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عنوان المحاضرة باللغة العربية: مقدمة في الطرق الحجمية

عنوان المحاضرة باللغة الإنكليزية : **Introduction to Volumetric Methods of Analysis**

## ***5.1 Introduction***

A quantitative analysis based upon the measurement of volume is called a volumetric or titrimetric method. Volumetric methods are much widely used than gravimetric methods because they are usually more rapid and convenient; in addition, they are often as accurate.

## ***5.2 Definition of Some Terms***

Titration is the process by which the quantity of analyte in a solution is determined from the amount of a standard reagent it consumes. Ordinarily, a titration is performed by carefully adding the reagent of known concentration until reaction with the analyte is judged to be complete; the volume of standard reagent is then measured. Occasionally, it is convenient or necessary to add an excess of the reagent and then determine the excess by back-titration with a second reagent of known concentration.

The reagent of exactly known concentration that is used in a titration is called a standard solution. The accuracy with which its concentration is known sets a definite limit upon the accuracy of the method; for this reason, much care is taken in the preparation of standard solutions. The concentration of a standard solution is established either directly or indirectly:

- 1- by dissolving a carefully weighed quantity of the pure reagent and dilution to an exactly known volume.
- 2- by titrating a solution containing a weighed quantity of a pure compound with the reagent solution.

In either method, a highly purified chemical compound called a primary standard is required as the reference material. The process whereby the concentration of a standard solution is determined by titration of a primary standard is called standardization.

The goal of every titration is the addition of standard solution in an amount that is chemically equivalent to the substance with which it reacts. This condition is achieved at the *equivalence point*. For example, the equivalence point in the titration of sodium chloride with silver nitrate is attained when exactly one formula weight of silver ion has been introduced for each formula weight of chloride ion present in the sample. In the titration of sulfuric acid with sodium hydroxide, the equivalence point occurs when two formula weights of the latter have been introduced for each formula weight of the former.

The equivalence point in a titration is a theoretical concept; in actual fact, its position can be estimated only by observing physical changes associated with equivalence. These changes manifest themselves at the *end point* of the titration. It is to be hoped that any volume difference between the end point and the equivalence point will be small. Differences do exist, however, owing to inadequacies in the physical changes and our ability to observe them; a titration error is the result.

A common method of end-point detection in volumetric analysis involves the use of a supplementary chemical compound that exhibits a change in color as a result of concentration changes occurring near the equivalence point. Such a substance is called an indicator.

### ***5.3 Reactions and Reagents Used in Volumetric Analysis***

It is convenient to classify volumetric methods according to four reaction types, specifically, precipitation, complex formation, neutralization (acid-base), and oxidation-reduction. Each reaction type is unique in such matters as nature of equilibria involved; the indicators, reagents, and primary standard available; and the definition of equivalent weight.

#### ***\* Primary standards***

The accuracy of a volumetric analysis is critically dependent upon the primary standard used to establish, directly or indirectly, the concentration of the standard solution. Important requirements for a substance to serve as a good primary standard include the following:

- 1- **Highest purity.** Moreover, established methods should be available for confirming its purity.
- 2- **Stability.** It should not be attacked by constituents of the atmosphere.
- 3- **Absence of hydrate water.** If the substance were hygroscopic or efflorescent, drying and weighing would be difficult.
- 4- **Ready availability at reasonable cost.**
- 5- **Reasonably high equivalent weight.** The weight of a compound required to standardize or prepare a solution of a given concentration increases directly with its equivalent weight. Since the relative error in weighing decreases with increasing weight, a high equivalent weight will tend to minimize weighing errors.

Few substances meet or even approach these requirements. As a result, the number of primary-standard substances available to the chemist is limited.

In some instances, it is necessary to use less pure substances in lieu of a primary standard. The assay (that is, the percent purity) of such a secondary standard must be established by careful analysis.

#### ***5.4 Standard Solution***

An ideal standard solution for titrimetric analysis would have the following properties:

- 1- Its concentration should remain constant for months or years after preparation to eliminate the need for restandardization.

- 2- Its reaction with the analyte should be rapid in order that the waiting period after each addition of reagent does not become excessive.
- 3- The reaction between the reagent and the analyte should be reasonably complete.
- 4- The reaction of the reagent with the analyte must be such that it can be described by a balanced chemical equation; otherwise, the weight of the analyte cannot be calculated directly from the volumetric data. This requirement implies the absence of side reactions between the reagent and the unknown or with other constituents of the solution.
- 5- A method must exist for detecting the equivalence point between the reagent and the analyte; that is, a satisfactory end point is required.

