1. **Write different types of complexometric titrations with suitable examples. Write the calcium gluconate assay's principle, reactions and Procedure**

Answer:

The quantitative analysis which involves formation complex by titration of EDTA, complexing agent with metal ions under determination, is termed as EDTA titrations or complexometric titration.

Principle:

In complexometry, a **Complex** or coordination compound is formed by the combination of a metal ion (either mono or poly valent) with a molecule that is capable of donating one or more electrons pair. Complexes formed are either non cyclic or Chelates (they have ring structure or cyclic))

The various type of EDTA titration or Complexometric titrations are as follows

1. Direct Titration:

Metal ion to be analyzed is Buffered to the desired pH and titrated directly with the standard EDTA solution. Before the end point, color of the solution is due to Metal indicator complex and at the end point, color is due to the free indicator.

M^{n+} + Na_2EDTA → $[M^n\text{-}Na_2EDTA]^{2-}$ + $2H^+$

Metal complexing agent Metal –EDTA complex

2.Back titration:

Excess of standard EDTA solution is added to an analyte metal ions, and Buffered to the desired pH. Unreacted EDTA is back titrated with another standard solution of metal ion i.e. either **zinc chloride/sulphate or Magnesium chloride/sulphate. The end point is detected by the adding an indicator which changes its color due to the formation of Zn-Indicator or Mg-Indicator complex**.

M^{n+} + Excess Na_2EDTA → M^n -Na_2EDTA complex
Un reacted Na_2EDTA + $MgSO_4$ → Mg- Na_2EDTA complex

At the end point,

$MgSO_4$ + Indicator → Mg- Indicator complex
(one excess drop) (blue color) (wine red color**)**

Replacement or substitution titration

This method is applied when analyte metal ion do not react satisfactorily with indicator to give sharp end point. Hence, Magnesium sulphate standard solution is added and desired pH is maintained by adding suitable buffer.

During titration, EDTA reacts with both metals to forms respective complexes.

Magnesium suphate also reacts with indicator to from colored complex i.e.Wine red color.

At the end point, one excess drop of EDTA displaces indicator from Mg-Indicator complex by forming Mg-EDTA complex and free Indicator shows Blue color.

Blank titration is performed with only MgSO4 and correction factor is applied.

M^{n+} + **Na_2EDTA → M^n -Na_2EDTA complex Mn: analyte and Mg**

At the end point:

Mg-InD Complex + Na_2EDTA → Free InD^- + $[Mg\text{-}Na_2EDTA]^{2-}$
(Wine red olor) (Blue color)

Alkalimetric titration

Na_2EDTA reacts - metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ions, which is then titrated with alkali, i.e. sodium hydroxide standard solution using suitable indicator to detect the end point.

M^{n+} + **Na_2EDTA → M^n -Na_2EDTA complex + $2H^+$**
Metals Disodium edetate Metal edetate complex Hydrogen

$2H^+$ + 2NaOH → H_2O + $2Na_+$
Alkali standard

Miscellaneous

Exchange reactions between the tetracyanonickelate(II) ion $[Ni(CN)_4]^{2-}$ (potassium salt) and the element to be determined, whereby nickel ions are set free is titrated with EDTA standard solution using an murexide or Bromopyrogallol indicator

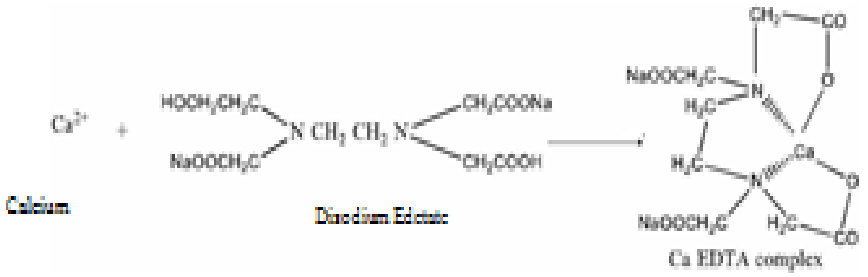
e.g. Silver and gold

$$[Ni(CN)_4]^{2-} + 2Ag^+ \rightleftharpoons 2[Ag(CN)_2]^- + Ni^{2+}$$

The principle involved in Calcium gluconate assay depends on substitution or displacement type of complexometric reaction.

