TITRIMETRIC (VOLUMETRIC) ANALYSIS

Titrimetric or volumetric analysis

- Titrimetric or volumetric analysis' is a method of quantitative analysis based on measuring the volume (or mass) of reagent T consumed for reaction with determined substance X. In other words, titrimetric analysis is an analysis based on titration.
- Titration is the process of determining substance X by the gradual addition of small amounts of substance T, during which a point (moment) when all substance X has reacted is determined in some way. Titration allows to determine the amount of substance X by the known amount of substance T added up to this point (moment), taking into account that the ratio in which X and T react is known from stoichiometry or otherwise.

- **A titrant** is a solution containing the active reagent T, which is used to perform titration.
- Titration is usually performed by adding titrant from a calibrated burette to a titration flask with the analyzed solution. An aliquot fraction of the analyzed solution is placed in the flask before titration.
- **An aliquot fraction(aliquot)** is a precisely known part of the analyzed solution sampled for analysis. It is often sampled using a calibrated pipette, and its volume is commonly denoted by symbol Vn.
- **Equivalent point (EP)** is a point (moment) during titration, at which the amount of added titrant T is equivalent to the amount of titrated substance X. Synonyms of EP are stoichiometric point, theoretic end point.

- **The end point** of titration (EPT) is a point (moment) of titration, at which a certain property of solution (for example, its color) changes noticeably (sharply). An EPT more or less corresponds to EP, but most commonly does not coincide with it.

- **An indicator** is a substance that exhibits a noticeable change at the EP or close to it. In the perfect case, the indicator is present in a sufficiently low concentration so that a significant amount of titrant T is not consumed in its transition range. A sharp noticeable change of indicator property (for example, its color) corresponds to EPT.

- **Indicator transition range** is the range of concentration of hydrogen ion, metal, or other ions, within which the human eye is capable of detecting a change in color shade, color intensity, fluorescence, or other property of a visual indicator caused by the change in the ratio of two corresponding forms of an indicator.

- **Titration degree** is the ratio of volume V(T) of added titrant to V(EP) of titrant corresponding to EP:

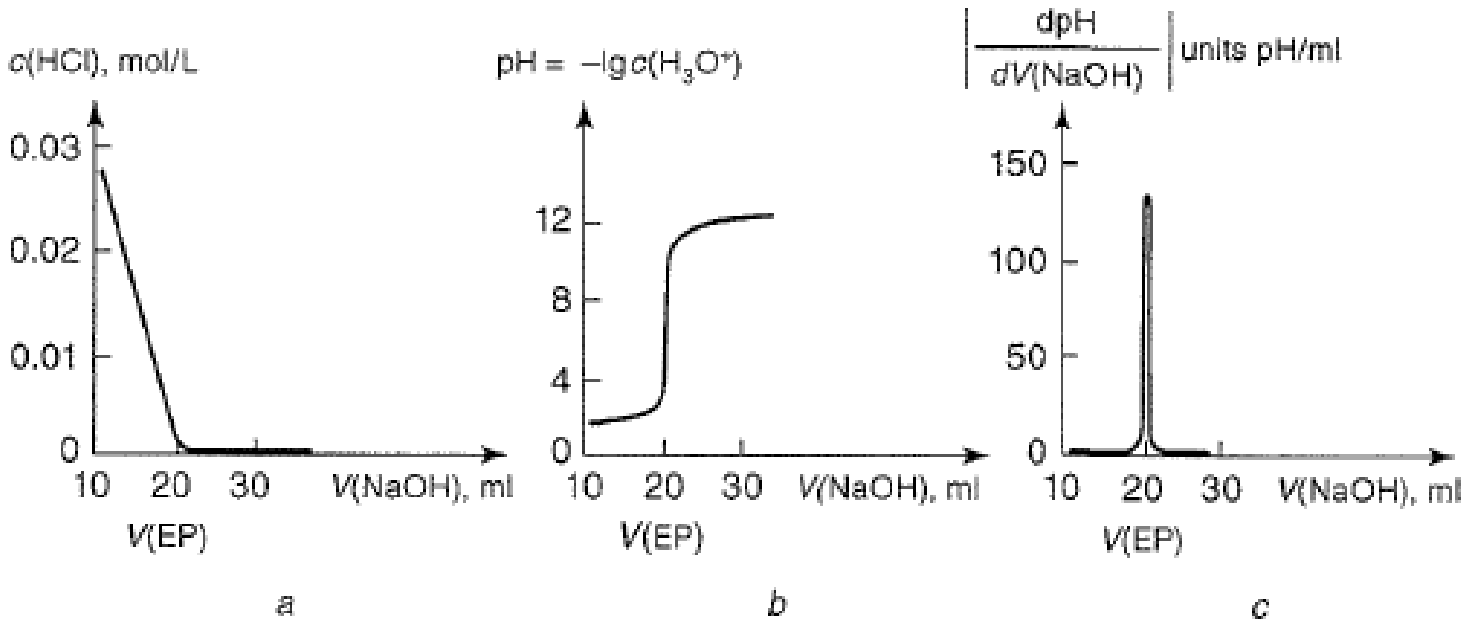
$$f = V(T)/V(EP).$$

In other words, the titration degree of a solution is the ratio of titrated substance amount to its initial amount in the analyzed solution.

