Pharmaceutical Analytical Chemistry I

الأستاذ الدكتور جمعه الزهوري (دكتوراه صيدلة-ألمانيا 1991)

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Principles of Titration

- Titration definition
- Analytical Tools
- Titration reaction
- Equivalent point
- Detection of equivalent point
- End Point
- Standard Solution
- Primary Standard Solution
- Secondary Standard Solution
- TitrationTypes(Direct, Back and Replacement)

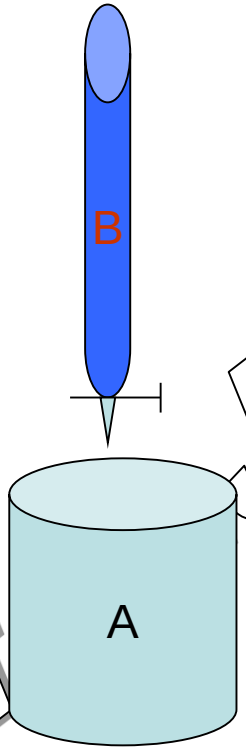
Principles of Neutralization Titrations

Titration

Titration The procedure whereby a measured volume of a standard solution reacts with an analyte to the point of chemical equivalence.

Principle of volumetric titration

$$A + B \longrightarrow C + D$$



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Equivalent Point

Analytical Tools

- **Burets** - Normal (not allowed in non-aqueous)
  - Half-automatic
  - Automatic
- **Pipets** - Volumetric
  - Graduated (not allowed in Titrations)
  - Micro-
- **Volumetric flasks**
- **Measuring Cylinder** (not allowed in Titrations)
- **Conical flask**
- **Burets Stand**

Normal burette

Buret

A graduated tube
From which
Accurately known
Volumes can be
Dispensed.

