Volumetric Analysis

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Volumetric Analysis

-is a branch of quantitative analysis, which depends upon the methods involving accurate measurement of volumes of liquid .

Titration also known as **titrimetry** ,-process of finding out the volumes of reagent required to bring out a definite reagent.

A reagent, called the *titrant* or *titrator* is prepared as a standard solution.

A known concentration and volume of titrant reacts with a solution of *analyte* or *titrand* to determine concentration.

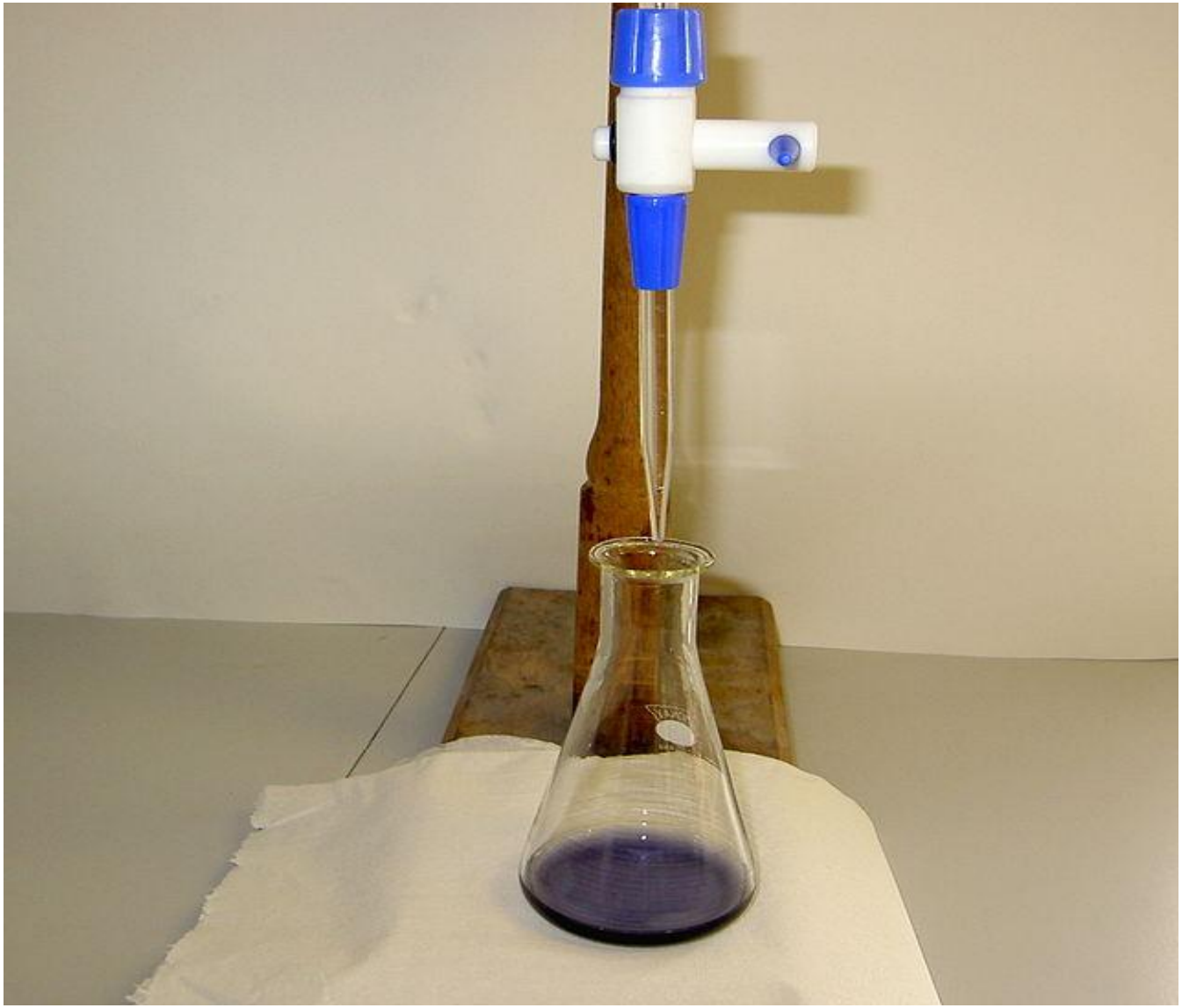
The volume of titrant reacted is called *titre*.

- The word "titration" comes from the Latin word *titulus*, meaning inscription or title.
- The French word *titre*, also from this origin, means rank.

Volumetric analysis originated in late 18th-century France.

Francois-Antoine-Henri Descroizilles developed the first burette (which was similar to a graduated cylinder) in 1791.

- Joseph Louis Gay-Lussac developed an improved version of the burette that included a side arm, and coined the terms “ pipette" and “burette" in an 1824.



Procedure

- A typical titration begins with a beaker orErlenmeyer flask containing a very precise volume of the analyte and a small amount of indicator(such as phenolphthalein) placed underneath a calibrated burette or chemistry pipetting syringe containing the titrant.

- Small volumes of the titrant are then added to the analyte and indicator until the indicator changes color in reaction to the titrant saturation threshold, reflecting arrival at the endpoint of the titration.

- Depending on the endpoint desired, single drops or less than a single drop of the titrant can make the difference between a permanent and temporary change in the indicator.

- Standard substances are divided into two types-Primary & Secondary standards

Primary standards -is a compound of sufficient purity from which a standard solution can be prepared by direct weighing of a quantity of it followed by dilution to give a definite volume of the solution.

The solution prepared by this method - Primary standard solution.

Requirements of a primary standard substance

1. It must easy to obtain, to purify, to dry, and to preserve in a pure state.
2. It should not be hygroscopic or deliquescent and must be stable in air.
3. Its composition should remain unaltered during its storage.
4. It should have high relative molecular mass so that the weighing errors may be minimized.
5. The substance must be readily soluble in water or the titration medium used.

Egs,

- Anhydrous sodium carbonate(Na_2CO_3)
- Crystalline oxalic acid ($H_2C_2O_4.2H_2O$)
- Mohrs salt($FeSO_4.(NH_4)_2SO_4.6H_2O$)
- Potassium dichromate ($K_2Cr_2O_7$)
- Copper sulphate($CuSO_4.5H_2O$)
- Arsenious oxide (As_2O_3)
- Potassium iodate (KIO_3)

Secondary standard solution

-A substance from which the direct preparation of a standard solution is impossible but whose solutions can be used as standard solutions if their concentrations are determined previously by suitable method.

Standardisation method- conc.of such substance are determined by titrating with the primary standard substance.

