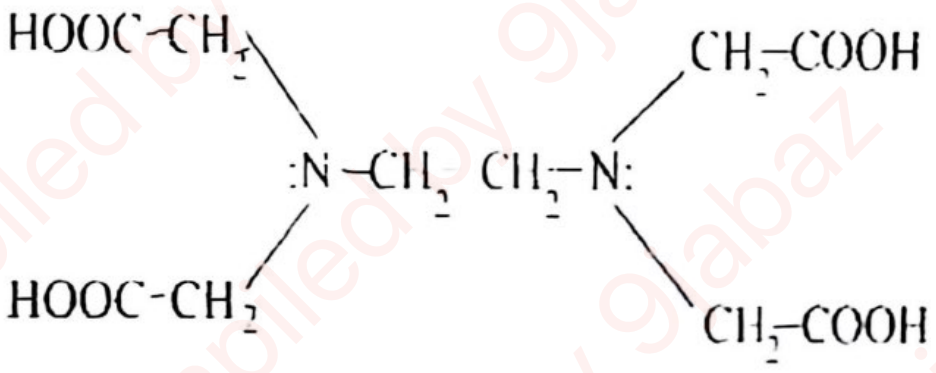
EDTA Titrations:

What is EDTA???

- ✓ EDTA is Ethylene Diamine Tetra Acetic acid.
- ✓ It has four carboxyl groups and two amine groups.

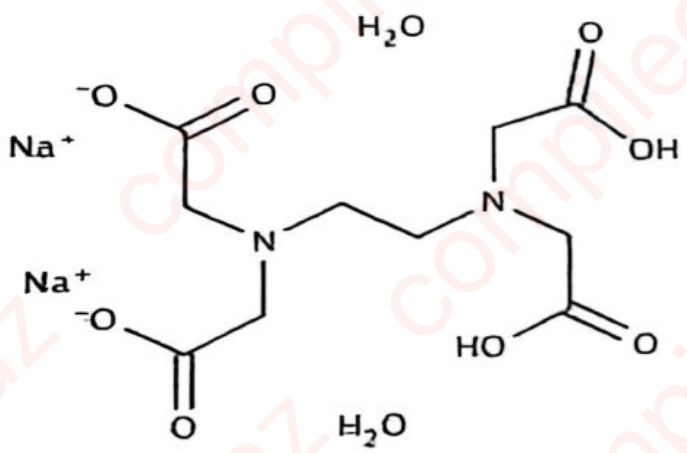
structure of EDTA

Commonly EDTA is rep esented in the acid form as H_4Y.



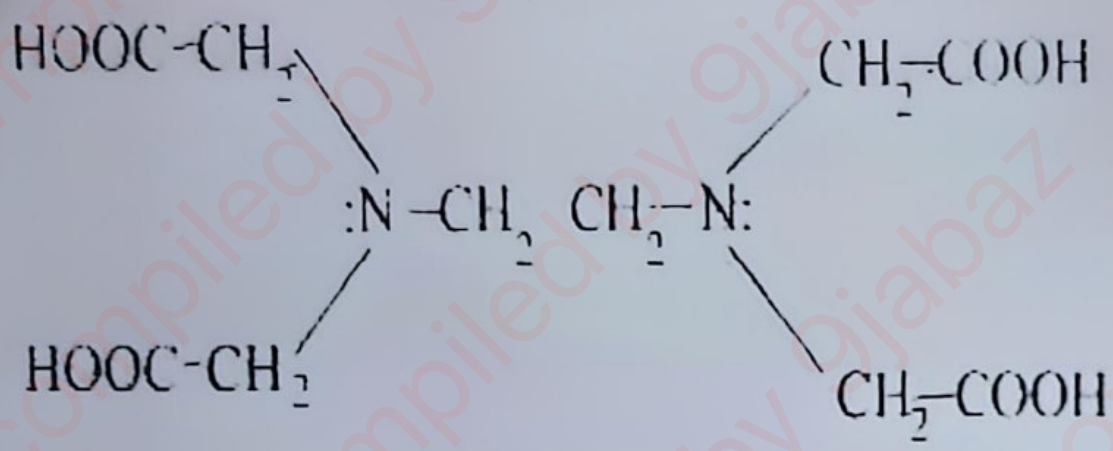
EDTA = H_4Y

Due to low solubility of acid form of EDTA in water, its disodium dihydrate EDTA salt i.e. $Na_2H_2Y.2H_2O$ is used



disodium dihydrate EDTA = $Na_2H_2Y.2H_2O$

Different Forms of EDTA



EDTA = H_4Y

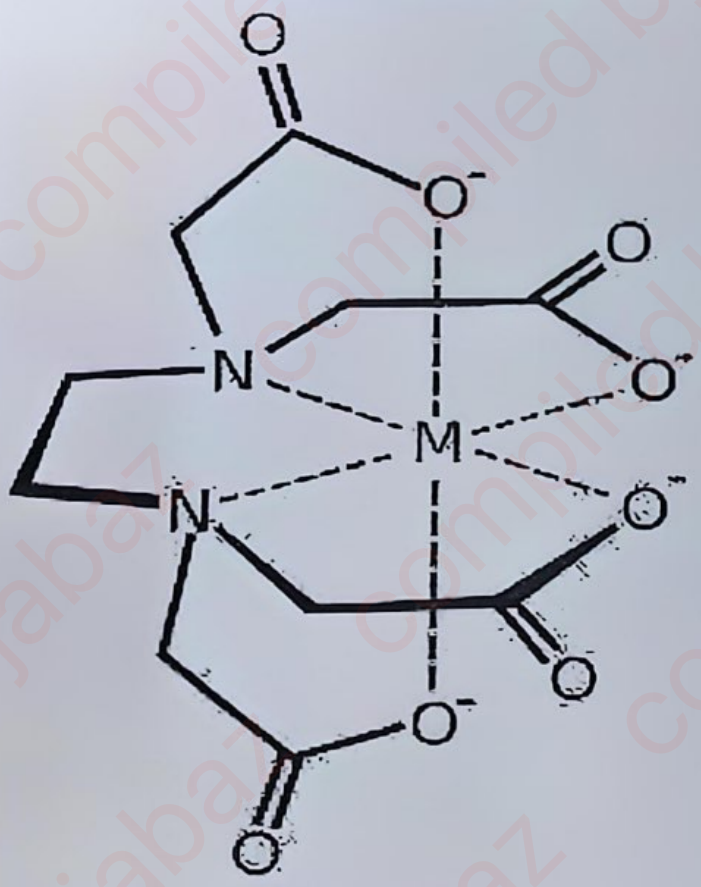
The fully protonated form H_4Y is only a major component in very acidic solutions (pH<3).