Normal Burette

Normal Burette with Schell Bach band

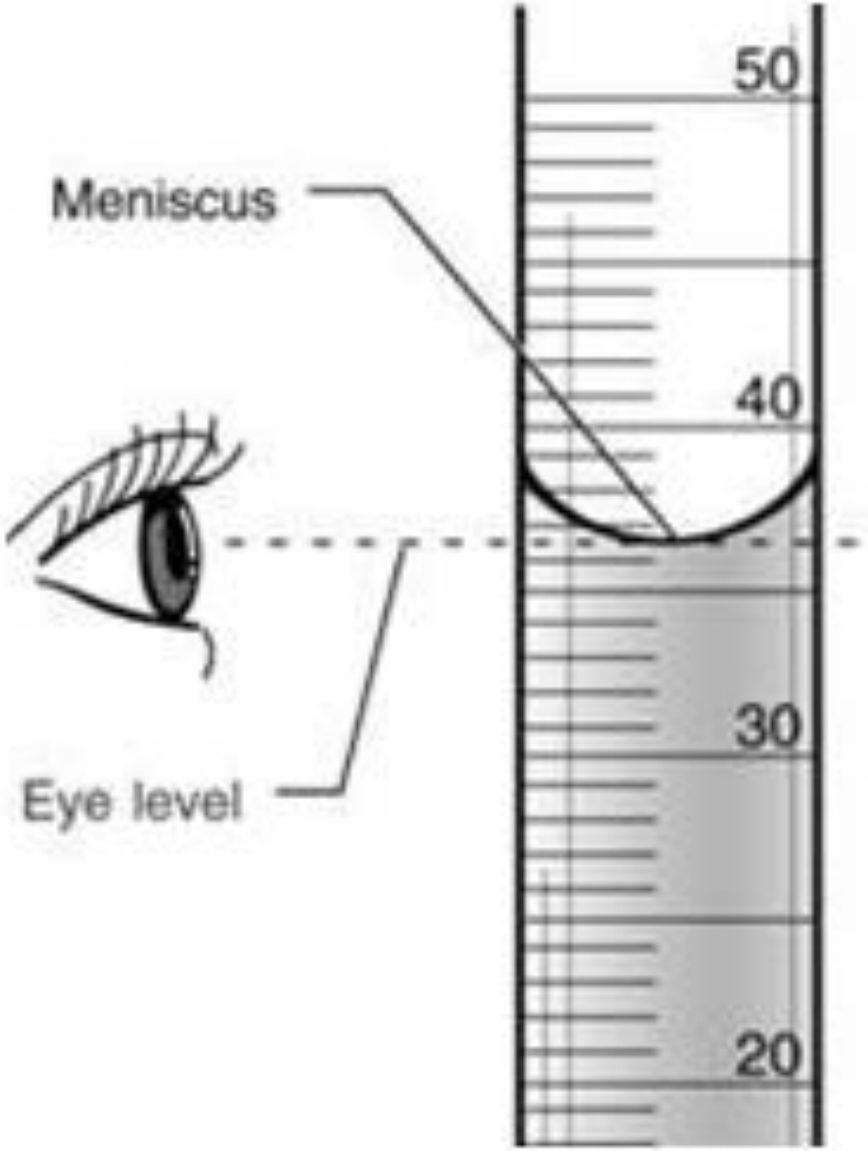
Half-Automatic
burette

Half-Automatic
Burette

Different Types of Burettes

Automatic Burette


19
20
21


50
40
30
20
Meniscus
Eye level

Never use your mouth to draw liquid into a pipette because of the possibility of accidentally ingesting the liquid being pipetted. Instead, a rubber suction bulb or a rubber tube connected to a vacuum source should be used.

A rubber suction bulb

Titration Reaction should be :

- ***Quantitative (Complete) - $K_{eq} > 10^8$***
  - 99.9% of analyte reacted.
  - right direction
- ***Stoichiometric***
- ***Rapid***
- ***Selective***
- ***Available suitable Indicator***

Detection of the Equivalent Point

Visual indicator

- **Color Change**
- **Color disappear**
- **Participate formulation**
- **Turbid formulation**

Measurement Property

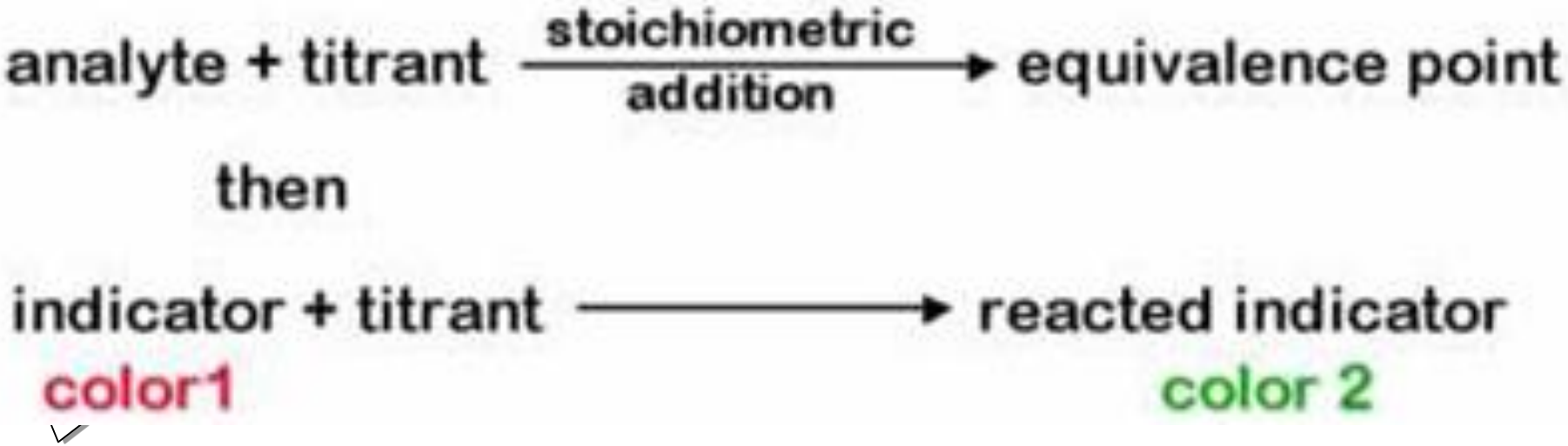
- **Electric Conductivity**
- **Electric Potential**
- **Electric Current**
- **Thermal Property**

- نقطة التكافؤ Equivalent Point:

هي النقطة التي تكون فيها حجم المحلول المضاف مكافىء ستيكومترياً لكمية المادة المراد تحديد تركيزها (Analyte)

- نقطة نهاية المعايرة End Point :

هي النقطة التي يكون فيها حجم المحلول المضاف كاف لتحديد نقطة التكافؤ



End point

The volume of titrant required for detection of the equivalence point. (When a physical change occurs)

Ideally, we want the equivalence point and the end point to be the same.

This seldom happens due to the methods used to observe end points.

Results in a titration error - overtitration.

Primary Standard solution

a solution of known concentration that is prepared from a ***Primary standard*** and used in a titrimetric analysis.