Disodium EDTA is a multidentate complexing agent or ligand has two pair of unshared electrons and donates them to Calcium ion to form cyclic or ring structured Ca-EDTA complex.

M^{n+} + **Na_2EDTA → M^n -Na_2EDTA complex + 2H+** **Mn: analyte and Mg**



At the end point:

Mg-InD Complex + Na_2EDTA → Free InD^- + $[Mg\text{-}Na_2EDTA]^{2-}$
(Wine red or Purple color) (Blue color) magnesium –EDTA complex

Procedure:

Conical flask: 0.5 g Calcium gluconate + 50 ml water + 5.0 ml of 0.05 M magnesium sulphate + 10 ml of strong ammonia solution

Calcium metal ion do not react satisfactorily with indicator to give sharp end point. Hence, Magnesium sulphate standard solution is added to increase the sensitivity of end point detection.

Ammonia –Ammonium chloride buffer is added to maintain desired pH =10 which is essential for the neutralization of H+ ions released in the complexation reaction, also Metal-EDTA complexes are more stable in alkaline condition.

Burette: 0.05 M disodium edetate a standard solution is used for titration

Indicator: 2 to 3 drops Mordant black II mixture added which acts as an indicator

In titration, EDTA reacts with both metals to forms respective complexes.

Magnesium suphate also reacts with indicator to from colored complex i.e.Wine red color.

At the end point, one excess drop of EDTA displaces indicator from Mg-Indicator complex by forming Mg-EDTA complex and free Indicator shows Blue color.

Blank titration is performed with only MgSO4 and correction factor is applied

From the volume of 0.05 M disodium edetate required, subtract the volume of the magnesium sulphate solution added or perform the blank titration

1 ml of the remainder of 0.05 M disodium edetate is equivalent to 0.02242 g of Calcium gluconate.

$$\% \text{ of Calcium gluconate} = \frac{\text{Titer(Sample-Blank)} \times \text{Molarity of DisodiumEDTA} \times \text{Factor} \times 100}{\text{Weight of Ca. gluconate taken} \times \text{Required Molarity}}$$

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2. Write the principle and steps involved in a barium sulfate assay. Describe co-precipitation and post-precipitation.

Principle involved in barium sulphate estimation

1. **Sample preparation**: Barium sulphate sample is converted to Barium carbonate by heating with *sodium carbonate and 5 g of potassium carbonate at 100ºC FOR 15min. After cooling it is suspended in water to remove impurities. Add acetic acid to crucible to dissolve traces of* Barium carbonate.

$$2BaSO_4 + Na_2CO_3 + K_2CO_3 \rightarrow Ba_2CO_3 + Na_2SO_4 + K_2SO_4$$

Barium sulphate sod.Carbonate Pot. Carbonate Barium carbonate sod.sulphate pot.sulphate

Cool in ice, and Barium carbonate solids are completely separated out are washed with 2 per cent w/v solution of *sodium carbonate until the washings are free* from sulphate

Barium carbonate solids are treated with 5ml of hydrochloric acid to convert it to barium chloride

$$Ba_2CO_3 + 4HCl \rightarrow 2BaCl_2 + 2H_2O + 2CO_2(g)$$

Barium carbonate hydrochloric acid Barium chloride

2. **Precipitation :** Add 10 ml of a 40% w/v solution of ammonium acetate, 25 ml of a 10% w/v solution of potassium dichromate + 10 g of urea. Cover, digest in an oven at 80° C to 85°C for 16 hours

$$2BaCl_2 + K_2Cr_2O_7 + 2NH_4OH \rightarrow 2BaCrO_4\,(s) + 2KCl + H_2O + 2NH_4Cl$$

Barium chloride Pot.dichromate Amm.hydroxide Barium chromate Pot.chloride *Amm. Chloride*

3. **Digestion:** Digestion of 16 hours converts complete and quantitative conversion of Barium chloride to barium chromate in alkaline condition by using urea(hydrolysed to Ammonia)

4. **Filteration :** Filter Barium chromate yellow precipitate while still hot using sintered-glass filter

5. **Washing:** wash with 0.5 per cent w/v solution of *potassium dichromate and finally with 2 ml of water prevent solubalization of precipitate*

6. **Drying:** Dry to constant weight at 105° C

. **7. Weighing :**
Weigh the residue after cooling in a desiccators using analytical balance**.**

