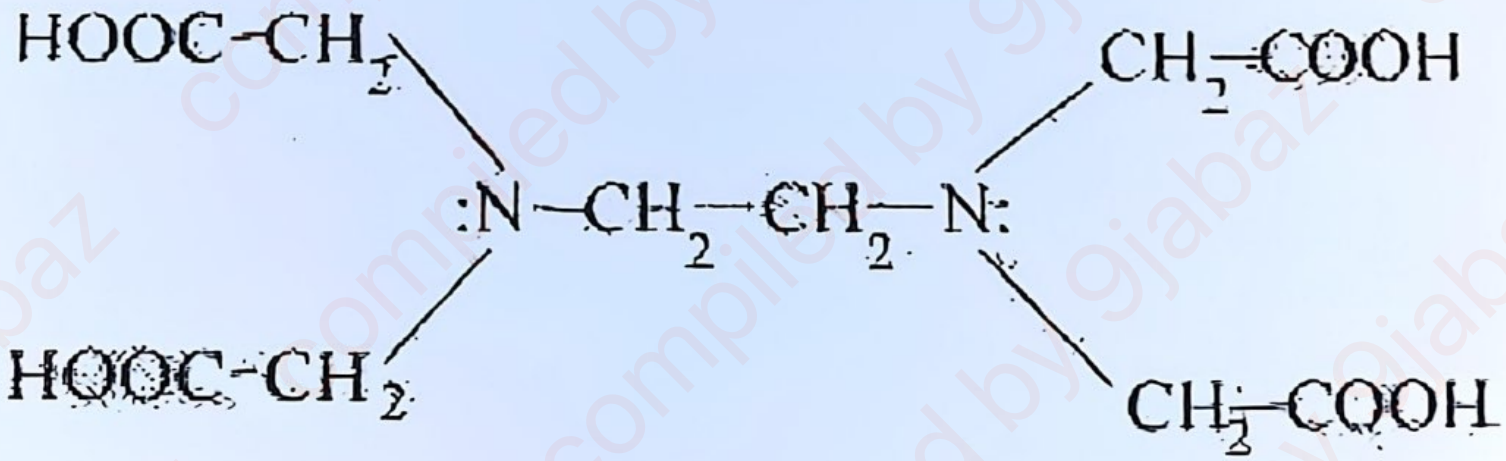
EDTA Titrations:

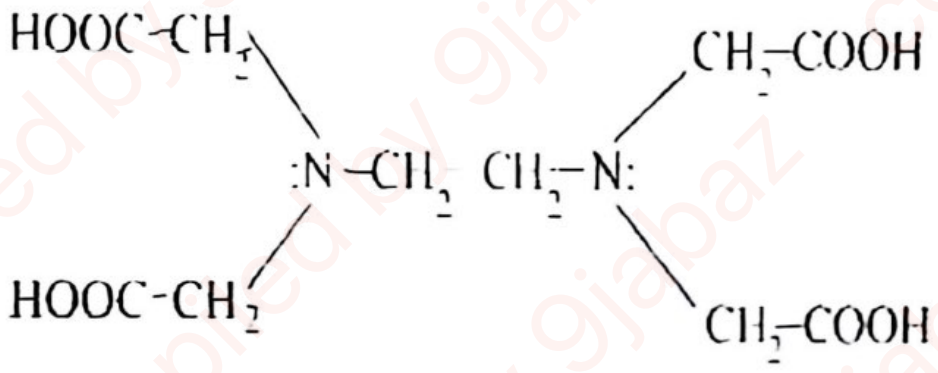
What is EDTA???