Throughout the pH range of 3 to 10 the species H_2Y^{2-} and H_3Y^- are predominant.

The fully unprotonated form Y^{4-} is dominant only in very basic solutions (pH>10).

EDTA has four carboxyl groups and two amine groups.

EDTA is polydenated ligand as it donate its six lone pairs of electrons for the formation of coordinate covalent bonds with metal cations to form Metal-EDTA complex.



Metal-EDTA complex

Stability of Metal-Ligand Complexes

The stability of complexes is influenced by a number of factors related to the ligand and metal ions.

1. Nature of the metal ion: Small ions with high charges lead to stronger complexes.

2. Nature of the ligand: The ligands forming chelates impart extra stability (chelon effect). For example the complex of nickel with a multidentate ligand is more stable than the one formed with ammonia.

3. Basicity of the ligand: Greater basicity of the ligand results in greater stability of the complex.

4. Size of chelate ring: The formation of five- or six - membered rings provides the maximum stability.

5. Number of metal chelate rings: The stability of the complex is directly related to the number of chelate rings formed between the ligand and metal ion. Greater the number of such rings, greater is the stability.

7. Steric effects: These also play an important role in the stability of the complexes.

Role of pH in EDTA titrations

-EDTA titrations are carried out in buffered solution of the metal ions to be estimated.

-The use of proper pH is important and is related to the stability constant of a metal-EDTA complex.

-E.g. Alkaline pH is required for the metals having low stability constant.

Low Alkaline to mild acidic pH is required for the metals having high stability constant.

- The dissociation reactions of acid form EDTA, H_4Y are also pH dependant. pH is also an important criteria for the proper functioning of the indicator substance.

Thus it is very important to maintain the pH during the EDTA titrations

Advantages of EDTA as titrant:

1. ETDA **form stable complex** with various metal ions.
2. The complexation occurs in a **single step** and hence the titration of the metal **produce a sharp change** in the metal ion concentration at the equivalence point.
3. The **Metal-EDTA complexes are all water soluble** and hence all studies can be performed in aqueous media.
4. EDTA **forms 1:1 complex with all metal ions** irrespective of all charge on the metal ions. The stoichiometry is hence same for all metal ions. The reaction can be represented as:

$$M^{n+} + H_2Y^{-2} + H_2O \longrightarrow MY^{(n-4)} + 2H^3O^+$$

Limitations of EDTA as titrant:

1. Formation of insoluble hydroxides:

   Many ETDA titrations are carried out under alkaline pH which may lead to formation of insoluble hydroxides or basic salts that may compete with the complexation process .

2. Lack of selectivity:

   Since EDTA forms stable complexes with most of the metal ions, it lacks selectivity if it is used to estimate a single metal cations from a solution of mixture of metal ions.

Absolute formation constant

EDTA forms 1:1 complex with all metal ions irrespective of all charge on the metal ions. The stoichiometry is hence same for all metal ions. If fully unprotonated form of EDTA (Y^{-4}) is react with metal ion as follows:

$$M^{+n} + Y^{-4} \rightleftharpoons MY^{(n-4)+}$$

Then absolute formation constant K_{MY} is given as,

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{+n}]\,[Y^{-4}]}$$

K_{MY} is also referred as absolute stability constant. Higher the value of K_{MY}, higher is the stability of complex formed.

Metal Cation	K_{MY}	Log K_{MY}	
Mg^{2+}	4.9×10^{8}	8.69	Group I Titrated in pH 8-11
Ca^{2+}	5.0×10^{10}	10.70	
Sr^{2+}	4.3×10^{8}	8.63	
Ba^{2+}	5.8×10^{7}	7.76	
Mn^{2+}	6.2×10^{13}	13.79	Group II Titrated in pH 4-8
Fe^{2+}	2.1×10^{14}	14.33	
Co^{2+}	2.0×10^{16}	16.31	
Ni^{2+}	4.2×10^{18}	18.62	
Cu^{2+}	6.3×10^{18}	18.80	
Zn^{2+}	3.2×10^{16}	16.50	
Cd^{2+}	2.9×10^{16}	16.46	
Al^{3+}	1.3×10^{16}	16.13	
Pb^{2+}	1.1×10^{18}	18.04	
Hg^{3+}	6.3×10^{21}	21.80	Group III Titrated in pH 1-4
Fe^{3+}	1.3×10^{25}	25.1	
V^{3+}	7.9×10^{25}	25.9	
Th^{4+}	1.6×10^{23}	23.2	

Conditional formation constant

In absolute formation constant only fully unprotonated form of EDTA (Y^{-4}) is taken consideration. EDTA is tetra protonic acid. It is represented as H_4Y. The four different stages of dissociation of this tetra protonic acid can be represented as follows:

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad K_{a1} = \frac{[H^+]\,[H_3Y^-]}{[H_4Y]}$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{-2} \qquad K_{a2} = \frac{[H^+]\,[H_2Y^{-2}]}{[H_3Y^-]}$$

$$H_2Y^{-2} \rightleftharpoons H^+ + HY^{-3} \qquad K_{a3} = \frac{[H^+]\,[HY^{-3}]}{[H_2Y^{-2}]}$$

$$HY^{-3} \rightleftharpoons H^+ + Y^{-4} \qquad K_{a4} = \frac{[H^+]\,[Y^{-4}]}{[HY^{-3}]}$$

✓Due to such important role of pH in complex formation with EDTA , normally the solution of metal ions are buffered so that the pH will remain constant.

✓In this way the Conditional formation constant (K'_{MY}) can be estimated and it is possible to calculate and construct the titration curve from which it is possible to judge the feasibility of the Complexometric titration.