The standardized solution are called-secondary standard solution

Egs, NaOH, HCl, H_2SO_4 , HNO_3 , $KMnO_4$

End point,equivalence point, or stoichiometric point **point**

- -of a chemical reaction is the point at which chemically equivalent quantities of acid and base have been mixed. It can be found by means of an indicator, most often phenolphthalein or by instrumental methods.
- Indicator- a substance which is used to indicate the completion of the reaction in a titration.

Standard solution-a solution of accurately known concentration. Or, a solution is one that contains a known amount of the solute per liter of the solution.

Properties of an ideal standard solution

1.Stable so that its concentration doesn't change with time.

2.Quick to react with the analyte so that the time between successive additions of the reagent can be minimized.

3.Capable of reacting selectively with the analyte as per simple balanced equation.

4.Capble of reacting completely with the analyte so aw to yield a satisfactory end point.

Division of Volumetric analysis

Divided into four

1. Acidimetry & alkalimetry
2. Permanganometry
3. Dichrometry
4. Iodometry & Iodimetry

1. Acidimetry & alkalimetry

Acidimetry -estimation of bases by titration with standard acid solution.

eg, estimation of NaOH using stad. Oxalic acid

$$2NaOH + H_2C_2O_4 \longrightarrow Na_2C_2O_4 + 2H_2O$$ Ph

Alkalimetry-estimation of acid by titration with standard base solution.

eg, estimation of HCl using stad. Oxalic acid

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$ MO

Acid –Base indicators

-are substance which are employed for the visual detection of the end point in acid-base titration, Because their colour change due to the pH change at the end point.

- they are weak organic acids or bases.

Eg. Phenolphthalein(a weak acid)

- Colour change-Pink to colourless
- Colour change in pH range

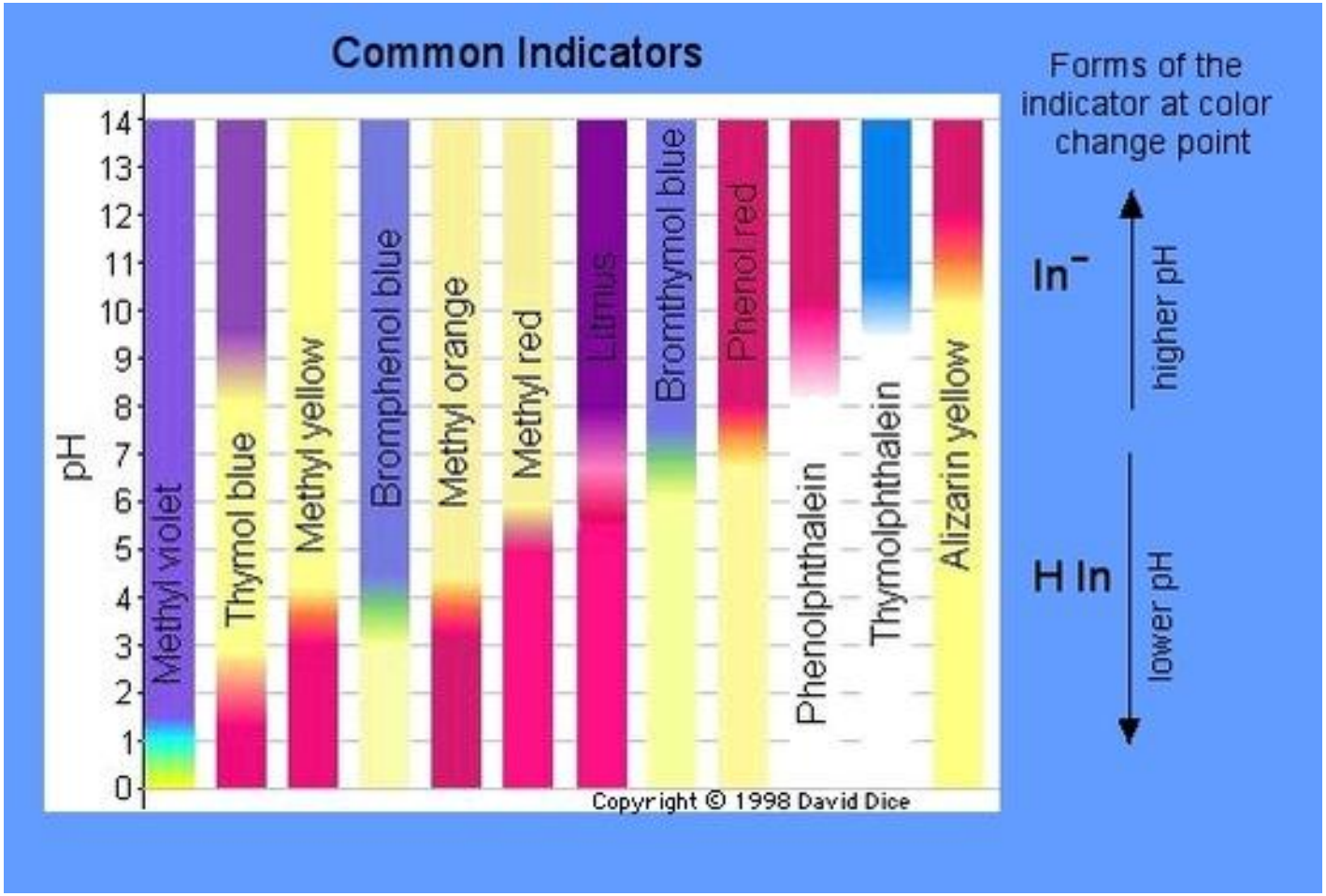
(colourless-acidic) 8—9.5(pink-base)

Methyl orange(weak base)