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



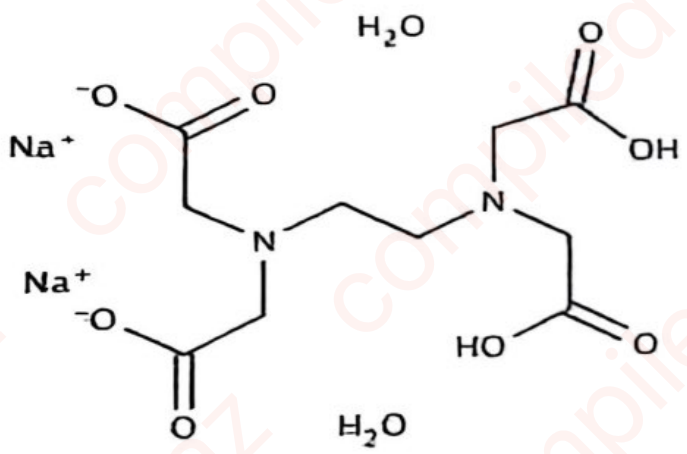
structure of EDTA

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



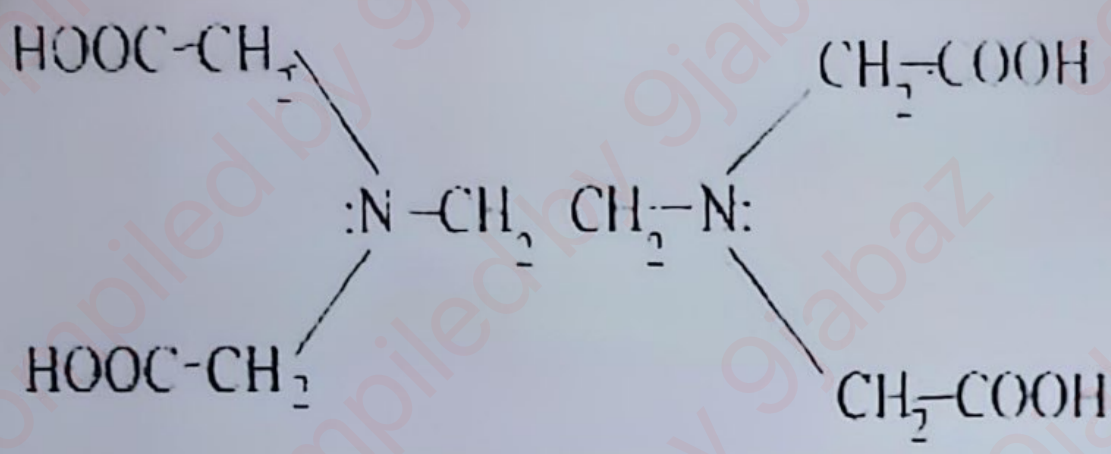
EDTA = H_4Y

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

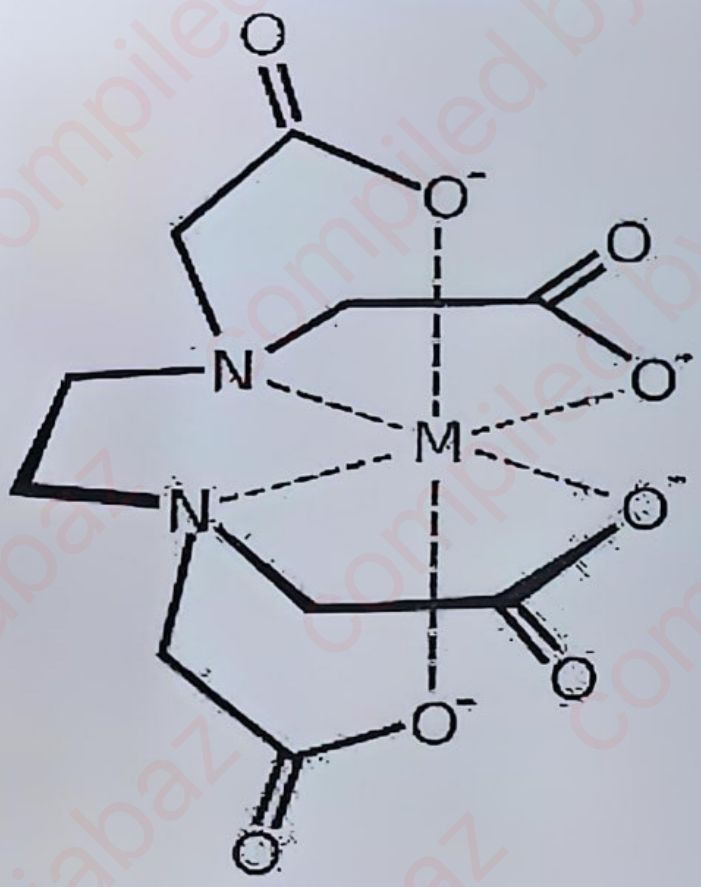
The fully protonated form H_4Y is only a major component in very acidic solutions (pH<3).

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. <u>Formation of insoluble hydroxides</u>:

   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. <u>Lack of selectivity</u>:

   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.

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

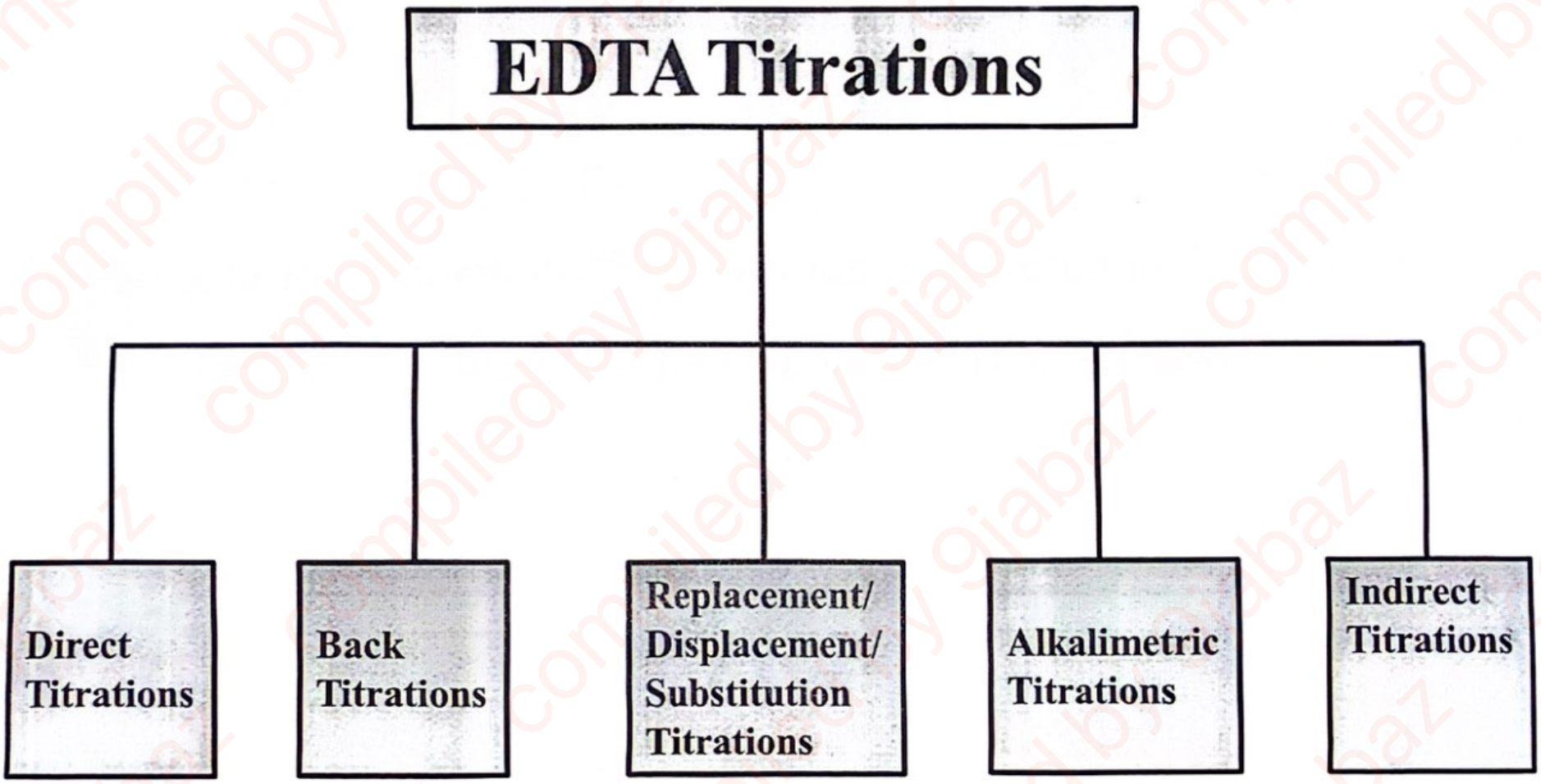
Stability of the Metal-Indicator complex K_{In}, is given by the equation