✓Instrumental methods used for end point detection in Complexometric titrations are : Spectrometric analysis, Ampheromtric analysis, Potentiometric analysis

Metallochromic indicator

✓The metallochromic indicators are organic compounds which are capable of forming intensely coloured complex with EDTA.

✓This metal –indicator complex is weaker than the Metal-EDTA complex and it has different colour than uncomplexed indicator.

✓During the course of titration, the metal ion from metal – indicator complex is replaced to form Metal-EDTA complex.

Requirement for Metal ion indicator

1. The colour must be sufficiently intense, so that a minimum amount of indicator can be used.
2. The colour contrast between the indicator and Metal-indicator complex should be readily observable.
3. The Metal-indicator complex should possess sufficient stability to ensure a sharp colour change, however it should be less stable than Metal-EDTA complex.
4. The change in equilibrium from metal-indicator complex to the Metal-EDTA complex should be sharp and rapid.

5. The colour reaction of the indicator should be selective.
6. The indicator must be very sensitive to metal ions so that the colour change occurs at near the equivalence point.
7. The indicator must be stable in the titration medium.
8. The indicator must be stable on storage also.
9. All the above requirements must be fulfilled in the pH range in which the proposed titration is to carried out.
10. It should be commercially available in adequate purity.

Theory of metal ion indicators

The reaction corresponding to use of a metal ion indicator in an EDTA titration can be represented as

$$M\text{-}In + EDTA \longrightarrow M\text{-}EDTA + In$$

This reaction will take place only if the M-EDTA complex is more stable than the M-In complex.

$$M + In \longrightarrow M\text{-}In$$

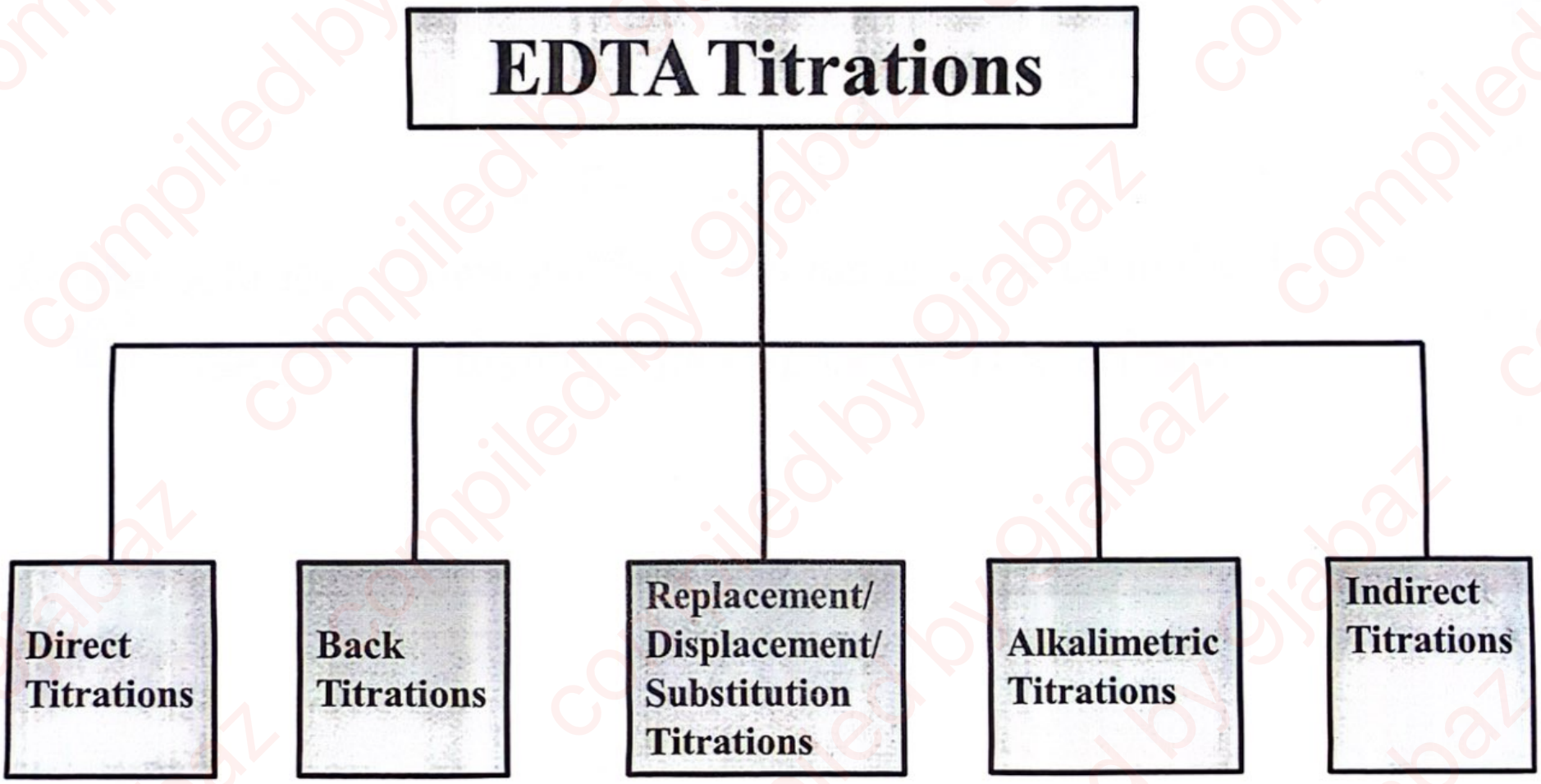
Stability of the Metal-Indicator complex K_{In}, is given by the equation

$$K_{In} = \frac{[M\text{-}In]}{[M]\ [In]}$$

Since, the indicator colour change also affected by the hydrogen ion concentration, so it is convenient to define the conditional indicator constant K'In which varies with pH.

For small the error, $K'_{In} > 10^4$ and the ratio of conditional formation constant of the metal-EDTA complex K'_{MY} to K'_{In} should be of the order 10^4 to provide a good end point.

Types of EDTA Titrations:



Direct Titrations:

- ✓ This is a direct determination of a metal ion by adding standard EDTA titrant to the sample solution.