Few volumetric reagents currently in use meet all of these requirements perfectly.

### ***5.5 End Point in Volumetric Methods***

End points are based upon a physical property which changes in a characteristic way at or near the equivalence point in the titration. The most common end point involves a color change due to the reagent, the analyte, or an indicator substance. Other physical properties, such as electrical potential, conductivity, temperature, and refractive index, have also been employed to locate the equivalence point in titration.

### ***5.6 Theory of Neutralization Titration for Simple Systems***

End-point detection in a neutralization titration is ordinary based upon the sharp change in pH that occurs near the equivalence point. The pH range with which such a change occurs varies from titration to titration and is determined both by the nature and the concentration of the analyte as well as the titrant. The selection of an appropriate indicator and the estimation of the titration error require knowledge of

the pH changes which occur throughout the titration. Thus, we need to know how neutralization titration curves are derived.

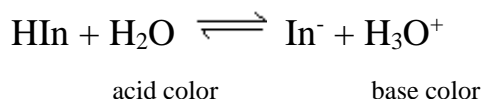
### ***5.7 Standard Solutions for Neutralization Titrations***

The standard solutions employed for neutralization titrations are always strong acids or strong bases because these react more completely than their weaker counterparts, and they therefore provide sharper end point. Standard solutions of acids are prepared by diluting concentrated acids.

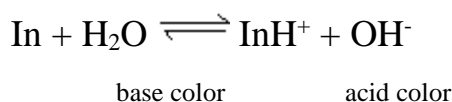
Standard solutions of bases are ordinarily prepared from solid bases.

### ***5.8 Acid-Base Indicators***

An acid-base indicator is a weak organic acids or a weak organic base whose undissociated form differ in color from its conjugate base or its conjugate acid form. For example, the behavior of an acid-type indicator, HIn, is described by the equilibrium:



Here, internal structure changes accompany dissociation and cause the color change. The equilibrium for a base-type indicator, In, is:



The equilibrium-constant expression for the dissociation of acid-type indicator takes the form:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}_3\text{O}^+]K_a = \frac{[\text{HIn}]}{[\text{In}^-]}$$

We then see that the hydronium ion concentration determines the ratio of the acid to the conjugate base from the indicator, which in turn controls the color of the solution.

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In<sup>-</sup>, particularly when the ratio [HIn]/[In<sup>-</sup>] is greater than about 10 or smaller than about 0.1. Consequently, the color change detected by an average observer occurs within a limited range of concentration ratios from about 10 to about 0.1. At greater or smaller ratios, the color appears essentially constant to the eye and is independent of the ratio. As a result, we can write that the average indicator, HIn, exhibits its pure acid color when:

$$\frac{[\text{HIn}]}{[\text{In}^-]} \geq \frac{10}{1}$$

and its base color when:

$$\frac{[\text{HIn}]}{[\text{In}^-]} \leq \frac{1}{10}$$

The color appears to be intermediate for ratios between these two values.

### 5.9 The Common Acid-Base Indicators

The list of acid-base indicators is large and includes a number of organic compounds. An indicator covering almost any desired pH range can ordinarily be found. A few common indicators are given in Table 5-1.

**Table 5-1 Some Important Acid-Base Indicators**

Common Name	Transition Range, pH	Color Change		Indicator Type
		Acid	Base	
Thymol blue	1.2-2.8 8.0-9.6	red yellow	yellow blue	1

Methyl yellow	2.9-4.0	red	yellow	2
Methyl orange	3.1-4.4	red	orange	2
Bromocresol green	3.8-5.4	yellow	blue	1
Methyl red	4.2-6.3	red	yellow	2
Bromocresol purple	5.2-6.8	yellow	purple	1
Bromothymol blue	6.2-7.6	yellow	blue	1
Phenol red	6.8-8.4	yellow	red	1
Cresol purple	7.6-9.2	yellow	purple	1
Phenolphthalein	8.3-10.0	colorless	red	1
Thymolphthalein	9.3-10.5	colorless	blue	1
Alizarin yellow GG	10-12	colorless	yellow	2
(1) Acid type $\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-$				
(2) Base type $\text{In} + \text{H}_2\text{O} \rightleftharpoons \text{InH}^+ + \text{OH}^-$				

### 5.10 Titration of a Strong Acid with a Strong Base

Strong acids and strong bases are completely ionized in their solutions, examples HCl and NaOH.



At the equivalence point, the hydronium and hydroxide ions are present in equal concentrations. The solution containing NaCl salt does not undergo hydrolysis, and the pH of the solution is 7.00.