Primary standard

A high purity compound used to prepare our standard solution or to standardize the solution with.

Primary standards

Desired properties of a primary standard

High purity

Stable in air and solution

Not hydroscopic

Inexpensive

Large formula weight

Soluble in our solvent

Reacts rapidly and stoichiometrically with our analyte

Few materials have all of these properties.

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Primary standard solutions

A material that is stable in a bottle may not remain that way in solution.

A primary standard solution should:

Have long term stability in your solvent.

React rapidly with your analyte

React completely with your analyte

Be selective for your analyte

The last requirement is often based on the procedure used.

Primary standards according to Bp

Substance name	Formula
Sodium carbonate, Anhydrous	Na_2CO_3
Sodium Chloride	NaCl
Arsenic Trioxide	As_2O_3
Potassium Iodate	KIO_3
Zinc (Granulated)	Zinc
Sulphanic acid	H_3NO_3S
Benzoic acid	$C_7H_6O_2$
Potassium H phthalate	KHph
Potassium Bromate	$KBrO_3$
Potassium Dichromate	$K_2Cr_2O_7$

Secondary standards

Suitable primary standards are not always available for a given titration.

You must often rely on a second material for your titrant.

It should always be standardized using a primary standard.

This second material is then considered a **secondary standard**.

Establishing the primary Standard Solutions

Two basic methods are used to establish the concentration of such solutions.

1- The direct method in which a carefully weighed quantity of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask.

Direct r e of primary on

- Example: F odium

a.

Sodium Ca rous Na_2CO_3 = 106.0

Weigh accu e substance and dissolved ted to 1 liter using volu

Establishing the primary Standard Solutions

2- **The standardization or calculation of standardization factor (F)} in which the secondary solution will be standardized against primary solution (or determination of the concentration of a solution through reaction with a primary standard).**

Primary standards substances and the secondary solution which standardized with it

Primary Standard substances	Secondary solution	Applied
Sodium Carbonate ,anhydrous	HCl, HNO_3, H_2SO_4	Acid-base (aqueous)
Potassium phthalate	$HClO_4$, NaOH	Acid-base (non-aqueous)
Benzoic acid {	$NaOCH_3, NaOC_2H_3$ $(C_4H_9)_4NOH$(=TBAH)	Base-acid (non-aqueous)
Sodium Chloride	$AgNO_3$	Precipitate
Zinc	EDTA-2Na	Complexometric
Arsenic oxide Potassium Bromate	I_2 , Ce^{+4} $Na_2S_2O_3$	Redox

Standardization of secondary solution

- **Example : To standardize approximately 0.1 N HCl solution we used 25 ml 0.1N Na_2CO_3 solution .The Average consume for the end point was 25.4 ml .What is the Standardization factor.**

$N_1V_1 = N_2V_2$

N_1x 25.4 = 0.1 x 25

N_1= 0.098

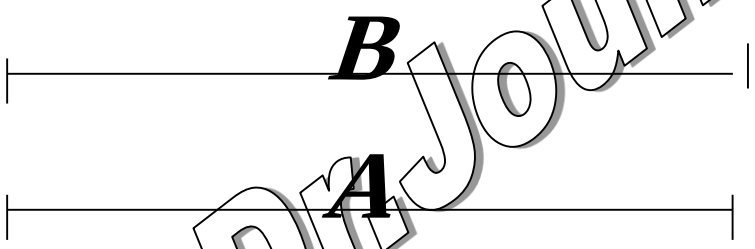
F = Practical Normality/Theoretical Normality