8. Calculation
1 g of the residue(Barium chromate) equivalent to 0.9213*i.e. Gravimetric factor* g of BaSO4.

$$\% \text{ of Barium sulphate} = \frac{\text{Weight of Barium chromate precipitate} \times 0.9213}{\text{Weight of the sample}}$$

The **contamination of the precipitate** by **substances** that are **normally soluble in the mother liquor is termed co-precipitation.**

Important types of co-precipitation

1. **Adsorption at the *surface* of the particles exposed to the solution**: It causes significant contamination of precipitates with large specific surface areas i.e. colloidal precipitate. It has no significance in crystalline precipitate
e.g. in determination of chloride ions, $AgNO_3$, a normally soluble compound, is co-precipitated with the AgCl precipitate.
Remedy: Digestion and washing with volatile electrolyte, re-precipitation are carried out to purify the precipitate.

   Mixed Crystal lattice: One of the ions in the crystal lattice of a solid is replaced by an ion of another element, provided the two ions have the same charge, their sizes differ by not more than about 5% and if their salts belong to the same crystal class.
   This Occurs in colloidal and crystalline precipitate.
   e.g. In the estimation of $BaCl_2$ analyte containing lead impurity, Co precipitation of lead sulfate occurs. Pb^{2+} ions replace some of the Ba^{2+} ions in the crystal lattice of $BaSO_4$ precipitate
   Remedies:
   Removal of interfering ion before final precipitation
   Different precipitating agent can be used

Occlusion :It is a type of coprecipitation in which a impurity or Foreign ions in the counter-ion layer is trapped within the growing crystal when rapid crystal growth occurs during precipitation
The amount of Occluded material is greatest in that part of the crystal that forms first and Occurs only in crystalline precipitate

Mechanical entrapment: It occurs when crystals lie close together during growth. Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.

Remedies for Occlusion & Mechanical entrapment:
Maintain low super saturation
Digestion i.e. rapid dissolving and re-precipitation at elevated temperature, opens the pockets and allow the impurities to escape in the solution

If any precipitation which occurs on the surface of the first precipitate *after* its formation, the process is called as post precipitation
Example: Magnesium oxalate separates out gradually upon the calcium oxalate primary precipitate

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Write a note about the conductometric titration of a strong acid versus a strong base using conductometry.

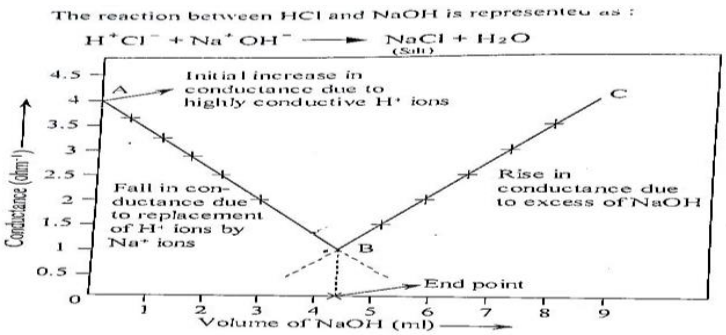
In Conductometric titrations, changes in the conductivity of the solution is measured which usually occur depending on the number & mobility of the ions which are removed or added from the solution.
At the end point there is a sharp change in the conductivity of the solution shown by the intersection of 2 lines in the graph which is a plot of conductivity Vs Titrant added.

Titration of Strong Acid Vs Strong base
Strong acid completely dissociates into H+ ions.

$H^+ + Cl^-$ + $Na^+ + OH^- \rightarrow$ NaCl + H2O

Hydrochloric acid Sodium hydroxide sodium chloride water

Initial conductance before titration is high because of the high concentration of highly conducting H^+ ions
During the titration H^+ ions are removed by neutralization with OH- ions of alkali resulting in decrease of Conductivity.
After the end point i.e. when all H^+ ions are neutralized, addition of excess alkali results in increase in conductivity because of the highly conducting OH^- ions.
The intersection of two lines gives the end point



4.Write about the construction and working of a glass electrode.

A glass electrode is a type of ion-selective electrode used primarily for pH measurement in potentiometry.