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

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:

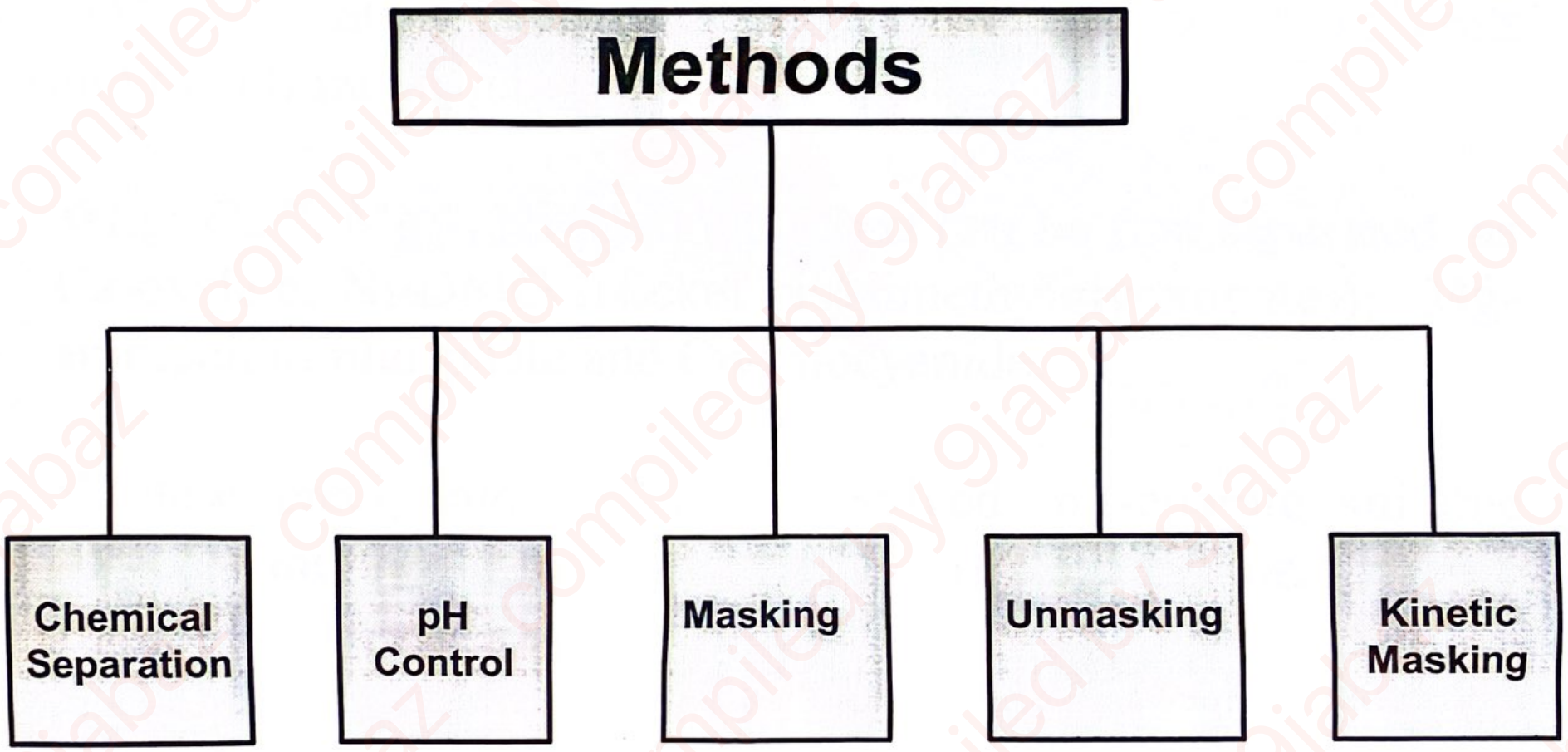
✓This method is used to determine the ions such as Halides, phospates, and sulphates that do not form complex with EDTA.

✓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.

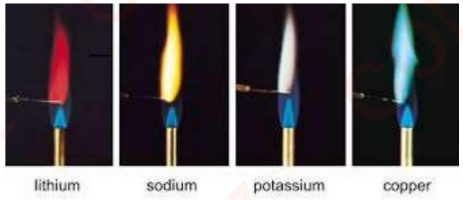
❖ Thus it is possible to determine Zn in the presence of Ca.

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

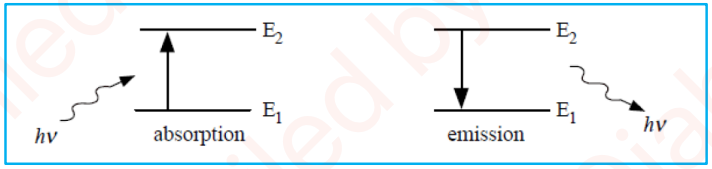
Principle:

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.