Metal ion + EDTA ⟶ [Metal-EDTA] complex

- ✓ The solution containing the metal ion is buffered to the desired pH *and titrated* directly with standard EDTA solution.
- ✓ Some auxiliary complexing agent such as tartarate can be added to prevent ~~the prevent~~ the precipitation of the hydroxide of metal ion.
- ✓ Cu^{+2}, Zn^{+2}, and Ni^{+2} can be determine by using direct titration method.

Back Titrations:

- ✓ This is method, an excess of standard EDTA is added to the sample solution of metal ion.
- ✓ The resulting solution will contain unreacted EDTA which is then back titrated with standard metal ion solution in the presence of indicator.

$ZnCl_2$, $ZnSO_4$, $MgCl_2$, $MgSO_4$ is used as standard metal ion solution.

- ✓ Al^{+3}, Co^{+2}, Pb^{+2}, Mn^{+2}, Hg^{+2}, and Ni^{+2} can be determine by using Back titration method

Replacement, Displacement or Substitutions Titrations:

- ✓ This is method, weak EDTA complex of another metal ion (M2) is added to the solution of metal ion (M1) to be determined.
- ✓ Mg-EDTA & Zn-EDTA are frequently used weak EDTAcomplex
- ✓ The weaker metal EDTA complex is replaced with strong metal EDTA complex.
- ✓ The equivalent amount of metal M2 freed from the weaker complex can be titrated with standard EDTA solution.
- ✓ This method is useful for the determination of Ca^{+2} ion.

Alkalimetric Titrations:

- ✓ This method, use the principle of liberation of free H^+ ions during the complexation.
- ✓ The reaction between metal ion and EDTA H_2Y^{-2} produce H^+.

$$M^{+n} + H_2Y^{-2} \longrightarrow MY^{(n-4)+} + 2H^+$$

- ✓ The free H^+ ions is titrated with standard solution of alkali like NaOH by using suitable acid-base indicator.
- ✓ The H^+ ions can also be determined by instrumental method.

Indirect Titration:

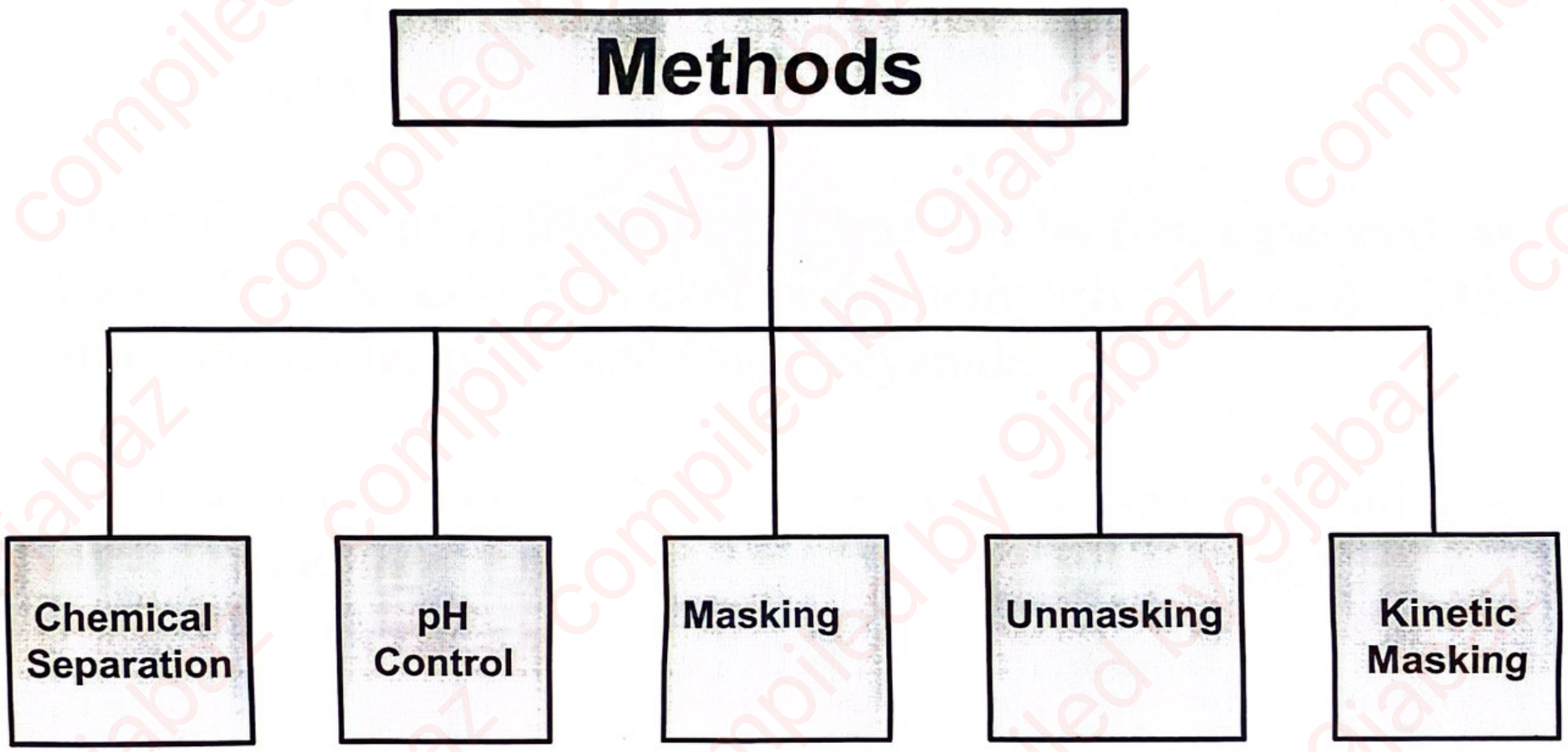
✓This method is used to determine the ions such as Halides, phospates, and sulphates that do not form complex with EDTA.

✓In the determination of sulphate ion, SO_4^{-2} ion solution is treated with excess of standard solution of Barium ion.

✓The formed precipitate of $BaSO_4$ is filtered off and unreacted Barium ions present in filtrate is titrated with EDTA.

✓In this way, we are able to indirectly determine the amount of sulphate ion present in the sample solution.