F =0.098/0.1 = 0.98

Standardization of NaOH solution using Potassium hydrogen phthalate

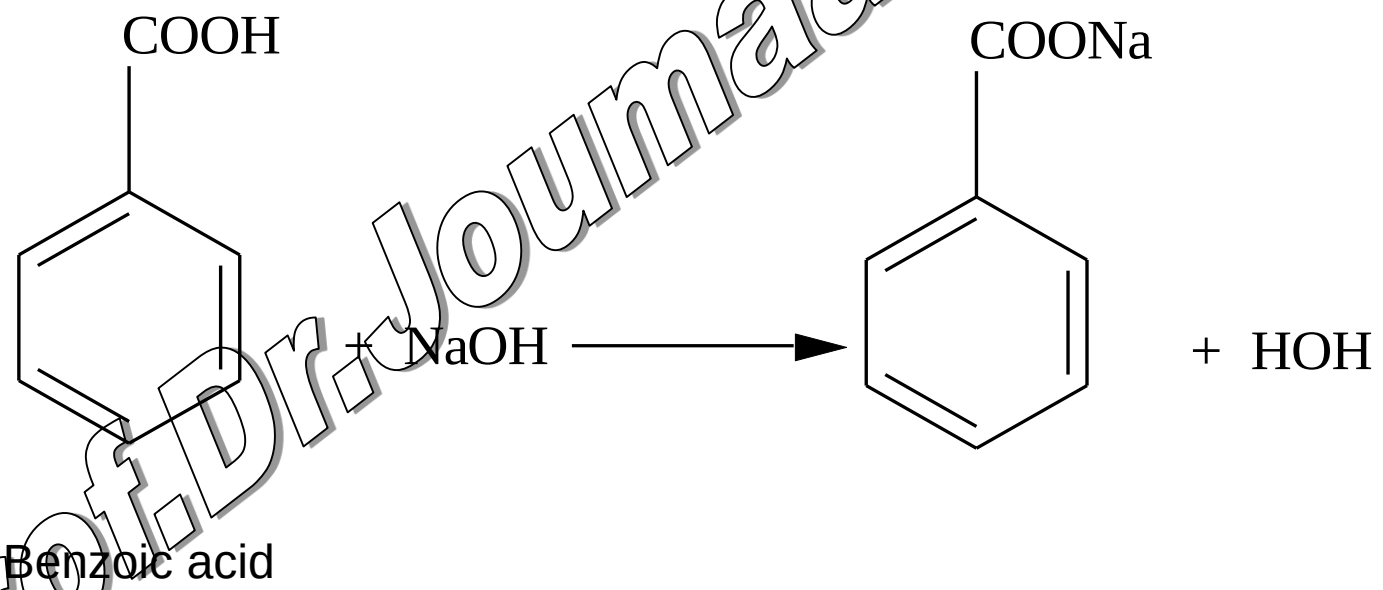
Direct Titration

- ***Direct titration is a process in which a standard solution (reagent) B is added to a solution of an analyte (A) until end-Point***



$$A \equiv B$$

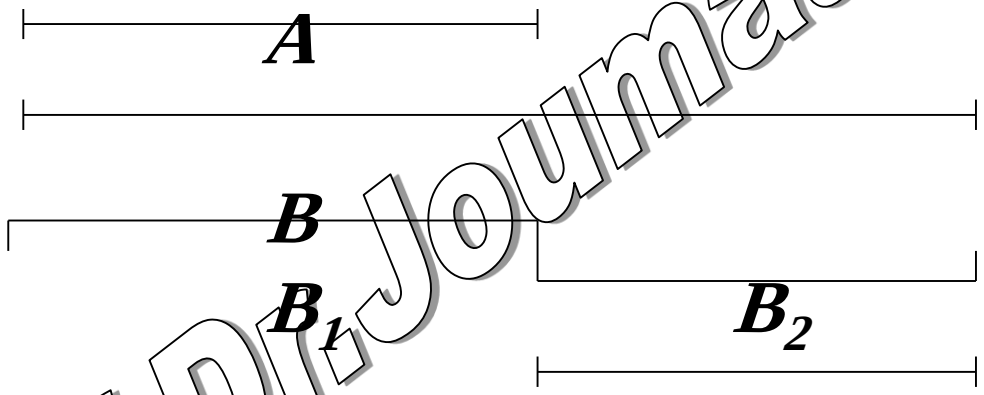
Direct Titration



Benzoic acid

Back-Titration

- ***Back-titration is a process in which the excess of a standard solution (B) used to consume an analyte is determined by titration with second standard solution (M). Back-titration are often required when the rate of reaction between the analyte an reagent is slow or when the standard solution lacks stability.***