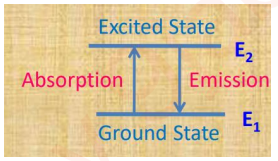
These excited atoms return to ground state and emit some radiations as a wavelengths .

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

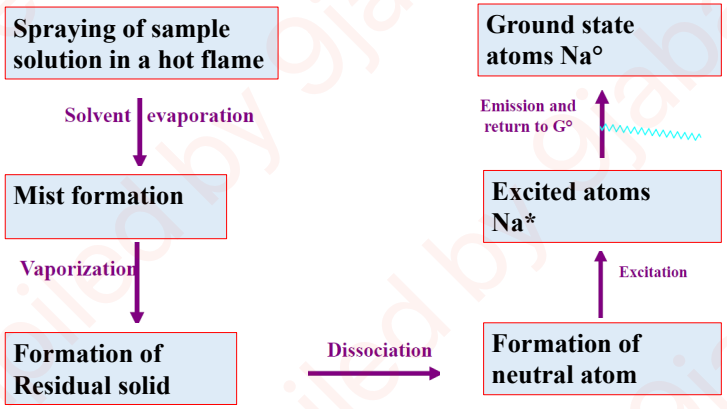
Types of Flames

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

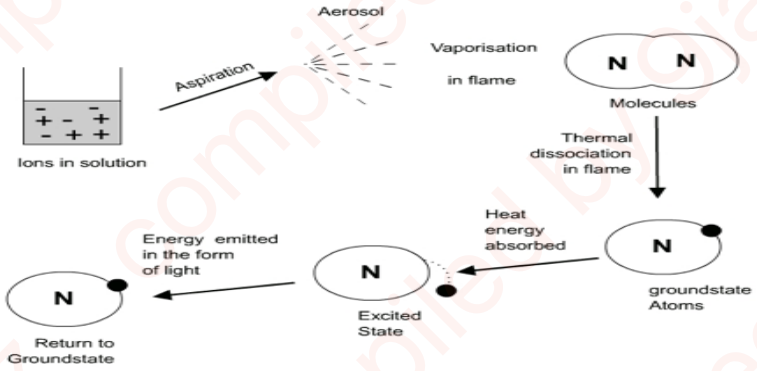


Fig 2: Brief overview of the process

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

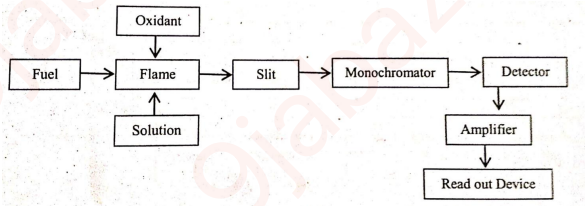
1) Concentration of analyte
2) Rate of formation of excited atoms in flame
3) Rate of introduction of sample in the flame
4) Temperature of the flame
5) Flame composition
6) Solvent used for dissolution

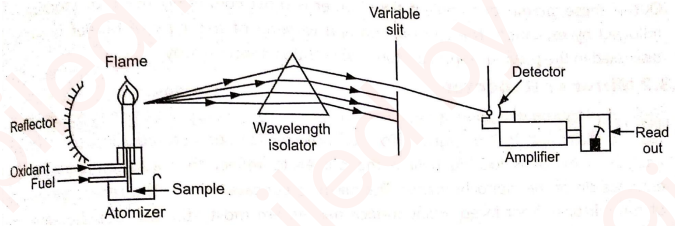
Alkali metals easily undergo ionisation , hence high temperature is not required for analysis of these elements. However for other elements including alkaline earth elements high temperature flame is preferred.

Flame Emission Spectroscopy

Instrumentation

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





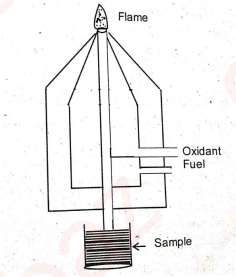
Flame Emission Spectroscopy

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

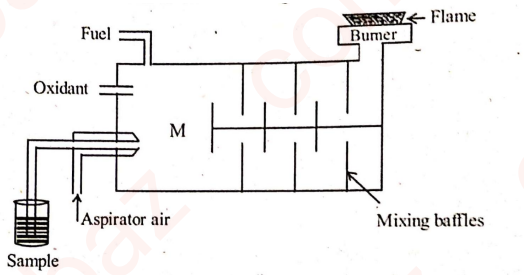
Flame Emission Spectroscopy

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.

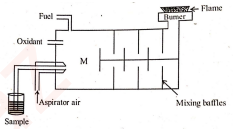
Flame Emission Spectroscopy

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.

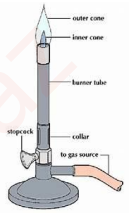
Flame Emission Spectroscopy

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.

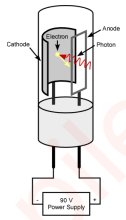


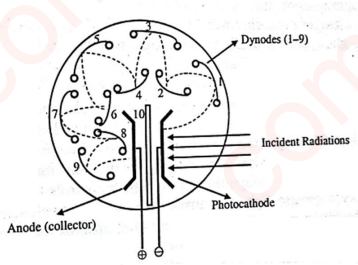
Photo Tube (Image Courtesy : http://people.whitman.edu/)

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:

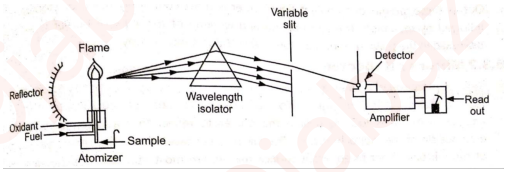
Amplifier is placed in between detector and read out device. It amplifies the signal received from the detector.