Methods of increasing the selectivity of EDTA as Titrations



Chemical Separation

❖In this technique, the selectivity is increases by separating the species from other components from the sample solution.

❖The separated species is then dissolved in suitable solvents and then titrated against EDTA using indicator.

❖Eg: Ca^{+2}, Mg^{+2}, Ni^{+2} and Cu^{+2} ions can be first separated as Ca-oxalate, Ni-DMG (Nickel bis(dimethylglyoximate)), Mg-ammonium phosphate and Cu-thiocyanide.

❖These precipitate are then dissolved in separate suitable solvents and then titrate against EDTA using indicator.

Control of acidity of pH of the solution

❖In this technique, the selectivity is increases by controlling the pH of the solution. That is depend on the hydrogen ion concentration.

❖So by adjusting the pH of the sample solution containing several metal ions, it is possible to allow only a single species to react with EDTA.

❖E.g.: Ca^{+2} can be determined in the presence of Mg^{+2} in strongly alkaline solution (pH < 10).

❖Trivalent ions like Bi+3, Fe+3 can be selectively determined from the solution of bivalent metal ions in strongly acidic solution (pH ~ 2).

Use of masking and demasking agents:

Masking agents act either by precipitation or by formation of complexes more stable than the interfering ion-EDTA complex. Masking is a process in which substance is prevented to take part in the reaction without physical separation of it. The reagent used in masking is known as masking agent

a) Masking by Precipitation

b) Masking by Complex formation

a) Masking by Precipitation: Many heavy metals e.g.- Co, Cu and Pb, can be separated either in the form of insoluble sulphides using Sodium sulphide, or as insoluble complexes using thioacetamide.

These are filtered, decomposed and titrated with disodium EDTA.

Other common precipitating agents are :

-sulphate for Pb and Ba,

-oxalate for Ca and Pb,

- fluoride for Ca, Mg and Pb,

- ferrocyanide for Zn and Cu,

- 8-hydroxy quinoline for many heavy metals.

Eg. Thioglycerol ($CH^2SH.CHOH.CH^2OH$) is used to mask Cu by precipitation in the assay of lotions containing Cu and Zn.

4.Potassium cyanide reacts with silver, copper, mercury, iron, zinc, cadmium, cobalt and nickel ions to form complexes in alkaline solution

5.Potassium iodide is used to mask the mercury(II) ion as $(HgI^4)^{2-}$ and is specific for mercury. It can be used in the assay of mercury(II) chloride.

6.Tiron (disodium catechol-3,5-disulphonate) will mask aluminium and titanium as colourless complexes. Iron forms highly coloured complex

7.Triethanolamine [N(CH2.CH2.OH)3] forms a colourless complex with aluminium, a yellow complex with iron(III), the colour of which is almost discharged by adding sodium hydroxide solution, and a green manganese(III) complex

Use of Demasking

In this technique, the one of the cation is first masked and remaining free cation is titrated with standard EDTA.

Then previously masked cation is damasked by using suitable reagent to get free cation. This free cation is then titrated by using standard EDTA.

Formaldehyde , chloral hydrate and methanol acetic acid mixture (3:1): use to demask cyanide complexes of cadmium and zinc

❖eg. Formaldehyde is used to damasked Zn-CN complex

$$[Zn(CN)_4] + 4HCHO + 4H^{+} \longrightarrow Zn^{+2} + 4HOCH_2CN$$

(Hydroxy ACN)

❖ This free Zn^{+2} ion is then titrated by using standard EDTA.

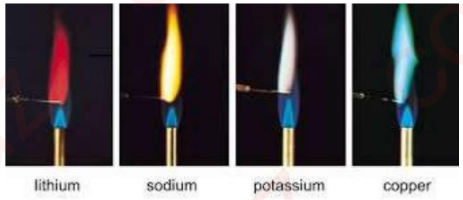
❖ Thus it is possible to determine Zn in the presence of Ca.

Flame Emission Spectroscopy (FES)

In flame emission spectroscopy, measurement of the radiation emitted by the excited atoms is measured and it is co-related to concentration of the sample.

FES is generally used for the determination of alkali and alkaline earth elements. (Na, K, Li, Ca, etc.).

This technique is useful for qualitative as well as quantitative analysis. Alkali and alkaline earth metals gives characteristic colour to the flame.



Flame Emission Spectroscopy (FES)

Wavelength emitted (flame colour) is used for qualitative analysis, while intensity of emission is related to the concentration.

This technique is mainly used in hospitals to measure the level of Na and K in body fluid and tissues.

Flame Emission Spectroscopy

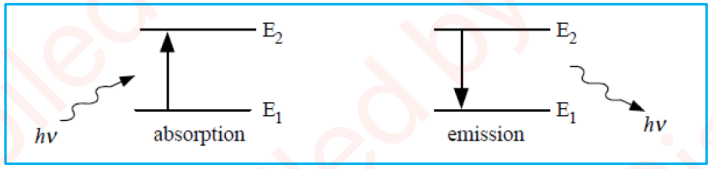
Principle:

Metallic salt solution introduced in flame in the form of mist. The flame evaporate solvent and form residual solid. These solid particles vaporize into gaseous state. These gaseous state molecules dissociate into neutral gaseous atoms or radicals.

Due to thermal energy, the atoms get excited to a higher energy level.

These excited atoms return to ground state and emit some radiations as a wavelengths .

The emitted wavelengths are specific for specific elements.



Flame Emission Spectroscopy

Principle:

Frequency of emitted light is calculated as

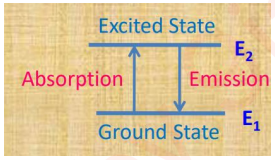
$h\gamma = E_2 - E_1$ ----------1

h= Plank's constant

γ =Frequency of emitted light

E_2= Higher energy level (Excited state)

E_1=Lower energy level (Ground State



Now $\gamma = C/\lambda$ ----------2 (C velocity of light and λ is frequency of emitted radiation)

Putting value γ of in eq.1

$hc/\lambda = E_2 - E_1$

$\lambda = hc/E_2 - E_1$

From the λ value , element present in the sample can be find out.