If the values of pH are plotted against the volumes of NaOH added, we obtain curve as shown in Figure 5-1, called titration curve for a strong acid with strong base.



***\* The effect of concentration***

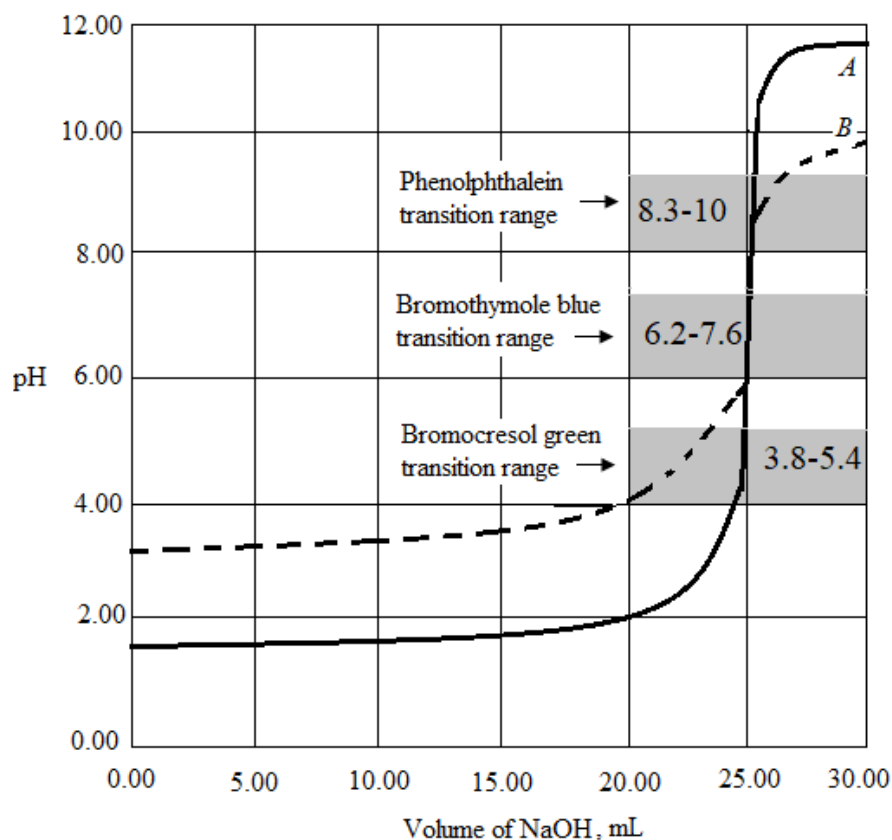
The effect of reagent and analyte concentrations on the neutralization titration curves for strong acids are shown by the plots in Figure 5-1. Note that with 0.1 M NaOH as the titrant, the change in pH in the equivalence-point region is large. With 0.001 M NaOH, the change is markedly less but still pronounced.

***\* Choosing an indicator***

Figure 5-1 shows that the selection of an indicator is not critical when the reagent concentration is approximately 0.1 M.

Here, the volume differences in titrations with the three indicators shown are of the same magnitude as the uncertainties associated with reading the buret; therefore, they are negligible. Note, however, that bromocresol green is unsuited for a titration involving the 0.001 M reagent because the color change occurs over a 5-mL range well before the equivalence point. The use of phenolphthalein is subject to similar objections. Of the three indicators, then, only bromothymol blue provides a satisfactory end point with a minimal systematic error in the titration of the more dilute solution.

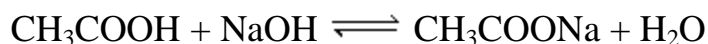
Titration curves for strong bases are derived in an analogous way to those for strong acids. The solution is neutral at the equivalence point.



**Figure 5-1 Titration Curves for HCl with NaOH. Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve B: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.**

### 5.11 Titration of a weak Acid with a Strong Base

Weak acid, like acetic acid, does not ionize in the solution completely. The equation for the reaction is:



At the beginning, the solution contains only a weak acid or weak base, and the pH is calculated from the concentration of the solute and its dissociation constant.