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

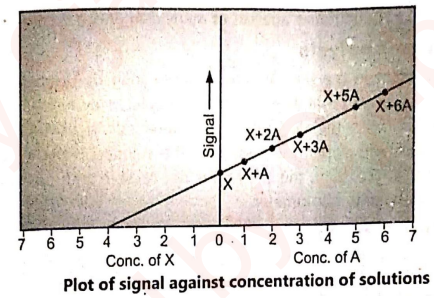
c) Calibration Curve Method

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:

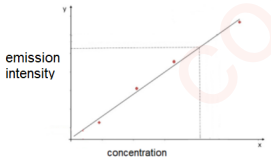
1) Series of standard solution is prepared.
2) Known amount internal standard (ex. Li) is added
3) Signal intensities of all standard solution having internal standard are measured.
4) Signal intensity of unknown solution is measured.
5) Graph of ratio of signal intensity vs concentration is plotted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

Introduction

- **Course Title:** Topics in Analytical Chemistry and Instrumentation
- **Course Code:** CHM 423
- **Credit:** 2
- **Course Instructors:** Profs. F. M. Adebiyi and Olabanji I.O
- **Course Description:** Topics will be chosen from the following :- sampling techniques; scope of EDTA titration; flame spectra and interferences; fluorescence and phosphorescence in analysis; analytical methods in mineral exploration, and proximate analyses.

- **Overall Learning Outcomes:**

- Learners should come away from this course with a sense of and appreciation for Analytical Chemistry and Instrumentation as an area of specialization in Chemistry.

- **Specific Objectives for the Course**

- Through this course, students should:

1. learn basic principles of sampling procedures for environmental matrices Viz., water, soil, air, geological material and vegetation.
2. learn the EDTA titration and uses
3. learn fluorescence and phosphorescence techniques in chemical analyses
4. learn some basic analytical methods in the natural resource exploration as well as in the proximate analyses
5. advance a native sense of significances of Analytical chemistry in the field of science and how they can be employed to make academic work more effective and efficient.

- ***TOPICS:*** Sampling techniques; Analytical Methods in Mineral Exploration, and Proximate Analysis

- Lecturer: *Prof. F. M. Adebiyi*

Module 1

SAMPLING OF ECOSYSTEMS

Definition of Terms

- A sample is a portion of material selected which possesses essential characteristics of the bulk of the original material.
- A sampling procedure consists of various steps i.e. technique (with various steps) used in the collection of the sample.
- A sampling unit may be defined as a minimum sized package in the consignment of material taken from any bulk sample.
- A gross sample is one which is prepared by mixing various portions or increments of sample.
- A sub sample is the smallest portion of the main sample just like a gross sample.
- An analyte is a substance or chemical constituent that is of interest in analytical procedure. It is important to note that experiments seek to measure the properties of analytes.

Transmission/transportation and Storage of Samples

- During transportation, the container, dust, moisture, oxygen, carbondioxide, light, heat and other environmental pollutants in atmosphere may contaminate the nature of the sample. It is therefore necessary to consider both the nature of the material that is being sampled and the tests that are to be made on the samples, while transporting it. Utmost care should be taken while drawing a sample from a population with a finite number of units to be examined. Since the process of sampling involves various operations like crushing, grinding and subdivision, thus contamination should not be permitted during these processes and also during storage. In addition to each operation, storage and transportation also contribute to the overall variance.

TYPES OF SAMPLING

1. Random sampling

Random sample is a sample collected at random/haphazard/casual from the target population. The ideal sampling plan provides an unbiased estimate of the target population's properties. This requirement is satisfied if the sample is collected at random from the target population. Despite its apparent simplicity, a true random sample is difficult to obtain. Haphazard sampling, in which samples are collected without a sampling plan, is not random and may reflect an analyst's unintentional biases. The best method for ensuring the collection of a random sample is to divide the target population into equal units, then assign a unique number to each unit and use a random number table to select the units from which to sample. A randomly collected sample makes no assumptions about the target population, making it the least biased approach to sampling. On the other hand, random sampling requires more time and expense than other sampling methods since a greater number of samples are needed to characterize the target population.

2. Judgmental sampling

The opposite of random sampling is selective or judgmental sampling, in which available information about the target population to help select samples is used. Because assumption about the target population are included in the sampling plan, judgmental sampling is more biased than random sampling; however, fewer samples are required. Judgmental sampling is common when we wish to limit the number of independent variables influencing the results of an analysis. For example, a researcher studying the bioaccumulation of polychlorinated biphenyls (PCBs) in fish may choose to exclude fish that are too small or that appear diseased. Judgmental sampling is also encountered in many protocols in which the sample to be collected is specifically defined by the regulatory agency.

For judgmental sampling, samples are collected from the target population using available information about the analyte's distribution, within the population.

3. Systematic sampling

This involves collection of samples from the target population at regular intervals in time or space. Random and judgmental samplings represent extremes in bias and the number of samples needed to accurately characterize the target population. Systematic sampling falls in between these extremes. In systematic sampling, the target population is sampled at regular intervals in space or time. For a system exhibiting a spatial heterogeneity, such as the distribution of dissolved oxygen in a lake, samples can be systematically collected by dividing the system into discrete units using a two-or three-dimensional grid pattern. Samples are collected from the centre of each unit, or at intersection of grid lines. When a heterogeneity is time-dependent, as is common in clinical studies, samples are drawn at regular intervals. When the target population's spatial or temporal heterogeneity shows a periodic trend, a systematic sampling leads to a significant bias if samples are not collected frequently enough.

4. Systematic-Judgmental sampling

This is a sampling plan that combines judgmental and systematic samplings' features. It involves combinations of the three primary approaches to sampling which is encountered in environmental studies when a spatial or temporal distribution of pollutants is anticipated. For example, a plum of waste leaching from a landfill can reasonably be expected to move in the same direction as the flow of groundwater.