Flame Emission Spectroscopy

The number of excited atoms N* per cm3 can calculated by using Boltzmann's Equation

$$N^*/N = Ae^{-Ea/KT}$$

N= Number of atoms in ground state

N*= Number of atoms in excited state

A= Constant for particular element

Ea= Difference in energy of two level (excitation energy)

K= Boltzmann constant

T temperature of flame in kelvin

Thus number of excited state atoms are depend on the flame temperature.

At higher temperature, number of excited atoms are more.

Flame Emission Spectroscopy

In Flame Emission Spectroscopy the number of excited state atoms depend on the flame temperature. As temperature of flame increases number of atoms in excited state also increases.

Flames used in FES

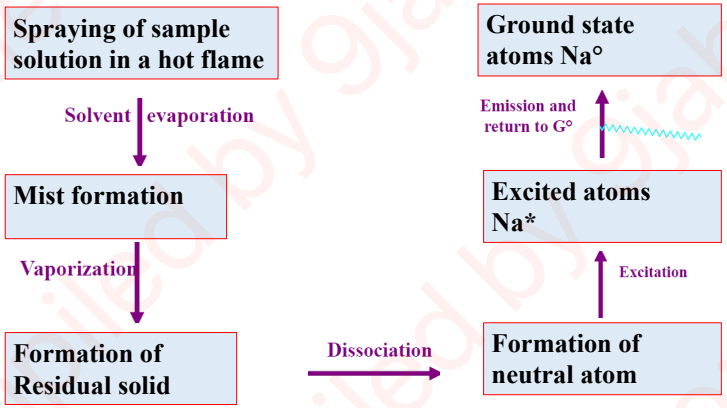
Types of Flames

Fuel / Oxidant	Temperature
acetylene / air	2200 °C
acetylene / O_2	3050 °C
Hydrogen /Air	2100 °C
Hydrogen /O_2	2780 °C
Methane/ Air	2000 °C
Methane/O_2	2700 °C
Propane/Air	1725 °C
Propane / O_2	2800 °C
Butane/Air	1900 °C
Butane / O_2	2900 °C

Selection of flame depends on the volatilization temperature of the atom of interest.

Flame Emission Spectroscopy

Events occur in FES



Flame Emission Spectroscopy

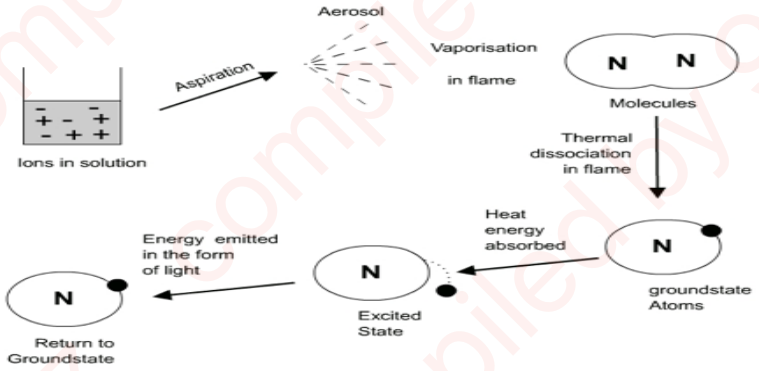


Fig 2: Brief overview of the process

Flame Emission Spectroscopy

Advantages of FES

1) It is more accurate method
2) It is faster technique
3) Detection sensitivity for alkali and alkaline earth metal is very good
4) Identification of one element in presence of other is possible
5) Easy to carry out

Disadvantages:

1) Only limited number of elements can be analyzed
2) Concentration required for analysis should be high
3) Sample in liquid form is necessary
4) There is possibility of spectral interference.

Flame Emission Spectroscopy

Factors affecting intensity of the flame

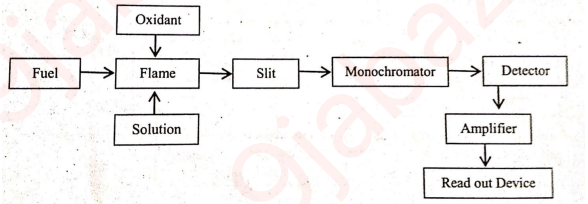
1) Concentration of analyte
2) Rate of formation of excited atoms in flame
3) Rate of introduction of sample in the flame
4) Temperature of the flame
5) Flame composition
6) Solvent used for dissolution

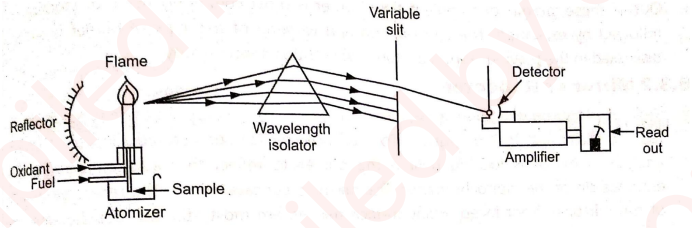
Alkali metals easily undergo ionisation , hence high temperature is not required for analysis of these elements. However for other elements including alkaline earth elements high temperature flame is preferred.

Flame Emission Spectroscopy

Instrumentation

1) Burner
2) Mirrors and slit
3) Monochromator
4) Detector
5) Amplifier
6) Read out device





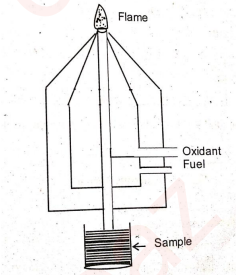
Flame Emission Spectroscopy

Instrumentation:

1) Burners:

Types of Burners

1) Total consumption burner:



Sample solution, fuel gas and oxidising gas are passed through separate inlet and mixed at the top of the flame.
Sample solution is converted tiny droplets, which on evaporation form residue and residue finally produce ground state atoms.