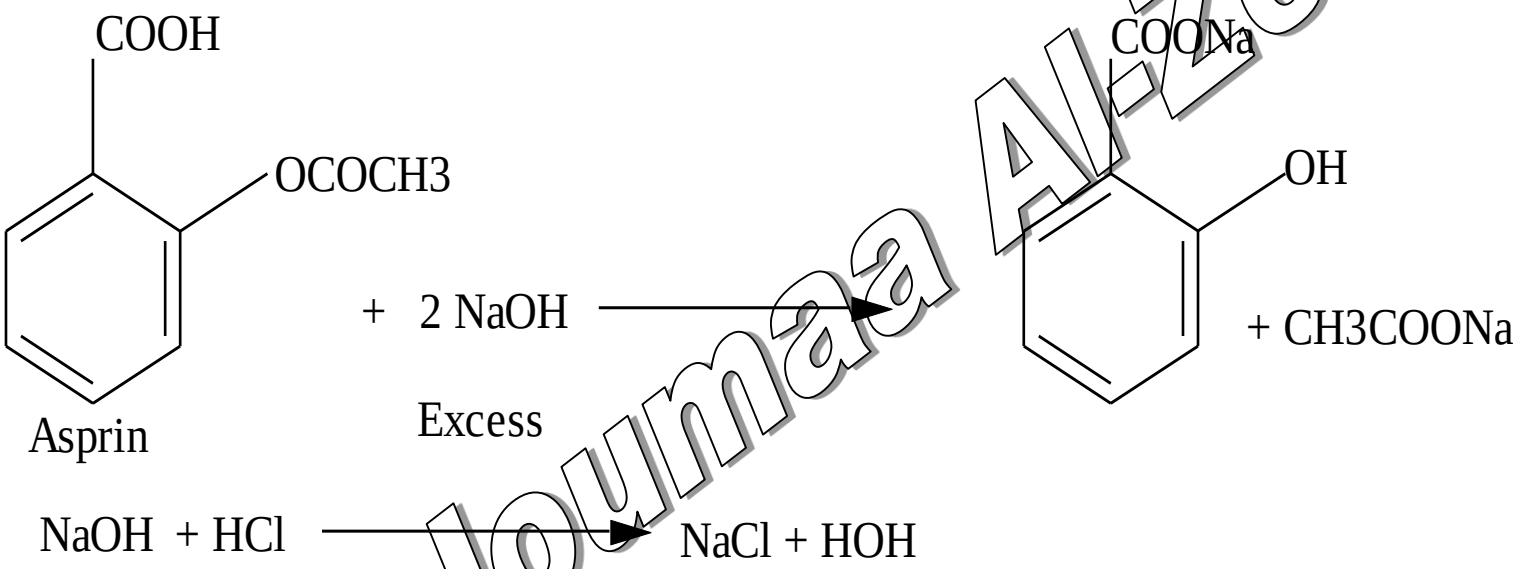


$M \equiv B_2$

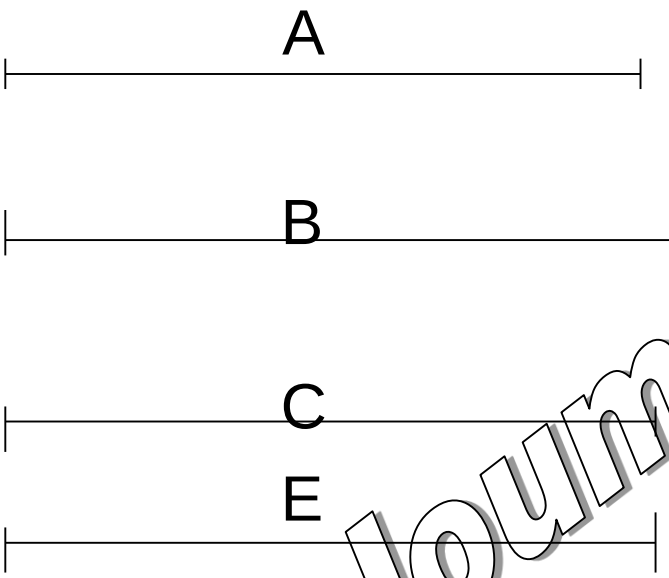
$B - B_2 \equiv B_1$

M

Back-titration



Replacement Titration



E = C = A

$$4\ NH_4Cl + 6HCHO \longrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$NH_4Cl \equiv HCl \equiv NaOH$$

Calculation methods in the Volumetric Titration

We depended on the equation and the Stoichiometric ratio.

- At eq.Point :

No. of Eq. in St.sol = No. of Eq. In analyte sol. (I)

N= No. of Eq / V ⟹ No. of Eq = N x V (II)

from I and II :

$$N_1 \times V_1 = N_2 \times V_2$$

Example 1

How many milliliters of 0.250 molar sodium hydroxide are required to neutralize 350.0 ml of 0.150 molar of hydrochloric acid.

Answer 210 ml

Example 2

How many milliliters of 0.250 molar Sodium hydroxide are required to neutralize 350.0 ml of 0.150 molar of sulphuric acid.

Answer 420 ml

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Q&A