5. Stratified sampling

This is a sampling plan that divides the population into distinct strata from which random samples are collected. Another combination of the three primary approaches to sampling is judgmental-random or stratified sampling. Many target populations are subdivided into distinct units or strata. For example, in determining the concentration of particulate Pb in urban air, the target population can be subdivided by particle size ($PM_{2.5}$ and PM_{10}), PM means particulate matter. In this case, samples can be collected in two ways. In a random sampling, differences in the strata are ignored, and individual samples are collected at random from the entire target population. In stratified sampling, the target population is divided into strata, and random samples are collected from within each stratum. Strata are analyzed separately, and then respective means are pooled to give an overall mean for the target population.

The advantage of stratified sampling is that the composition of each stratum is often more homogeneous than that of the entire target population. When true, the sampling variance for each stratum is less than that when the target population is treated as a single unit. As a result, the overall sampling variance for stratified sampling is always at least as good as, and often better than, that obtained by simple random sampling.

6. Convenience sampling

This is a sampling plan in which samples are collected because they are easily obtained. In convenience sampling, sample sites are selected using criteria other than minimizing sampling error and sampling variance. For example, in a survey of groundwater quality, samples can be collected by drilling wells at randomly selected sites, or by making use of existing wells. The latter method is usually the preferred choice. In this case, cost, expedience, and accessibility are the primary factors used in selecting sampling sites.

General Steps in Sampling Techniques

The ultimate objective of most geochemical analysis programmes is to describe the true variation of analyte's concentration or the concentrations of several analytes in some domain of the natural world which is under investigation such as sediment in streams, an area thought to contain a mineral deposit, or airborne particulate matter downwind from an industrial plant e.t.c.

The laboratory analysis of rocks, minerals or environmental materials pass through the following stages of geochemical investigation

(a) Thinking – (i) to decide on geochemical objectives (e.g., problem to be solved) (ii) to design investigation, to achieve objective
(b) Sampling – collect samples
(c) Analysis – (i) prepare sample for analysis (ii) decompose sample – solution (if necessary) (iii) examine the sample
(d) Interpretation (i) assess quality of samples and analysis (ii) geochemical analysis
(e) Conclusion – draw conclusions and/or recommend action

Common decisions to be taken in the design of a sampling technique

1. The medium to be sampled (e.g., solid, liquid etc.)
2. What the sample is intended to represent (e.g., the analytes dissolved in water, or those present in suspended solids (particle > 0.45 μm)).
3. The size of sample required (i.e., by mass or volume)
4. The number of samples required
5. The spatial distribution of the sample sites (e.g., sampling density)
6. Weather temporal variation in the sample media is important (e.g., for stream waters)
7. How the quality of the sampling can be estimated (what methods are applicable) for estimating precision/variance and bias of sampling)
8. What levels of sampling errors will be acceptable?
9. What scheme of sample identification is to be used (as part of a quality assurance scheme for monitoring sample progress)?

General guidelines for sampling various media

1. Atmosphere

Sampling of an atmosphere may refer to either the gas phase or the suspended particulate matter. Gas-phase sampling may be required in the open air or in restricted environments. Both types of sampling are susceptible to rapid temporal and spatial fluctuations due to meteorological and social factors. *In-situ* continuous field monitoring of air quality, particularly in urban locations, is now replacing laboratory analysis.

The optimum positioning and orientation of samples, together with the timing and duration of the sampling, all need to be investigated in designing the sampling protocol.

Particulate sampling equipment (air particulate sampler) consists of a pump drawing air at a known rate through a filter membrane such as 10 μm or glass fibres to collect the suspended particles. The duration of the particulate sampling can be calculated to ensure the expected concentration of the analyte is sufficiently high above the analytical detection limit (e.g ×100) so that acceptable precision can be attained. This is known as active sampling.

- **Passive sampling** involves chemical analysis of gaseous S and N compounds. The sample concentrations are achieved by passing the air sample through a suitable trapping medium e.g., an absorbing solution or an impregnated filter paper. The chemical methods for the analysis of gaseous N and S pollutants are classified as acidimetric, colorimetric and coulometric techniques.
- **Acidimetric technique** involves the determination of the free H^+ produced following the adsorption of the gas in an oxidizing solution.
- **Colorimetric method** involves interaction in solution of the gas or its hydrolysis or oxidation products with a colour-forming reagent followed by spectrophotometric measurement of the colour.
- **Coulometric method** involves measurement of the electrical current produced when strongly oxidizing or reducing pollutant gases react with KI or KBr solution in an electrochemical cell.

2. Water

Filtration is carried out immediately after the sample is taken, to prevent adsorption of dissolved elements onto the suspended matter. For analyzing cations, it is normal to acidify the solution to 0.1 M (~ 1% by volume) with high-purity HNO_3, immediately after filtration, to minimize solute deposition on to the container walls. A separate, non-acidified sample should be taken if anions are to be determined and some analyses (e.g., pH and alkalinity) may need to be carried out in the field.

Plastic bottles (e.g., polypropylene) soaked overnight in acid (1 M analytical grade) are appropriate containers unless organic constituents are to be determined. Seasonal variability is particularly pronounced in lake water, spatial variation of composition has also been recognized as a serious problem. For polluted water/effluent, the sampling protocol must prescribe appropriate safety measures to protect operator's health.

3. Soil

A hand-held auger with a thread of 15 by 2.5 cm is ideal for most soil sampling, while wet-strength bags are a good storage medium. The sampling of soils should ideally be accompanied by a systematic description of the type of soil. The most appropriate depth or horizon to be sampled can be determined by an orientation survey. The B horizon for example is often sampled for mineral exploration in temperate climates. The other sampling parameters such as the sample weight, the number of sub samples to be combined into one sample and whether the surface vegetation should be removed prior to sampling, all need detailed consideration.