Advantages:

1) High sensitivity 2) No risk of explosion

Disadvantages:

1) Clogging is possible 2) Poor reproducibility
3) Noisy operation
4) Rate of sample introduction depends on viscosity of solution

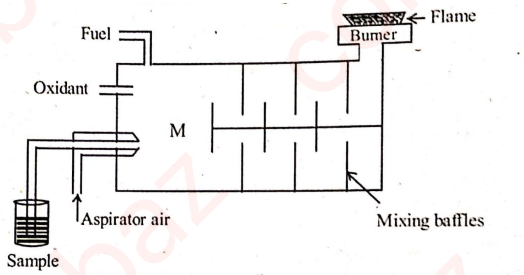
Flame Emission Spectroscopy

Instrumentation:

1) Burners

Types of Burners

2) Laminar flow /Premix burner:



Sample solution, fuel gas and oxidising gas are mixed in mixing chamber

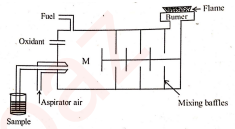
This mixture is then passed through a series of baffles where thorough mixing and formation of uniform droplets of the sample take place.

Flame Emission Spectroscopy

Instrumentation:

1) Burners:

Types of Burners



2) Laminar flow /Premix burner:

Advantages:

1) Atomization efficiency is high as droplets are finer
2) Sensitivity is very high sensitivity due to mixing baffles.
3) Good reproducibility
4) Little tendency to clog
5) No noisy operation

Disadvantages:

1) Rate of sample introduction is slow
2) Possibility of explosion in mixing chamber.
3) Selective evaporation of mixed solvent can lead to analytical errors.

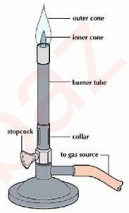
Flame Emission Spectroscopy

Instrumentation:

1) Burners:

Types of Burners

3) Mecker burner:



This burner was used in earlier days.

It used natural gas as fuel and air as oxidant

Flame temperature is low, hence only used for easily ionizable elements.

Advantages:

1) Burner cap can cooled easily.
2) Possibility of flashing back is less.

Disadvantages:

1) Only used for alkali metals
2) Flame is not homogeneous
3) Produce relatively low temperature

Flame Emission Spectroscopy

Instrumentation:

2) Mirrors:

It is important component in FES placed behind the flame. It collects all radiations emitted by the flame and focus towards the monochromator. Generally concave mirror is used. It creates inverted image of the flame, of equal size, at the location of the flame.

3) Slits:

Entrance and exit slits are used to control incoming and outgoing radiation

Flame Emission Spectroscopy

Instrumentation:

4)Monochromator:

Monochromator: It is the combination of the components from entrance slit to exit slit. There are two types of monochromators used in FES are Prism or grating. For more accuracy gratings are used and hence cost of instrument increases. In simple FES filter can be used. Overall cost of instrument is based on monochromator. The low cost instruments are useful for routine analysis or simple analysis.

Flame Emission Spectroscopy

Instrumentation:

4) Monochromator:

i) Prism:
It is triangular shape piece of glass or quartz. It work on refraction phenomenon.

ii) Diffraction Grating:

It is dispersing element that can isolate a selected band of wavelength. It is prepared by ruling a large number of parallel equidistance groves upon highly polished metallic surface. Approximately 15,000 to 30,000 groves per square inch are present on diffraction grating, these groves acts as scattering centers.

Flame Emission Spectroscopy

Instrumentation:

5) Detectors: a) Phototube

Detector convert the radiation energy into electrical signal. In Flame Emission Spectroscopy, radiation emitted by excited state atoms is detected by using photosensitive detector. In Flame Emission Spectroscopy phototube and photomultiplier tubes are used as a detectors.

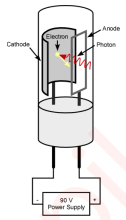


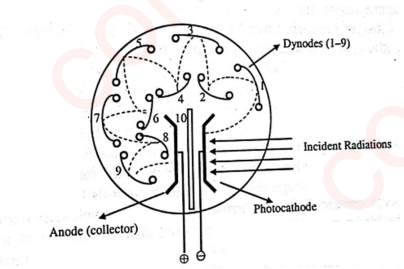
Photo Tube (Image Courtesy : http://people.whitman.edu/)

A phototube consists of an anode and a light-sensitive cathode. These are placed in an evacuated glass or quartz bulb. Approximately 100 volt potential difference is applied across the two electrode. When radiation (photon) strikes on surface of cathode, ejection of an electrons take place. These ejected electrons strikes on the surface of anode and current start flowing. This low intensity current needs amplification for measurement.

Flame Emission Spectroscopy

Instrumentation:

5) Detectors: b) Photomultiplier tube



Photomultiplier tube
Construction:

It contain photosensitive half cylinder of metal which act as cathode.

Inner surface of cathode is coated with light sensitive material like Cs_2O, Ag_2O and K_2O.

It consist of 9 dynodes which having coating of cesium metal which emits several electrons (2 to 5).

These electrons are collected by collecting electrode (anode).

Flame Emission Spectroscopy

Instrumentation:

5) Detectors: b) Photomultiplier tube

Working:

When light strike on cathode surface, it eject electrons due to photoelectric effect.

These electrons strike on the surface of first dynode and ejection of 2 to 5 electrons take place.

These electrons strike on surface of second dynode and ejection of more electron take place.

This process is continued up to 9^{th} dynode. Emitted electrons are collected by collecting electrode and current begin to flow. This current is amplified and measured by read out device.

Advantages:

1) It is very fast (response time is 10^{-9} second)
2) High sensitivity for U.V. and visible region.

Flame Emission Spectroscopy

Instrumentation:

6) Amplifier:

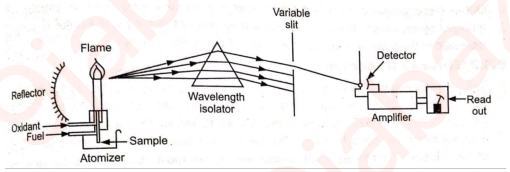
Amplifier is placed in between detector and read out device. It amplifies the signal received from the detector.

7) Read out device:

Galvanometer is used as read out device

Flame Emission Spectroscopy

Measurement by FES:



1) Sample is dissolved in suitable solvent.
2) Solution along with fuel and oxidant are aspirated to the flame.
3) Ground state atoms are produced
4) Ground state atoms goes to excited state and return to ground state by emitting radiation.
5) Radiation passed through monochromator and strike on detector.
6) Amplifier amplify detector response and give to read out device.

Flame Emission Spectroscopy

Interferences in FES:

Interference : Any process which causes error in determination is called interference.