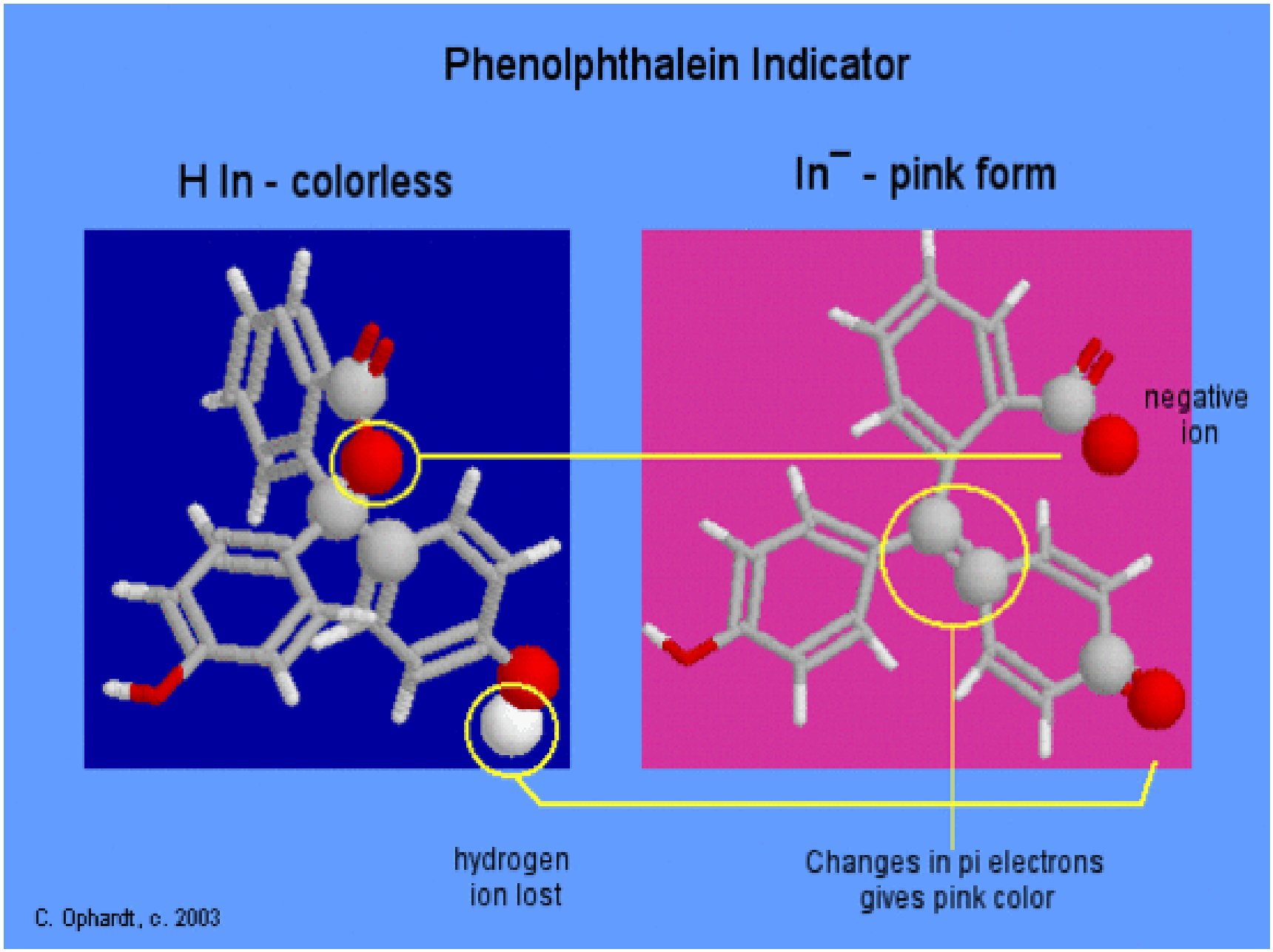
- Colour change- Golden yellow to red orange
- Colour change in pH range

(red orange -acidic) 3.1—4.4(Golden yellow - base)

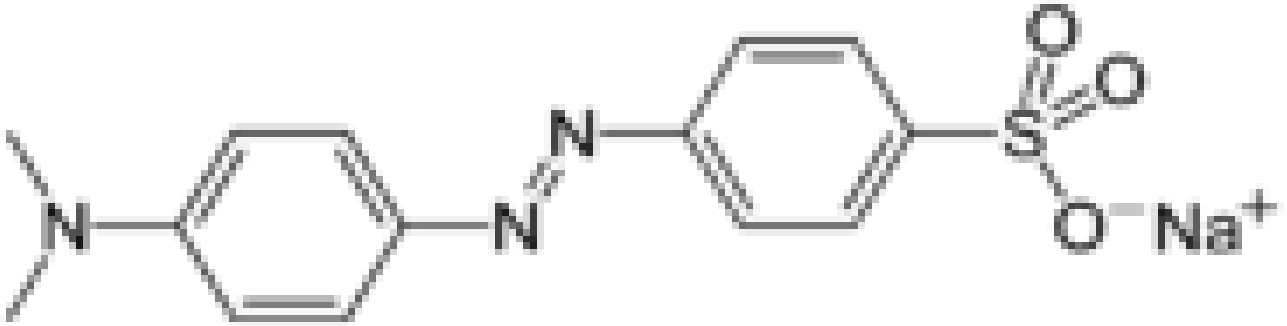
Acid –Base Indicator



Phenolphthalein Indicator



Methyl Orange



1.Strong acid -strong base titrations

Strong acid –HCl, HNO_3 ,H_2SO_4

strong base- NaOH, KOH

-Just before the completion of the reaction Ph of the solution in the conical flask is 10.

-But at end point the Ph is suddenly drops to about 3.5.

i.e., PH range 10-3.5

-can use Ph(pH)—9.5 to 8

MO(pH)—4.4 to 3.1

2. Strong acid –weak base titrations

Strong acid –HCl, HNO_3 ,H_2SO_4

Weak base- Na_2CO_3 , K_2CO_3 , NH_4OH

pH range at he vicinity of the end point 7.5-3.5

-can't be use Ph(pH)—9.5 to 8

can use MO(pH)—4.4 to 3.1

3. weak acid – strong base titrations

Strong Base– NaOH, KOH

Weak acid-oxalic acid, acetic acid

pH range at he vicinity of the end point 10-6.5

-can be use Ph (pH)—9.5 to 8

can't be use MO (pH)—4.4 to 3.1

4. weak acid – weak base titrations

No sharp change in the vicinity of the end point.

Gradual change from 7.5 to 6.5.

-so ph or MO are not used for this titration.

-it is done using conductometric titrations

Table 5.2 : Some acid-base indicators

Indicator	*pH range and colour change*
Thymol blue	← Red — 1.2 – 2.8 — Yellow →
Methyl orange	← Red — 3.1 – 4.4 — Yellow →
Methyl red	← Red — 4.2 – 6.3 — Yellow →
Bromothymol blue	← Yellow — 6.0 – 7.6 — Blue ⟶
Cresol red	← Yellow — 7.2 – 8.8 — Red ⟶
Phenolphthalein	← Colour-less — 8 – 9.5 — Pink ⟶
Alizarin yellow	← Yellow — 10.1 – 12 — Red ⟶

General shapes of different neutralization titration Value

most suitable indicator for it.