4. Sediment

A simple polythene-scoop is required for sampling of surface stream sediment. Wet-strength paper bags, with fold-over closure tabs are a convenient storage medium, unlike polythene bags, they can be transferred directly to an oven. The part of sediment to sample cannot be left to subjective judgment. For example, only active stream sediment should be sampled, avoiding any collapsed bank material. It should be sampled only from a specified depth interval (e.g., top 2 cm) which would be in the oxidizing zone of the sediment. The trace element composition of the sediment changes markedly in this oxidized zone where precipitation of iron and manganese causes elevation of base metal concentrations due to co-precipitation or adsorption mechanisms. The decision to avoid anthropogenic contamination or to sample the sediment in a deliberately non-representative manner (e.g., taking only the <170 µm fraction is bias in favour of adsorbed bioavailable trace metals), and this must be determined by the geo-chemical objectives of the project and whether the surface vegetation should be removed prior to sampling all need detailed consideration.

5. Rock

For rock sampling, the simplest method is to take chip samples of unweathered material from exposures using a hammer. Representative in this situation is problematic as the exposed rock may differ in composition to the unexposed rock. Furthermore, rock will often break along planes of the weakness that are liable to have been altered and therefore be chemically unrepresentative. Systematic litho-geochemical sampling may therefore require sampling at a regular interval using a diamond drill core. This method, however, poses its own possibility of bias, in form of contamination by the drilling materials. Rock chips produced by percussion drilling can be used as an alternative but information on sample depth is usually inaccurate. Sample bags made of canvas or thick polythene are usually robust enough to prevent cross-contamination between rock samples. It is prudent to split core in half lengthways, sampling one half and storing the other as reserve.

6. Herbage/Vegetation

The sampling of herbage such as plants, leaves, fruits, bark and roots has the particular problem of the identification of the species required. Furthermore, there is the selection of the most appropriate part of the plant, and the optimum time of year for sampling the plant in question. Care must be taken to minimize the effect of soil contamination that can be very pronounced for certain elements that are preferentially excluded by the plant. Careful washing often fails to remove all the soil particles and the extent of the degree of contamination then needs to be estimated experimentally. This can be achieved using electron microprobe analysis, or by comparison between different acid decomposition.

Sample preparation

The objectives of sample preparation are

(i) To remove unwanted contaminant (e.g., suspended matter from water)

(ii) To preserve the essential features of the sample composition until analysis takes place

(iii) To convent the form of the sample material into one suitable for chemical analysis

(iv) In some cases, to separate or concentrate a particular constituent

Dissolution procedures for geophysical and environmental samples

i. Acid leaching

Aqua regia is commonly used as the leaching acid, although nitric acid alone and occasionally acid mixture may be recommended for specialized applications. Aqua regia (3:1 HCl: HNO_3) will leach many metals notably base metals (Cu, Cd, Mn, Pb etc.). The effectiveness of aqua regia for sample attack and dissolution is thought to be due to the complexing power of the chloride ion and to the catalytic effect of O_2 and NOCl present as the reaction takes place. Occasionally, reversed aqua regia 3:1 HNO_3: HCl may be preferred.

Advantages of using aqua regia

- compared with evaporation using HF or fusion techniques is that volatile components (As, Hg, S, Sb, Se etc.) can be retained.

ii. HF acid digestion

Dissolution using HF in combination with another strong minimal acid having a higher boiling point, is widely used procedure for opening up silicate-based minerals. Either HF + HNO_3 or HF + perchloric acid ($HClO_4$) in a Teflon beaker or platinum crucible on a hot plate or under an infrared lamp is used.

iii. Digestion by fusion

Fusing a silicate sample with an appropriate flux is the most complete but rigorous method for sample dissolution. There are no known silicate minerals that cannot be brought into complete solution when fused with the appropriate flux. The most commonly used fluxes are sodium carbonate and sodium hydroxide (salts of alkali metals) but have now been largely replaced by lithium metaborate ($LiBO_3$) and lithium tetraborate ($Li_2B_4O_2$).

Procedure

The normal procedure is to mix 0.5 g of sample carefully with 1.5 g of flux in a platinum crucible, and heat to 900°C in an electric muffle furnace or over a burner for approximately 30 minutes. The mixture is cooled and H_2O + 10 mL HNO_3 is added to the crucible containing the fusion mixture. A stirring bead in magnetic bar is placed inside the crucible, the solution placed on a magnetic stirrer and the solution stirred until the fusion mixture has fully dissolved.

Instrumental Analysis in Mineral Exploration and Exploitation (MEE)

Instrumental Analysis (IA) plays a critical role in different facets of Mineral Exploration and Exploitation (MEE) to establish many important aspects like physical characterization of ore, its mineralogical and chemical composition to establish overall grade, composition of its constituent ore/gangue minerals and mineral extraction products, quality assurance and quality control during various operations, value addition, characterization of processed waste and creation of wealth from such waste. IA is carried out by various techniques for different parameters that are broadly of two categories, viz., physical and chemical methods. For accurate IA, proper and thoroughly cleaned sampling and sub-sampling are necessary for quality data analysis, interpretation and decision.

a. Physical Methods of Instrumental Analysis in MEE

- These include the methods for determination of density, porosity, permeability, magnetic susceptibility, mineral – rock – ore characterization by petrological-microscope study, crystal properties by X-ray Diffraction (XRD) study, thermal properties, radioactivity and luminescence of minerals, ores and rocks.

b. Chemical Methods of Instrumental Analysis in MEE

- Chemical analysis of rocks and ores, their constituent, and mineral extraction products, obtained during their processing, is carried out by diverse instrumental techniques. In MEE, it provides critical information, like **(i)** grade of ore samples (required for calculation of ore reserves); **(ii)** chemical nature of rock samples (as acidic, intermediate, basic and ultrabasic); **(iii)** chemical composition of rocks and ores in terms of major (> 1 wt. %), minor (0.1-1 wt. %), trace [< 0.1% (< 1000 – 10 parts per million, ppm or g/ton)] and ultra-trace (< 10 ppm or 10,000 parts per billion, ppb or mg/ton) elements;

