reagent of known concentration is referred to as a standard solution. It is typically delivered from a **buret**; the solution delivered by the buret is called the **titrant**. (In some instances, the reverse may also be carried out where a known volume of the standard solution is taken and it is titrated with the analyte of unknown concentration as the titrant). The volume of titrant required to just completely react with the analyte is measured. Since we know the reagent concentration as well as the reaction stoichiometry between the analyte and the reagent, we can calculate the amount of analyte.



The Requirements of the Titration

The requirements of a titration are as follows:

-There must be a well-defined and known reaction between the analyte and the titrant.

-The reaction should be rapid.

-There should be no side reactions; the reaction should be specific.

-There should be a marked change in some property of the solution when the reaction is complete. This may be a change in color of the solution or in some electrical or other physical property of the solution.

-The point at which an equivalent or stoichiometric amount of titrant is added is called the **equivalence point**. The point at which the reaction is observed to be complete is called the **end point**, that is, when a change in some property of the solution is detected.

-The reaction should be quantitative. That is, the equilibrium of the reaction should be far to the right so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy. If the equilibrium does not lie far to the right, then there will be gradual change in the property marking the end point.

Example

In the titration of acetic acid in vinegar with sodium hydroxide,,,

A well-defined reaction takes place:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

-Analyte: acetic acid
-Titrant: NaOH

-This ionic reaction is very rapid.

-In this example, there should be no other acids present (no side reactions).

-In the titration of acetic acid with sodium hydroxide, there is a marked increase in the pH of the solution when the reaction is complete. A color change is usually brought about by addition of an indicator.

-Suitable indicators:
Thymol blue (pH range 8.0-9.6) yellow to blue
Phenolphthalein (pH range 8.3-10.0) colorless to pink

Standard Solutions and Standardization

A **standard solution** is prepared by dissolving an accurately weighed quantity of a highly pure material called a **primary standard** and diluting to an accurately known volume in a volumetric flask. Alternatively, if the material is not sufficiently pure, a solution is prepared to give approximately the desired concentration, and this is standardized by titrating a weighed quantity of a primary standard.

Standardization is the process of determining the exact concentration of a solution.

For example, sodium hydroxide is not sufficiently pure to prepare a standard solution directly. It is therefore standardized by titrating a primary standard acid, such as potassium acid phthalate (KHP). Potassium acid phthalate is a solid that can be weighed accurately.

A solution standardized by titrating a primary standard is itself a secondary standard. It will be less accurate than a primary standard solution due to the errors of titrations.

A primary standard should fulfill these requirements:

(1) It should be 100.00% pure, although 0.01 to 0.02% impurity is tolerable if it is accurately known.

(2) It should be stable to drying temperatures, and it should best able in definitely at room temperature. The primary standard is always dried before weighing.

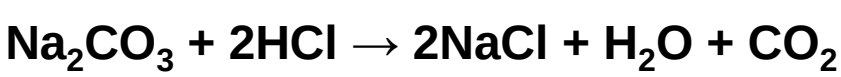
(3) It should be readily and relatively inexpensively available.

(4) Although not essential, it should have a high formula weight. This is so that a relatively large amount of it will have to be weighed. The relative error in weighing a greater amount of material will be smaller than that for a small amount.

(5) If it is to be used in titration, it should possess the properties required for a titration listed above. In particular, the equilibrium of the reaction should be far to the right so that a sharp end point will be obtained.

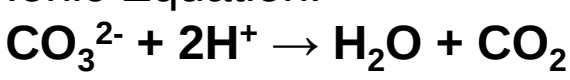
Example

An approximate 0.1 M hydrochloric acid solution is prepared by 120-fold dilution of concentrated hydrochloric acid. It is standardized by titrating 0.1876 g of dried primary standard sodium carbonate:



$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

Ionic Equation:



$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$

The titration required 35.86 mL acid. Calculate the molar concentration of the hydrochloric acid.

Solution

n Na_2CO_3 = n HCl / 2
n Na_2CO_3 = 0.1876 / 105.99 = 0.00177 mol
n HCl = 0.00177 x 2 = 0.00354 mol
M_{HCl} = n / V (L)
M = 0.00354 / 0.03586 = 0.09872 M

Classification of Titration Methods

There are **four** general classes of volumetric or titrimetric methods.

(1) Acid–base titrations

(2) Precipitation titrations

(3) Complexometric titrations

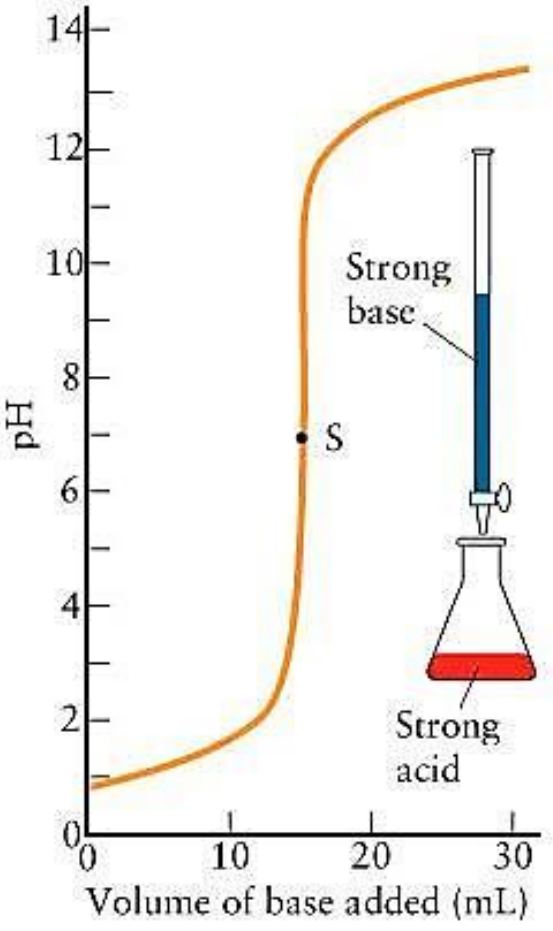
(4) Oxidation-reduction titrations (redox titrations)

Acid–Base Titrations

Many compounds, both inorganic and organic, are either acids or bases and can be titrated, respectively, with a standard solution of a strong base or a strong acid.