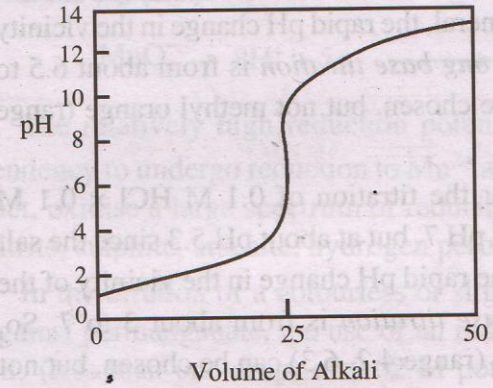


Fig. 5.1 (a) : Strong acid-strong base titration

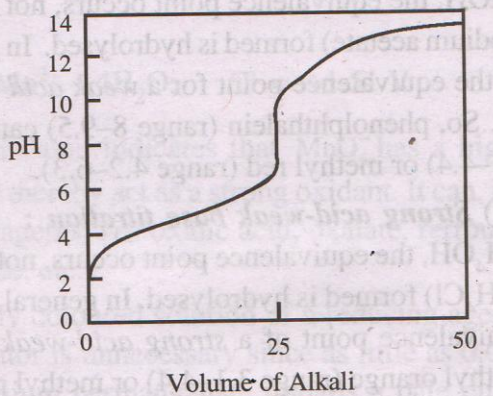
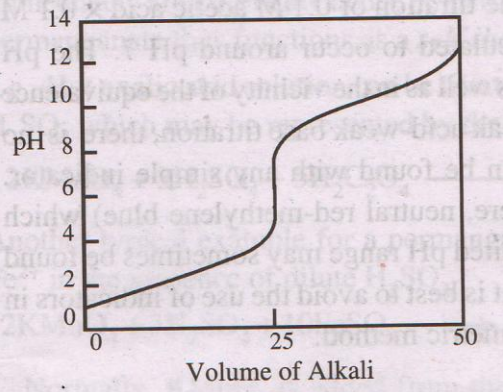
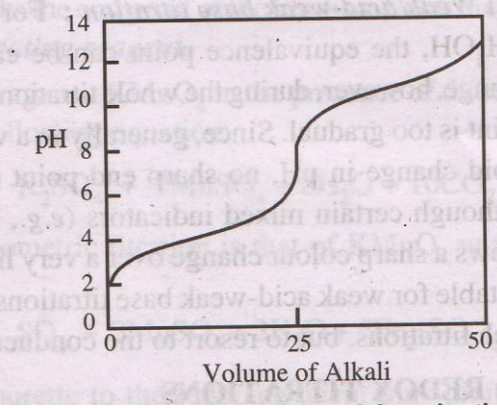
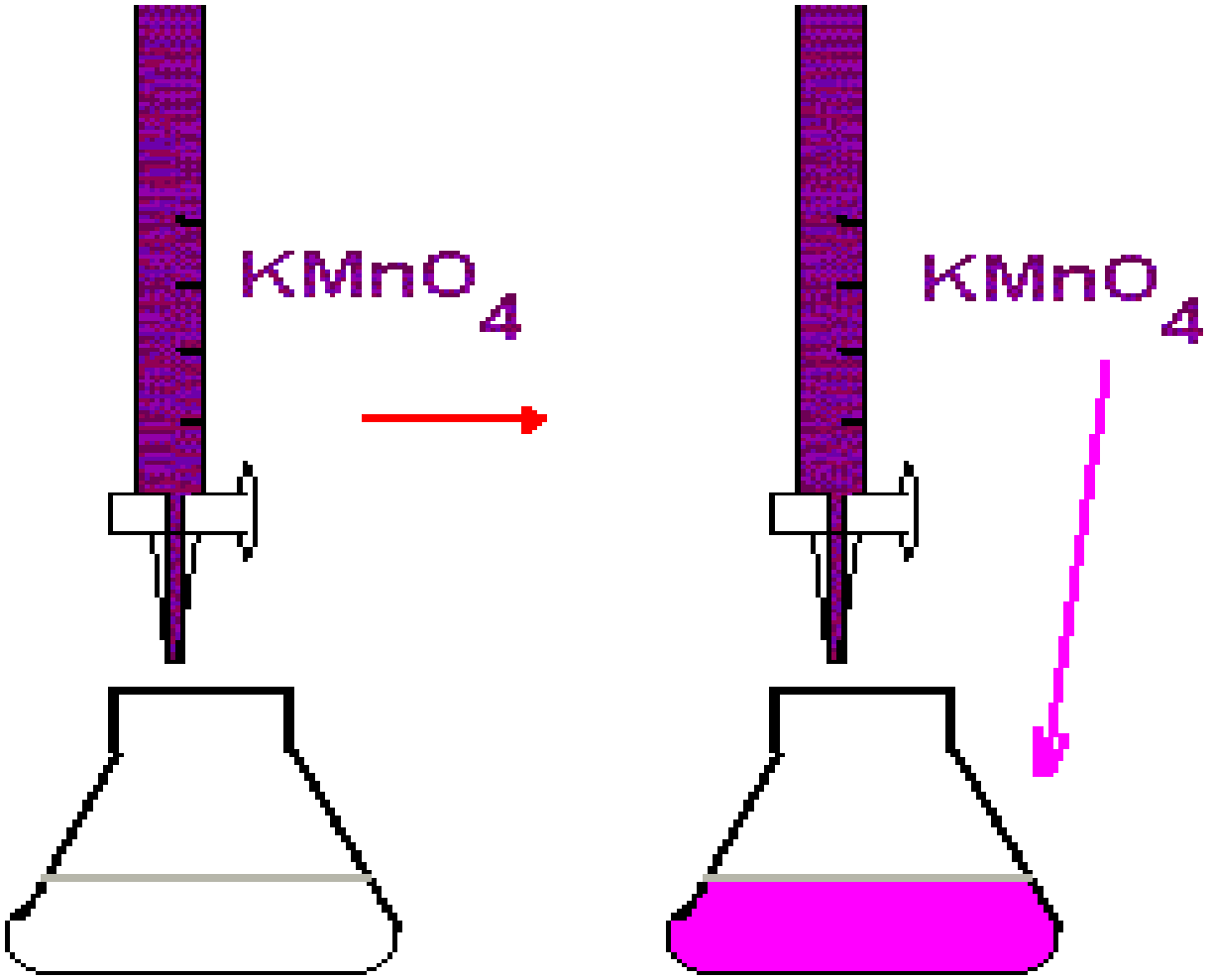


Fig. 5.1 (b) : Weak acid-strong base titration





Redox titrations



Redox titrations

- Chemical reaction involved in oxidation and reduction.
- Oxidizing agent are titrated against the reducing agent
- Common oxidents are-

Potassium permanganate-permanganometry

Potassium dichromate-Dichrometry

Cerium (IV) sulphate -Cerimetry

I_2 - Iodometry or Iodimetry

Permanganometry

- Oxidising agent- $KMnO_4$- self indicator
- -it is a powerful oxidizing agent in acid medium and it gets easily reduced to colourless manganous ions in redox reactions.