- **(iv)** nature of matrix (e.g., silicate, oxide and carbonate) of analyzed samples; **(v)** possible co-/by-products in ores; **(vi)** presence and content of precious metals like Au, Ag in ores with no mineralogical expression, e.g., invisible Au and Ag in some sulphides; and **(vii)** nature and amount of impurities in mineral extraction products. Chemical analysis of geological samples is carried out either for elemental (or in oxide form of elements) or isotopic composition. For elemental (or oxide) composition, the usual chemical methods of analysis are as follows: Gravimetry, Titrimetry, Spectrophotometry, Flame Photometry, Emission Spectrography (DC-arc or AC-spark), Atomic Absorption Spectrometry (AAS), X-Ray Fluorescence Spectrometry (XRFS – either Wavelength- or Energy-Dispersive, W/ED or Total reflection, TXRF), Instrumental Neutron Activation (INA), Inductively Coupled Plasma - Optical/Atomic Emission Spectrometry (ICP – O/AES), ICP – MS (Mass Spectrometry), Electron Micro Probe (EMP) and Fluorimetry. Of these, the first two are absolute methods and the rest are comparative methods that require appropriate standards for calibration and analysis. Depending upon geochemical nature, expected concentrations and type of matrix of the sample to be analyzed, specific methods amongst the above need to be selected for analysis of its elements. It may be noted that until ~1960s, chemical analysis of geological materials was done by classical and rapid methods, which are time-consuming, cumbersome and detailed chemical manipulations. These are superseded by instrumental methods that have modern analytical technology that is possible due to notable advances in micro mini aturization of electronic and computational technology.

PROXIMATE ANALYSIS

- The proximate composition of foods includes moisture, ash, lipid, protein and carbohydrate contents which are expressed as the content (%) in the food, respectively. These food components may be of interest in the food industry for product development, quality control (QC) or regulatory purposes. Analyses used may be rapid methods for QC or more accurate but time-consuming official methods. Sample collection and preparation must be considered carefully to ensure analysis of a homogeneous and representative sample, and to obtain accurate results. Estimation methods of moisture content, ash value, crude lipid, total carbohydrates, starch, total free amino acids and total proteins are put together in a lucid manner.

Precisely, in industry, the standard proximates are:

- Ash, Moisture, Proteins, Fat and Carbohydrates. Analytically, four of the five constituents are obtained via chemical reactions and experiments. The fifth constituent, carbohydrates, are calculated based on the determination of the four others. Proximates should nearly always account for 100% of a food product; any deviation from 100% displays the resolution of the chemical test, as small variations in the way each test is performed accumulate or overlap the compositional make-up.

There are additional ingredients that may fall under the category of one of the five constituents. Carbohydrates, for example, include but are not limited to:

- Dietary fibers
- Sugars
- Sugar alcohol

Whereas ash includes but is not limited to:

- Dietary minerals e.g. sodium, potassium, iron, calcium
- Vitamins e.g. β-Carotene, retinol, vitamin D_3, vitamin D_2, B vitamins

Although proximates do not give the entire nutritional assay, they are an inexpensive way to track deviations in the quality of foods.

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- D.A.Skoog, D.M. West and F.J. Holler. 1992. Fundermental Principle of Analytical Chemistry, Seventh Edition, Saunders College Publishers, Fort Worth

Department of Chemistry
Obafemi Awolowo University
Ile-Ife, Nigeria

TOPICS IN ANALYTICAL CHEMISTRY (CHM 423) 2024/2025 Mid-semester Exam **Instructions:**
Answer all questions **Time: 60 minutes**

Q1

b. (i). Write the structure and Molecular formula for EDTA
(ii). Write two other names for EDTA
(iii). What is the basic principle involved in EDTA titration?
(iv). Mention one indicator used in EDTA titration
(v). How many EDTA is/are in operation

b. (i). Give stepwise account of the procedure involved in increasing selectivity of EDTA by Chemical separation.
(ii). Explain the role of pH in EDTA titration.
(iii). What is/are the advantage(s) of EDTA as titrant?

c. Explain the principle of Flame Emission Spectroscopy (FES).

2a. Explain briefly the general guidelines for the sampling of the soil.

b. In not more than *four* lines in each case, describe the following terms as applied in the field of Environmental Chemistry: **i.** Sampling procedure and **ii.** Sampling unit ·

c. Itemize *four* objectives of sample preparation **(15 marks).**

CHM 423 - Practice questions

1 (a) An Environmental Chemist is working on the assessment of aerial (air) pollution of Ile-Ife metropolis using air particulates as indicators. The grant for the work was facilitated by the Federal Ministry of Environment, Nigeria. Name and describe the best sampling method you would recommend for the researcher to use.

(b) Supposing your Research project (CHM 421/CHM 422) topic is "Mineralogy of herbage" within Obafemi Awolowo University Farm, Ile-Ife". Describe briefly the general guidelines for the sampling of the herbage.

(c) In not more than *four* lines in each case, describe the following terms as applied in the field of Environmental Chemistry: **i.** Sample **ii.** Sampling procedure **iii.** Sampling unit **iv.** Gross sample and **v**. Analyte

2 (a) List *four* objectives of sample preparation

(b). A Geoscience student of Elizade University, Ilara Mokin, Ondo State wish to carry out rock analysis for his B.Sc degree research project and he is looking up to you as a student of "GREAT IFE" for advice. Convince him to use chemical methods of instrumental analysis as applied in Mineral exploration and exploitation (MEE) by stating *five* critical information these methods can provide.

(c) Classify and describe briefly the chemical methods for the analyses of gaseous N and S compound pollutants.

(d) i. Explain briefly the term proximate composition **ii.** State how the five standard proximates in industry can be obtained analytically.