The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH with a pH meter.

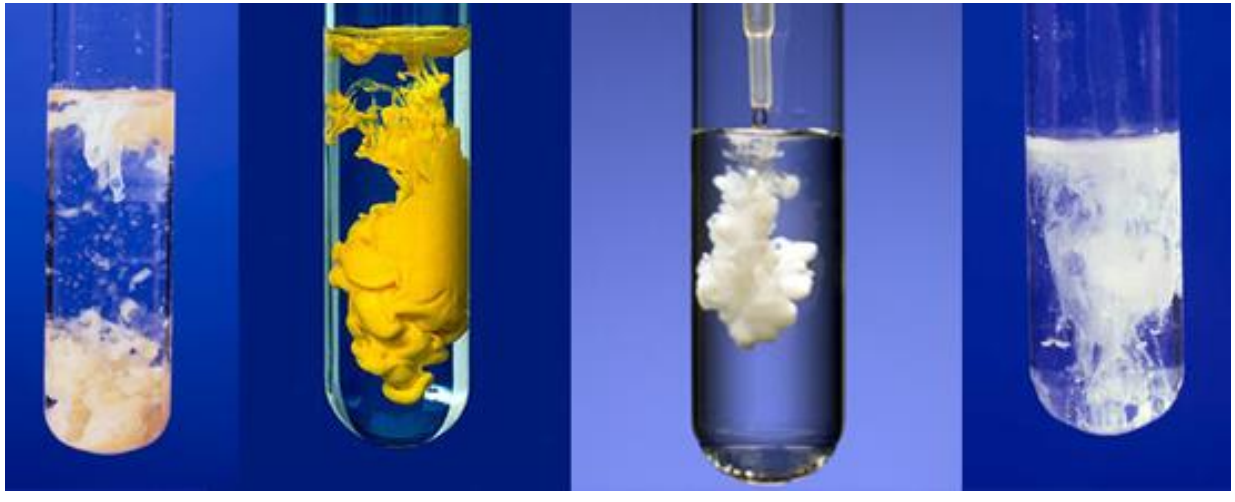
The acidity and basicity of many organic acids and bases can be enhanced by titrating in a nonaqueous solvent. The result is a sharper end point, and weaker acids and bases can be titrated in this manner.



Precipitation Titrations

In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate.

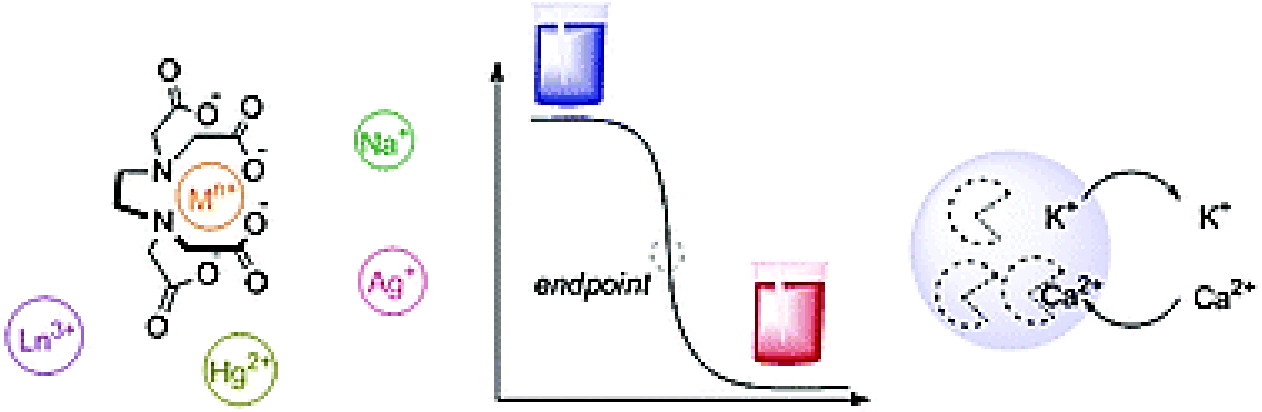
Again, indicators can be used to detect the end point, or the potential of the solution can be monitored electrically.



Complexometric Titrations

In complexometric titrations, the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion.

The titrant is often a chelating agent. Ethylenediaminetetraacetic acid (EDTA) is one of the most useful chelating agents used for titration. It will react with a large number of metal ions, and the reactions can be controlled by adjustment of pH. Indicators can be used to form a highly colored complex with the metal ion.



Reduction–Oxidation Titrations

These “redox” titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

There must be a sufficiently large difference between the oxidizing and reducing capabilities of these agents for the reaction to go to completion and give a sharp end point; that is, one should be a fairly strong oxidizing agent (strong tendency to gain electrons) and the other a fairly strong reducing agent (strong tendency to lose electrons).

Appropriate indicators for these titrations are available; various electrometric means to detect the end point may also be used.

Real Life Uses of Titration

Some real life uses of titration:

- Medical uses
- Pharmaceutical industry
- Cosmetic industry
- Food industry and nutrition uses
- Determine the fatty acids in food
- Wine industry
- Acid rain
- Science and education
- Cleaning material industry
- Wastewater analysis
- Biodiesel production
- Aquarium water testing
- Paint makers


Thank You!