Oxi.agnt (redn) redu.agnt(oxidn)

$$\overset{+1\ +7\ -8}{KMnO_4} + 3H_2SO_4 + 5\overset{+2\ +6\ -8}{H_2C_2O_4} \rightarrow K_2SO_4 + \overset{+2\ \ -2}{MnSO_4} + 8H_2O + 10\overset{+4\ \ -4}{CO_2}$$

$H_2C_2O_4$- 2+2x+-8=0 x=3

CO_2 –oxi.no. of C =+4(increases -oxidation-redu.agent)

- Egs, Hot oxalic solution X $KMnO_4$ in dil. H_2SO_4
- Fe^{2+} X $KMnO_4$ in dil. H_2SO_4
- Not use Conc.H_2SO_4 &(conc.or dil.) HCl ,HNO_3 because these are oxidising agent hence it interfere the reaction.
- *It is a secondary stad.sub. and standardized using stad. solution of stad. sub.like crystalline oxalic acid, Mohrs salt etc.*

Dichrometry

- Oxidising agent- $K_2Cr_2O_7$ - indicator
- -it is a powerful oxidizing agent in acid medium.
- It oxidizes reducing agent like ferrous sulphate, nitrite, sulphate etc.
- In acid medium dichromate is reduced to green Cr^{3+} ions

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + Fe_2(SO_4)_3$$

Two methods are used to detect the end point

i) External indicator-end point detected by testing a drop of the solution with potassium ferricyanide.

-ferrous ions give blue colour with ferricyanide due to the formation of prussian blue, $KFe(Fe(CN)_6)$.

-end point no blue colour ,hence no ferrous ion.

ii) Internal indicator-

a. N-phenyl anthranilic acid (0.1% solution in 0.005 M NaOH).
b. Diphenylamine(1%soln. in conc. H_2SO_4)
c. Sodium diphenylamine sulphonate (0.2 % aqu.soln.)

Redox Indicator(oxidation reduction indicators)

-Indicators indicate end point due to the change in the potential difference in accordance with the Nernst equation.

$$E = E^{o} + \frac{2.303RT}{nF} \log \frac{(\text{oxidised state})}{(\text{reduced state})}$$

-near to the end point a sudden change in the potential takes place.

-certain compounds responds to the sudden change in potential and undergo a colour change.

-such compounds used to mark the end points of redox titrations.

- Redox indicator is one which marks the end point of a titration by undergoing a colour change in response to a sudden change in potential that occurs in the vicinity of the equivalence point.
- It shows different colours in oxidized and reduced form.

Eg, $Indicator_{ox} + ne^- \longleftrightarrow Indicator_{red}$

colour A *colour B*

- *The potential of E_{In} of the system at 298 K is given by the Nernst equation.*

$$E_{In} = E^{o}_{In} - \frac{0.059}{nF} \log \frac{(In_{red})}{(In_{ox})}$$

E^{o}_{In} = standard electrode potential

Eg, Fe^{2+} X dichromate in dil. H_2SO_4 (1 M) and phosphoric acid(0.5M).

Reduction form –diphenylamine- Oxidation form

(colourless) (violet)

Reduction -N-phenyl anthranilic acid –Oxidation

(colourless) (red violet)

Iodimetry & Iodometry

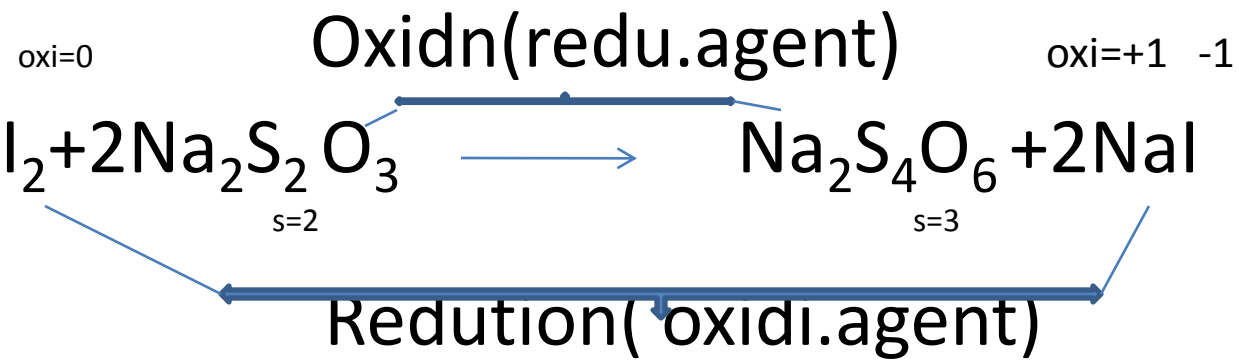
-titrations in which oxidizing agent is *Iodine.*

Iodimetry-direct titrations of as standard solution of Iodine against a reducing agent.

Iodometry-Titrations of Iodine liberated from a chemical reaction with a reducing agent.

Reducing agent: Sodium thiosulphate, arsenious oxide, sodium arsenite etc.

Eg, Iodine oxidises sodium thiosulphate to sodium tetrathionate



Indicator: Starch is added at the end of the titration. It reacts with Iodine to form a Blue coloured complex. When all Iodine is reduced to Iodide, the blue colour varnishes- the end point.

Iodine is slightly soluble in water. Conc. In aqueous Iodine decreases during handling due to its volatility.

To overcome this,

Iodine solution is usually prepared by dissolving Iodine in aqueous potassium Iodide solution forms triiodide ion(I_3^-)

$$I_2 + I^- \longleftrightarrow I_3^-$$

An oxidant like $KMnO_4$ or $K_2Cr_2O_4$ can be oxidise KI to an equivalent amount of Iodine.

Eg,

$$KMnO_4 + 8\,H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + I_2$$

Similarly,

$$K_2Cr_2O_7 + 14HCl + 6KI \longrightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

The liberated iodine then titrated against sodium thiosulphate using starch as indicator.

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

This is the basis of Iodometric methods.

Copper sulphate also estimated Iodometrically.