- **A titration level** is magnitude order (10^{-x} of concentration of titrant solution used

- **A titration curve** is a plot of concentration change c(X) of determined substance X or any associated feature of the system (solution) against the volume V(T) of titrant T added. The value of C(X) during titration changes by several orders of magnitude; therefore, the titration curve is often plotted in coordinates IgC(X) — V(T).

Titration curves



Different types of calculated curves for titration of 20 ml of 0.1 mol/L HC1 solution with equimolar NaOH solution: a — a linear titration curve; b — logarithmic titration curve; c — a differential titration curve

REQUIREMENTS FOR REACTIONS IN TITRIMETRIC ANALYSIS

- 1. The reaction must proceed according to a strictly defined stoichiometric equation. Side reactions must be eliminated.
- 2. The reaction must proceed quantitatively, i.e., almost to the end. Equilibrium in the system must be completely shifted to the side of reaction products. The degree of conversion of an initial substance into reaction products at EP must be at least 99.90-99.99%. The equilibrium constant must be sufficiently large.
- 3. The reaction must proceed quickly so that equilibrium is established almost immediately at any moment of titration. Sometimes, in order to accelerate the achievement of equilibrium, the solutions are heated, or catalysts are added to them.
- 4. The reaction must allow determining EPT near EP precisely and conveniently.

REAGENTS USED IN TITRIMETRIC ANALYSIS

- **Primary standard substance (primary standard)** is a high-purity substance used to determine titrant concentration (to standardize titrant), which is based on the stoichiometry of their interaction, or it can be used itself to prepare titrant solution with a precisely known concentration.
- **Secondary standard substance (secondary standard)** is a substance used for standardization; the content of an active component in it is determined using the primary standard.

REAGENTS USED IN TITRIMETRIC ANALYSIS

- **A standard solution** is a solution with a known concentration of an active substance.
- **A primary standard solution** is a standard solution prepared from the primary standard substance, whose concentration is known by mass of this substance in a certain volume (or mass) of the solution.
- **A secondary standard solution** is a solution whose concentration is determined by standardization or prepared according to the known mass of the secondary standard substance.
- **Standardization** is the process of determining the concentration of the active reagent in solution (most often by titration with standard solution).

Methods for expressing concentrations in titrimetric analysis

- Molar concentration c(A) is the amount of dissolved substance A in moles contained in one liter of solution:

$$c(\mathrm{A}) = n(\mathrm{A})/V(\mathrm{A}) = m(\mathrm{A})/M(\mathrm{A})V(\mathrm{A}),$$

- Molar equivalent concentration c (1/z A), or normality (previous name) is the amount of dissolved substance A in moles corresponding to the equivalent of A contained in one liter of solution:

$$c({}^{1}/_{z}\,\mathrm{A}) = n({}^{1}/_{z}\,\mathrm{A})/V(\mathrm{A}) = m(\mathrm{A})/M({}^{1}/_{z}\,\mathrm{A})V(\mathrm{A}),$$

- Titer T (A) of dissolved substance A is a mass of dissolved substance A contained in one milliliter of a solution:

$$T(\mathrm{A}) = m(\mathrm{A})/V(\mathrm{A}) = c({}^{1}/_{z}\,\mathrm{A})M({}^{1}/_{z}\,\mathrm{A})/1000,$$

Methods of individual weights and pipetting

During titration, either a predetermined mass of the analyzed substance or precisely measured volume of the analyzed solution can be taken. According to this, two methods are distinguished:

- the method of individual weights
- method of pipetting.

Method of individual weights

- In the method of individual weights, an exact sample weight m(À) of substance A is weighted using an analytical balance, quantitatively transferred to a titration flask, dissolved by adding a certain amount of solvent to the flask, and the resulting solution is titrated. In this case, it is not necessary to measure the volume of the titrated solution.

$$n(^1/_z\,\mathrm{A}) = m(\mathrm{A})/M(^1/_z\,\mathrm{A}),\ n(^1/_z\,\mathrm{T}) = c(^1/_z\,\mathrm{T})V(\mathrm{T}),$$

$$c(^1/_z\,\mathrm{T})V(\mathrm{T}) = m(\mathrm{A})/M(^1/_z\,\mathrm{A}).$$

$$c(^1/_z\,\mathrm{T}) = m(\mathrm{A})/M(^1/_z\,\mathrm{A})V(\mathrm{T})$$

Pipetting method

- In the pipetting method, an aliquot is sampled using a calibrated pipette, which corresponds to the precisely measured volume F(X) of the analyzed substance X solution with an unknown molar equivalent concentration C(1/zX), and the aliquot is titrated with standard titrant solution with molar equivalent concentration c(1/zT).