At the equivalence point, the solution contains only the salt, and the pH is calculated from the concentration of this product. The solution containing  $\text{CH}_3\text{COONa}$  salt, undergoes hydrolysis as shown in the equation:



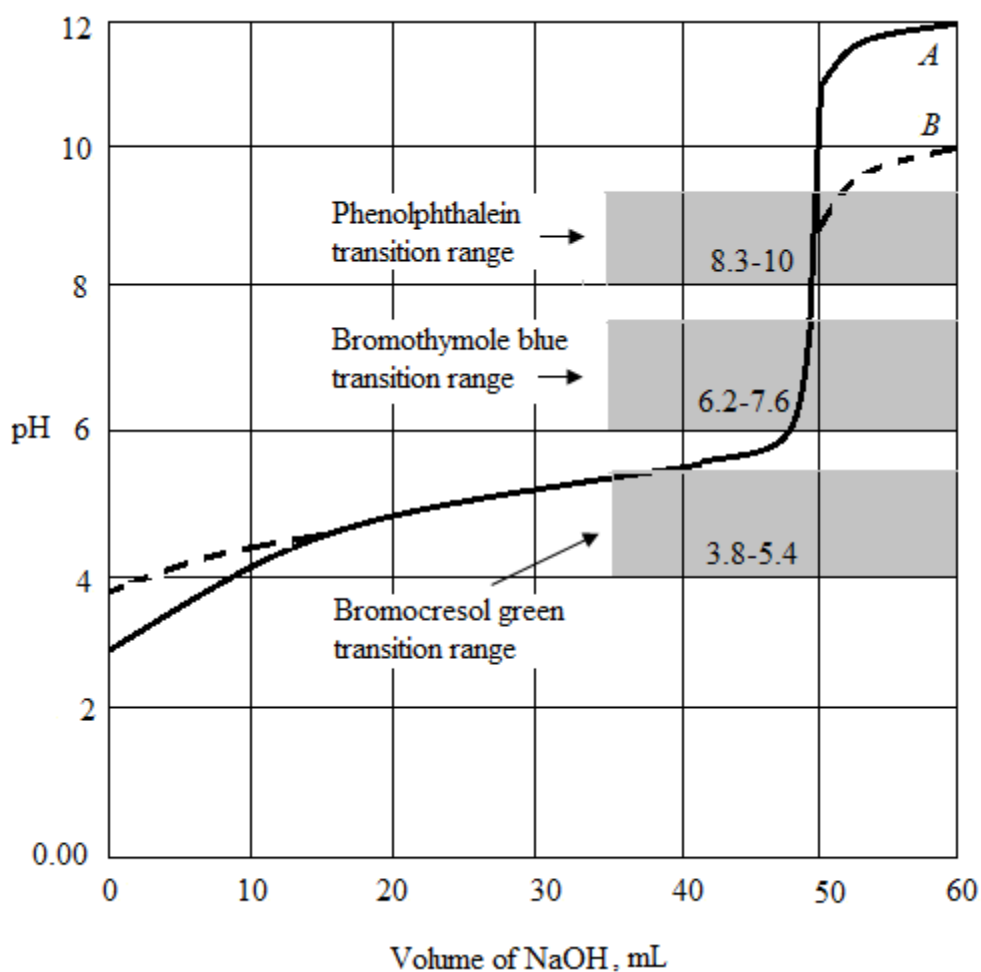
which increases the hydroxide ions concentration over the concentration of hydrogen ions, because NaOH ionizes completely and the  $\text{CH}_3\text{COOH}$  ionizes partially. The pH of the solution is 8.72. The titration curve is shown in Figure 5-2.

**\* *The effect of concentration***

The initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (curve B).

**\* *Choosing an indicator***

Figure 5-2 shows that the choice of indicator is more limited for the titration of a weak acid than for the titration of a strong acid. The bromocresol green is totally unsuited for titration of 0.1000 M acetic acid. Bromothymol blue does not work either because its full color change occurs over a range of titrant volume from about 47 mL to 50 mL of 0.1000 M base. An indicator exhibiting a color change in the basic region, such as phenolphthalein, however, should provide a sharp end point with a minimal titration error.



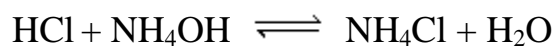
**Figure 5-2 Titration Curves for  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$ . Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.**

The end-point pH associated with the titration of 0.001000 M acetic acid (curve B) is so small that a significant titration error is likely to be introduced regardless of indicator. Use of an indicator with a transition range between that of phenolphthalein and that of bromothymol blue in conjunction with a suitable color comparison standard, however, makes it possible to establish the end point in this titration with decent precision.

### ***5.12 Titration of a Strong Acid with a Weak Base***

The calculations needed to draw the titration curve for a weak base are analogous to those for a weak acid.

Consider the titration of HCl, (a strong acid) and ammonium hydroxide (a weak base). The equation for the reaction is:



The pH at the equivalence point, is less than 7.00 (5.28), due to the hydrolysis of the ammonium chloride, and formation of HCl, which is more ionized than NH<sub>4</sub>OH.