Here excess KI added to the $CuSO_4$ Solution which results in the liberation of equivalent amount of I_2.

$$CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$$

$$CuI_2 \longrightarrow Cu_2I_2 + I_2$$

The liberated iodine is titrated against sodium thiosulphate using starch as indicator

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Principles of Colorimetric Analysis

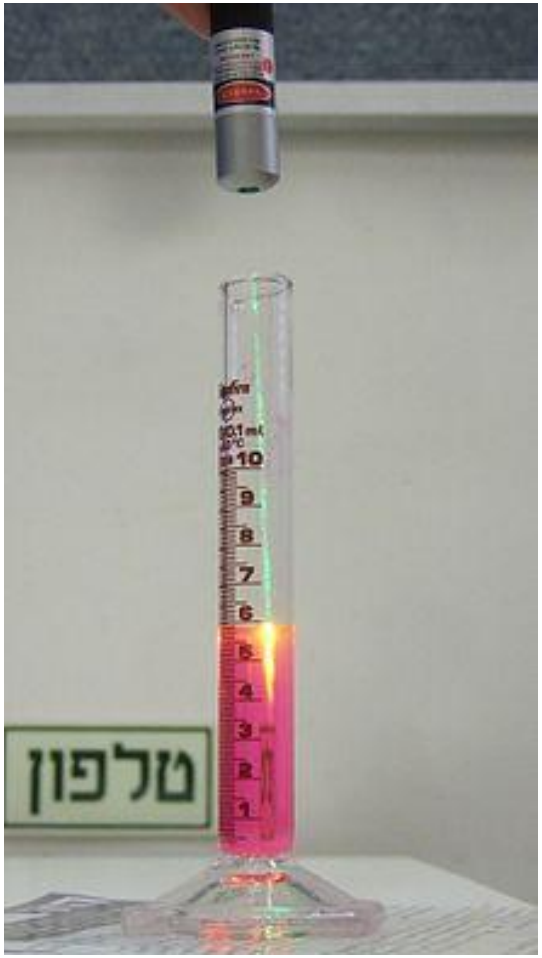
Colorimatry-is an analytical technique involving the measurement of intensity of light absorbed in the visible region.

-It based on the Beer-Lambert Law.

Beer-Lambert Law- Absorption of light:

states that when a beam of monochromatic radiation passes through a solution of an absorbing substance, the rate of decreases of intensity of radiation with thickness of the solution is directly proportional to the intensity of incident radiation as well as concentration of the solution

An example of Beer–Lambert law: green laser light in a solution ofRhodamine 6B. The beam intensity becomes weaker as it passes through solution



- Mathematically,

$$-dI/dx \propto I\ c$$

I= intensity of radiation, c= conc. of the solution

$$-dI/dx = k\ I\ c$$

k= constant, characteristic of both the radiation and the medium

or, $$-dI/I = -k\ c\ dx$$

If I_o = incident intensity.

I_x = emergent intensity after passing through a thickness x of the medium.

$$\int_{Io}^{Ix} dI/I = -kc \int_{o}^{x} dx$$

$$\ln I_x / I_0 = -k\ c\ x$$

$$\log I_x / I_0 = \frac{-k}{2.303}\ c\ x$$

$$\log I_0 / I_x = \frac{k}{2.303}\ c\ x$$

$$\log I_0 / I_x = \varepsilon\ c\ x$$

k/ 2.303= ε new constant=molar absorption coefficient or molar excitation coefficient when conc. expressed in $molL^{-1}$ and thickness in cm.

$$A = \varepsilon\ c\ x$$

$A = \log I_0 / I_x$ ، A= absorbance or optical density of the solution

$$\varepsilon = \frac{1}{c\ x} \log \frac{I_0}{I_x}$$

When $I_x = (1/10)\, I_0$, $c = 1 mol^{-1} L^{-1}$

then, $$\varepsilon = \frac{1}{x}$$

Hence, the molar absorption coefficient or molar extinction coefficient is defined as the reciprocal of the thickness of a 1 molar solution which reduces the intensity of radiation to $1/10^{th}$ of its initial value.

For a given solvent and a radiation of a given frequency ε is a characteristic of a solute

ε- units - $Lmol^{-1} cm^{-1}$

The ratio of emergent light intensity(I_x) to the incident light (I_0) is called transmittance (T).

Transmittance (T)= I_x / I_0

Since, A= log I_0 / I_x A= -log T

Limitations ., only valid if,

1. The solution is dilute,
2. There is no solute solvent interaction,
3. The molecular state of the solute does not change with change in concentration.

Applications

The law is used for the estimation of a substance in a solution by comparing its light absorbance with that of a solution of it of known concentration.

Instruments used--colorimeters and spectrophotometers.

Colorimetry -quantitative analysis

-used for the estimation of the concentration of a substance.

-measured by comparing the relative absorption of radiation by the substance in a test solution with respect to the known concentration of the substance.

Or, the variation of the colour of a system with change in concentration of some component forms the basis of colorimetric analysis.

Colour may be inherent in the desired component(analyte) itself or it may be developed by inducing the formation of a coloured compound by the addition of a suitable reagent to the analyte solution.

Eg, in determination of Fe^{2+} ,the colour developing reagent is ammonium thiocyanate in acidic medium.

The intensity of colour (extent of absorption) of the sample is then compared with those of appropriate standards, ie, with those obtained by treating solutions of known concentration of the substance in the same manner.

eg., Nesslers method for ammonia in 1856.

-found that on adding alkaline solution of HgI_2 and KI to a dil.solution of NH_3 produced a yellow to reddish brown colloid with colour determined by the concentration of ammonia.

A comparison of the sample's colour to that for a series of standards was used to determine the concentration of ammonia.

Equal volumes of the sample and standards were transferred to a set of tubes with flat bottom.

The tubes are placed in a rack equipped at the bottom with a reflecting surface , allowing light to pass through the solution.

The colours of sample and standards were compared *visually* by looking down through the solutions.

In visual colorimetry,

natural or artificial white light used as light source.

-determination are usually made with visual colour comparison with the help of an instrument called colorimeter or colour comparator.

Colorimetry is the forefather of modern molecular absorption spectroscopy.

According to Beer-Lambert law,

$$\log I_0 / I_x = A = \varepsilon c x \text{ ---------- (1)}$$

I_0 = intensity of incident light, I_x = intensity of transmitted light

A=Absorbance(optical density) of the solution

c = concentration of the solution in mol dm^{-3}

x =thickness of the solution column

ε= molar absorption coefficient.

- From, eqn (1),it follows that absorbance (A) of the solution in a transparent or optical cell (called *Cuvette*) of fixed length (x) is directly proportional the concentration (c) of the solution.
- This means that a plot of 'A' against 'c' will be straight line passing through the origin is called the calibration curve.
- A series of dilute solutions of known concentration of a substance are prepared and their absorbance (A) measured using the instrument photoelectric colorimeter.