Interferent is the substance present in the sample, blank or standard solution which affects the signal of the analyte.

1) Spectral Interference:

When emission lines overlap with each other, then this kind of interference is observed.

Emission of an interfering species either overlap or lies so close to the analyte band that resolution by the monochromator become difficult.

This interference arises when flame temperature is very high. At high temperature number of spectral lines are produced.

Spectral interference is very common in FES.

Example: Iron line at 3247.28 A^0 overlap with copper line at 3247.54 A^0

Aluminium line at 3082.15 A^0 overlap with vanadium line at 3082.11 A^0

Flame Emission Spectroscopy

Interferences in FES:

2) Ionization Interference:

Due to high flame temperature ionization of atoms take place.

FES is used for analysis of alkali and alkaline earth elements. Ionization energy of these elements is low , hence ionization interference is most common in FES

To overcome this effect easily oxidisable elements are added to the solution

Example: During analysis of sodium , potassium is added in the solution. Potassium undergo ionization and electrons are produced in the flame which help to prevent ionization of sodium in.

Flame Emission Spectroscopy

Interferences in FES:

3) Chemical Interference:

Because of formation of stable compound which cannot undergo decomposed at flame temperature.

Example Aluminum and magnesium form a thermally stable mixed oxide, thus low results are obtained for magnesium in presence of aluminum..

This process leads to lower number of atoms in the flame for excitation.

Example: Analysis of calcium: If phosphate ions present in the analyte solution, formation of calcium phosphate stable compound is observed.

This interference can be avoided by adding excess of lanthanum salt in the analyte solution. Lanthanum preferentially combines with phosphate ions and calcium will be unaffected.

Flame Emission Spectroscopy

Interferences in FES:

4) Anion error:

Anions interfere as components of salt and acid

Example: Chloride and sulphate can cause this type of interference.

5) Cation –Cation Interference:

Presence of metal cations of Na and K can cause this type of interference . This decrease the signal intensity.

Flame Emission Spectroscopy

Interferences in FES:

6) Background Absorption :

It is caused by absorption of the species other than the atoms at resonance wavelength.

It is wavelength dependent phenomenon and gives a positive error in the analysis.

It can be minimized by using Deuterium arc background correction (continuum source)

Flame Emission Spectroscopy

Applications of FES:

1) Qualitative analysis:

Alkali and alkaline earth elements can be detected by this technique. It is fast, simple and accurate technique.

2) Quantitative analysis:

For quantitative analysis, liquid sample is introduced into the flame and the intensity of radiation is measured. The quantitative analysis of alkali and alkaline earth elements can be done by using the following method.

a) Standard Addition Method

b) Internal Standard Method

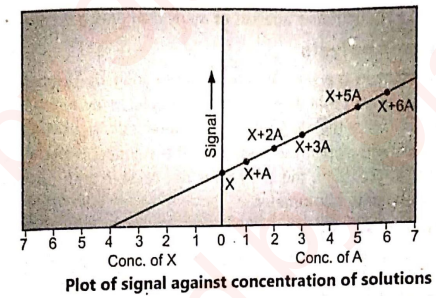
c) Calibration Curve Method

Flame Emission Spectroscopy

Applications of FES:

2) Quantitative analysis:

a) Standard addition method:



Plot of signal against concentration of solutions

1) Signal intensity (emitted radiation) of unknown sample(X) is measured.

2) Series of solution containing fixed amount of unknown (X) and different amount of standard is prepared.[(X+A), (X+2A), (X+3A), (X+4A), (X+5A), (X+6A)]

3)Signal intensity of each solution is measured and plot of signal vs concentration (X+A) is plotted.

4) Concentration of unknown solution(X) can determined by the intersection of the curve with the concentration axis.

Flame Emission Spectroscopy

Applications of FES:

2) Quantitative analysis:

b) Internal standard method:

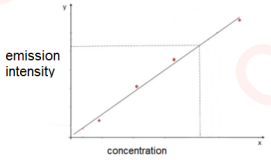
1) Series of standard solution is prepared.
2) Known amount internal standard (ex. Li) is added
3) Signal intensities of all standard solution having internal standard are measured.
4) Signal intensity of unknown solution is measured.
5) Graph of ratio of signal intensity vs concentration is plotted and concentration of unknown solution is determined.

Flame Emission Spectroscopy

Applications of FES:

2) Quantitative analysis:

c) Calibration curve method:



1) Series of standard solutions of element to be analyzed is prepared
2) Emission intensity of each standard solution is measured.
3) Emission intensity of unknown solution is measured.
4) Calibration curve of emission intensity vs concentration of standard solution is plotted.
5) Concentration of unknown solution is find out by extrapolation method.

Flame Emission Spectroscopy

Applications of FES:

3) Simultaneous Multielement Analysis:

Analysis of more than one element can be done by using FES. By using vidicon detector system multielement analysis is possible.

4. Miscellaneous Applications:

a) Soil and Water Analysis:

It is used in agriculture field for soil and water analysis. Sodium, magnesium, potassium, calcium, iron content of soil and water can be analyzed by FES.

It is useful for deciding proper fertilizer required for soil.

b) Food Analysis: This technique is very useful in analysis of food products. Fresh milk can be studied for there nutritional value. Butter milk, fruit juices, soft drinks and alcoholic beverages can be analyzed by FES.

Flame Emission Spectroscopy

Applications of FES:

4. Miscellaneous Applications:

c) Medicine and Biology:

Sodium and Potassium level from body fluid can be analyzed by FES

d) Geology, Industry and other field:.

Waste water analysis from industry is carried out by using FES.

Analysis of raw material and finished product

Analysis of geological materials such as minerals, ores, clay, petroleum etc.

Flame Emission Spectroscopy

Preparation of standard solutions:

1. Standard solution of sodium ions:

2.542 g Sodium chloride is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of sodium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 µg (microgram) of sodium ions

2. Standard solution of potassium ions:

1.909 g Potassium chloride is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of potassium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 µg (microgram) of sodium ions

Flame Emission Spectroscopy

Preparation of standard solutions:

3. Standard solution of Lithium ions:

5.324 g Lithium carbonate is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of lithium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 µg (microgram) of sodium ions