$$c(^1/_z\mathrm{X}) = c(^1/_z\mathrm{T})V(\mathrm{T})/V(\mathrm{X}).$$

$$m(\mathrm{X}) = c(^1/_z\mathrm{X})(M\,^1/_z\mathrm{X})V_p$$

CLASSIFICATION OF TITRIMETRIC ANALYSIS METHODS

- **Acid-base titration (neutralization method)** is titration based on the reaction of proton transfer from one reacting particle to another in solution. It includes acidimetry and alkalimetry.
- **Oxidation-reduction (redox) titration (redoxometry)** is titration accompanied by a transition of one or more electrons from donor ion or molecule (reducing agent) to an acceptor (oxidizing agent).
- **Precipitation titration** is a type of titration, during which the titrated substance is precipitated from solution due to interaction with the titrant.
- **Complexometric titration** is titration of a substance with a compound solution that interacts with the titrated substance forming a weakly dissociating soluble complex.

TYPES OF TITRATION USED IN TITRIMETRIC ANALYSIS

- Direct titration
- Back titration
- Indirect titration, or titration with substituent (substitution titration)

Direct titration is a type of titration during which the determined substance directly titrated with standard titrant solution or vice versa. The results of direct titration results are calculated similarly to the described above pipetting method

$$n(^1/_z\mathrm{X}) = n(^1/_z\mathrm{T}),$$

$$c(^1/_z\mathrm{X})V(\mathrm{X}) = c(^1/_z\mathrm{T})V(\mathrm{T}),$$

$$c(^1/_z\mathrm{X}) = c(^1/_z\mathrm{T})V(\mathrm{T})/V(\mathrm{X}),\ \mathrm{T}(\mathrm{X}) = c(^1/_z\mathrm{X})M(^1/_z\mathrm{X})/1000,$$

$$m(\mathrm{X}) = c(^1/_z\mathrm{X})M(^1/_z\mathrm{X})V_f = \mathrm{T}(\mathrm{X})V_f,$$

Back titration {titration by residue) is titration of unreacted substance, which has been added as a standard solution in excess to the analyzed solution. The precisely known volume V(T1) of standard substance T, solution with molar equivalent concentration c(1/zT,) is added to an aliquot of an analyzed solution with a volume of V(X)n. The determined substance X reacts with T, completely. Then, unreacted excess of substance T, is titrated with a standard solution of titrant T2.

$$n(^1/_z\mathrm{T}_1) = n(^1/_z\mathrm{X}) + n(^1/_z\mathrm{T}_2),$$

$$c(^1/_z\mathrm{T}_1)V(\mathrm{T}_1) = c(^1/_z\mathrm{X})V(\mathrm{X}) + c(^1/_z\mathrm{T}_2)V(\mathrm{T}_2),$$

$$c(^1/_z\mathrm{X}) = [c(^1/_z\mathrm{T}_1)V(\mathrm{T}_1) - c(^1/_z\mathrm{T}_2)V(\mathrm{T}_2)]/V(\mathrm{X}).$$

Indirect titration (substitution titration) is titration, during which a determined substance does not react directly with a titrant, and is determined indirectly by using a stoichiometrically proceeding reaction leading to the formation of another substance that reacts with the titrant.

$$\underset{}{X} + \underset{\text{excess}}{A} = \underset{\text{substituent}}{B}$$

The formed substituent B is titrated with a standard solution of titrant T:

$$B + T = D$$

$$n(^1/_z X) = n(^1/_z B) = n(^1/_z T),$$

$$c(^1/_z X)V(X) = c(^1/_z T)V(T),$$

$$c(^1/_z X) = c(^1/_z T)V(T)/V(X),\ T(X) = c(^1/_z X)M(^1/_z X)/1000,$$

$$m(X) = c(^1/_z X)M(^1/_z X)V_к = T(X)V_к',$$

METHODS FOR DETERMINING END POINT OF TITRATION

There exist two groups of methods for determining EPT: **visual** and **instrumental**.

METHODS FOR DETERMINING END POINT OF TITRATION

- **Visual methods**. The reaction is controlled visually by monitoring color change (or other property) of a specially added indicator /

1. In case of indicator visual methods, an indicator is added to a titrated solution. Depending on the specifics of titrated solution and titrant, various indicators are used: acid-base, redox, precipitation, metalchromic, adsorption, metal fluorescent, fluorescent, chemiluminescent, screening, extraction. The most important of these indicators are considered below when describing different types and methods of titration.
2. Non-indicator visual methods are based on color of titrant or titrated substance. EPT is determined by titrant coloration or titrated substance discoloration.

- **Instrumental methods.** EPT is determined by changing physical-chemical properties of a solution, such as fluorescence, optical density, potential, specific electrical conductivity, current strength, radioactivity, etc. Changes in physico-chemical properties are recorded using various instruments.