Calibration Curve

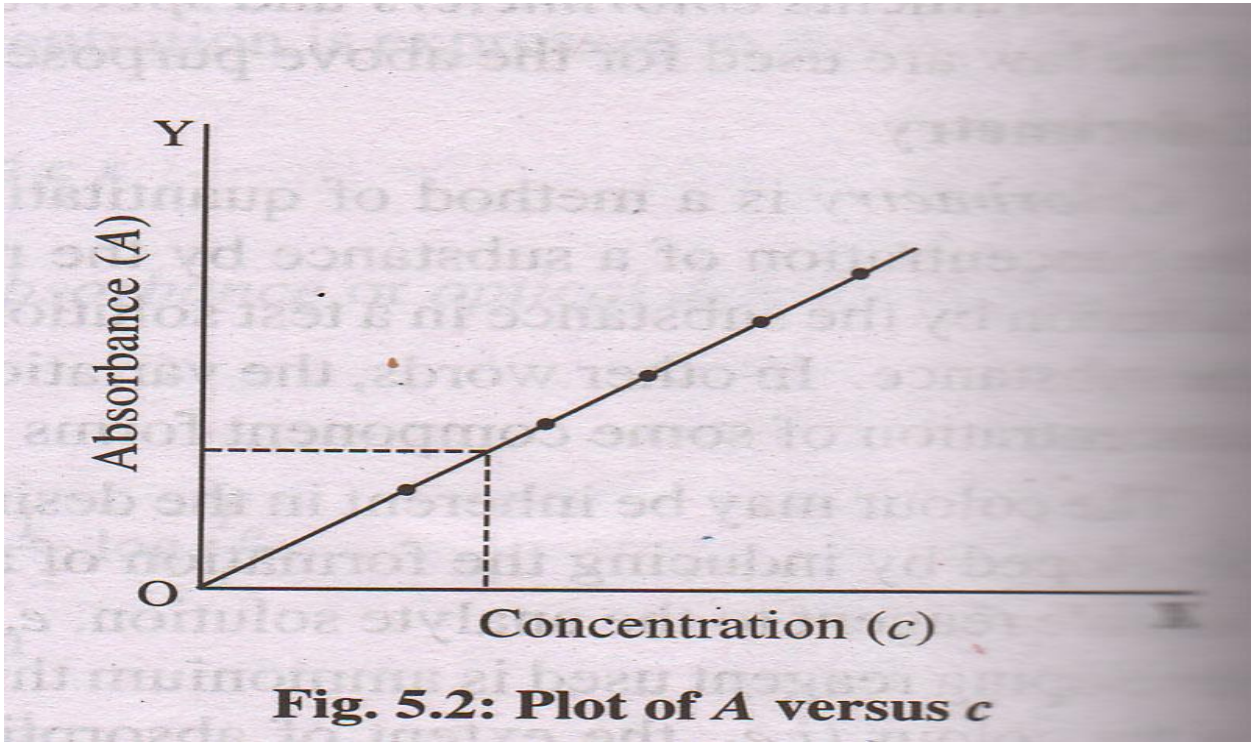


Fig. 5.2: Plot of *A* versus *c*

- Absorbance measurement under similar conditions is made with the solution of the substance of unknown concentration.
- From the measured absorbance the calibration line is then used to determine the unknown concentration

- Photoelectric colorimetry, a photoelectric colorimeter is used to detect the absorbence of the sample solution.
- Photoelectric cell carries the functions that the human eyes carried out in visual colorimeter.
- White light(source) allow to pass through the filters to produce narrow band of wavelength.
- Filters- materials in the form of plates of coloured glass or gelatin etc.-which transmit only a limited spectral region.
- Filter is placed between source and the sample
- Hence only a single optical path between the source and detctor, the instrument is called a single –beam instrument

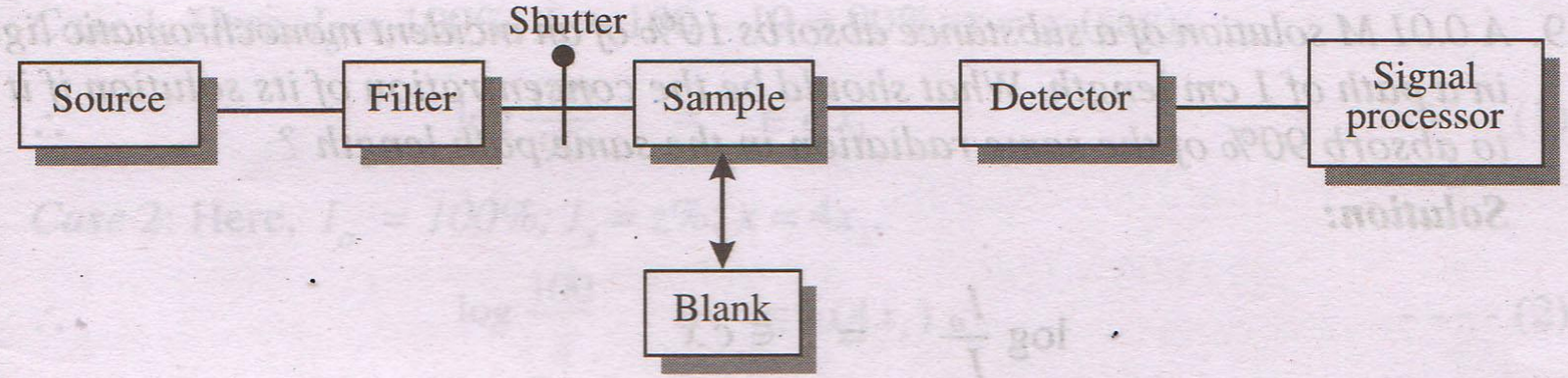


Fig. 5.3: Flow-diagram of a photoelectric colorimeter

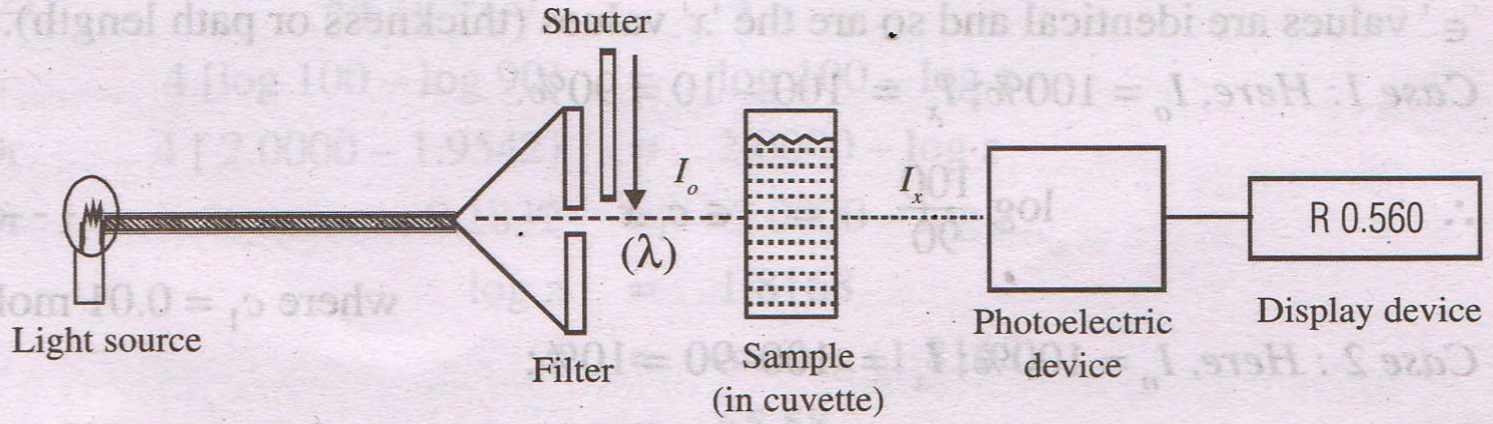
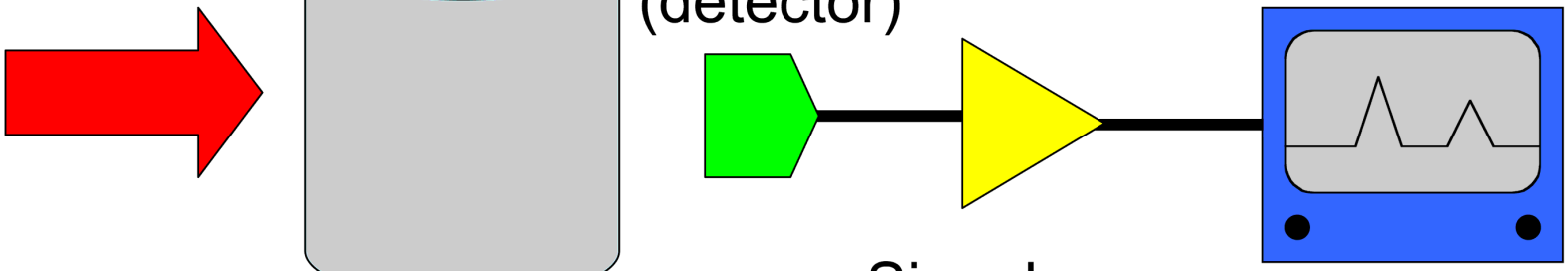


Fig. 5.4: Schematic diagram of a single-beam spectrophotometer

The instrument is calibrated to 0% T while using a shutter to block the source radiation from the detector. After removing the shutter, the instrument is calibrated to 100% *T* using an appropriate blank. The blank is then replaced with the sample and its transmittance (*T*) is measured. Direct measurement of the absorbance (*A*), which is related to the transmittance (*T*) as: $A = -\log T$, is also possible in modern instruments.

Analytical Instrument



Input Transducer (detector)

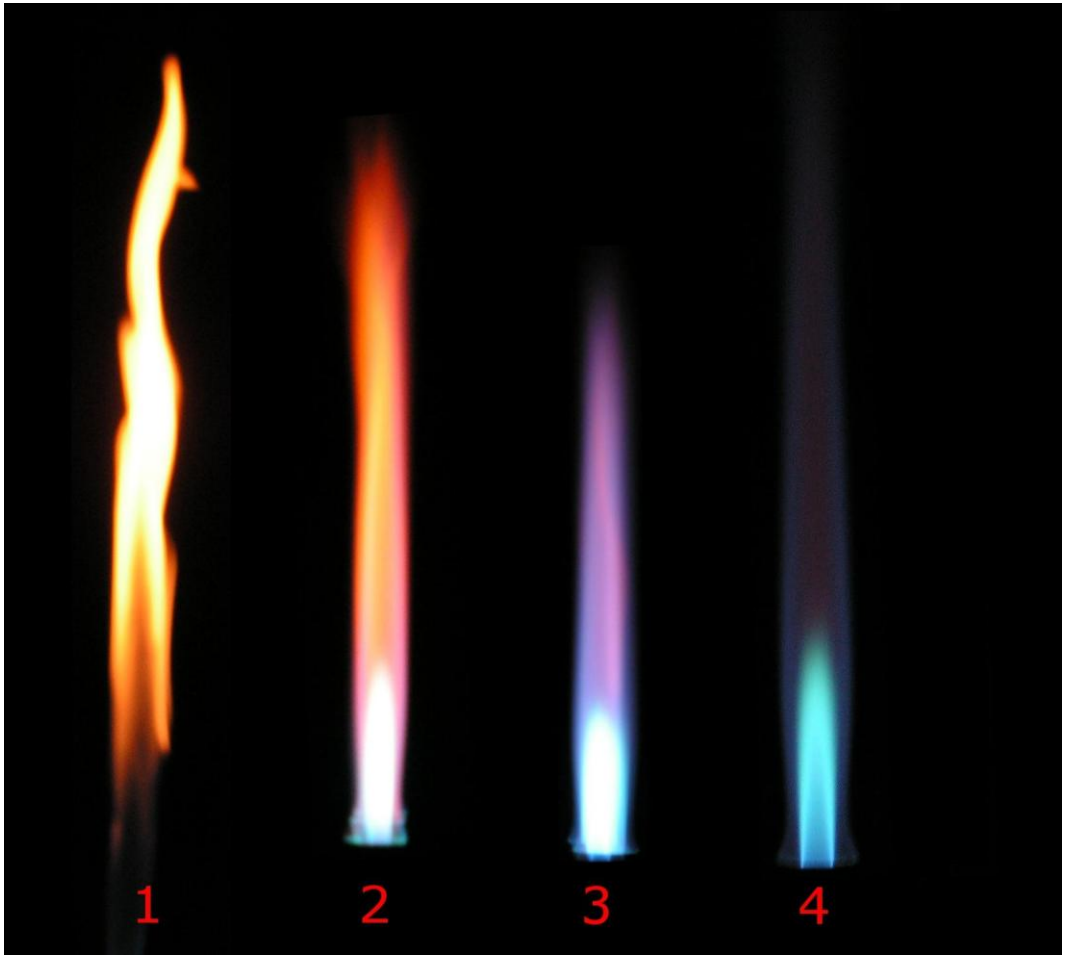
Stimulus:
- light
- heat
- current
- voltage

Sample

Signal Processor
- amplifier
- digitizer

Readout:
- meter
- plotter
- computer

BUSEN FLAME



Cu