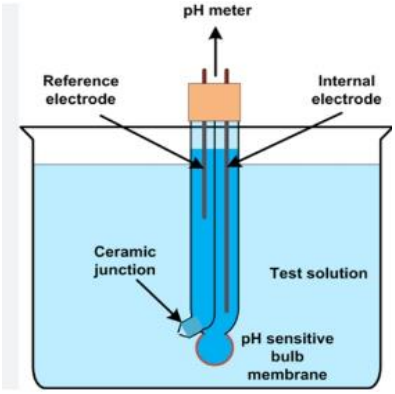
Construction of Glass Electrode

a) **Thin Glass Membrane: It is** made of soft glass i.e.silicate (alkali metal oxides) with thickness of 0,05 to 0.2mm thickness at which rapid exchange of H^+ ions occurs.

b) Internal Reference Electrode and inner solution: Inside the electrode, there is a silver-silver chloride (Ag/AgCl) electrode or a calomel electrode (Hg/Hg_2Cl_2) immersed in 0.1 M HCl which has a known and stable pH and maintains constant potential.

c) External Reference Electrode(If inbuilt internal reference electrode is not available)

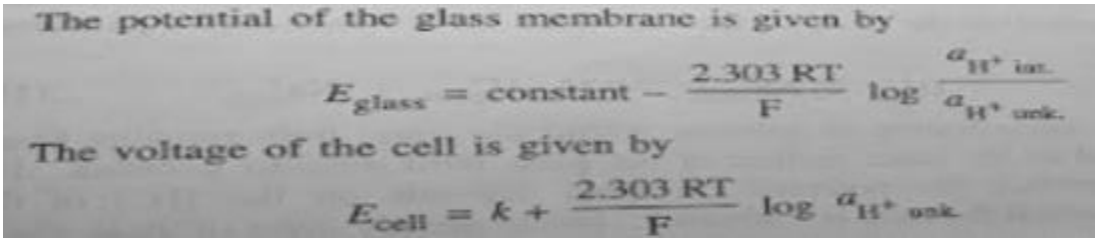
A separate reference electrode, such as a calomel electrode (SCE) or Ag/AgCl electrode, is used to provide a stable reference potential. It is placed in the test solution and connected to the measurement circuit.



Working:

1. The glass electrode is immersed in the solution whose pH needs to be measured
2. Hydrogen Ion Exchange at the hydrated gel layer on both sides of Glass Membrane takes place.
   The outer surface comes into contact with the test solution, while the inner with the internal solution (0.1 M HCl).

3. The difference in H^+ ion concentration between the test solution and the internal solution generates a potential difference across the glass membrane.
This potential is governed by the Nernst equation


The potential of the glass membrane is given by

$$E_{glass} = \text{constant} - \frac{2.303\,RT}{F} \log \frac{a_{H^+ \text{ int.}}}{a_{H^+ \text{ unk.}}}$$

The voltage of the cell is given by

$$E_{cell} = k + \frac{2.303\,RT}{F} \log a_{H^+ \text{ unk.}}$$

Advantages:

1. Used in the presence of oxidants and reductants, organic compounds, viscous media, colored, turbid or colloidal solutions
2. Simple to operate,
3. pH range of 0-14

Disadvantages:

1. It is very fragile and minute abrasion on membrane causes the damage
2. Cannot be used in acid fluoride solution
3. Cannot be used at high temperature for prolonged period.

Application:

1. Measurement of pH
2. Cation selective glass electrodes are used for Na^+, K^+, Li^+, $NH4^+$, Ag^+, and for Determination of Ca^{2+}, Na^+, K^+ in biological fluids

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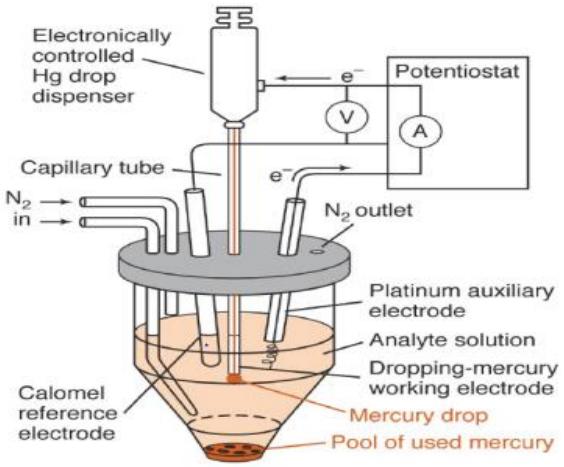
7. Describe the construction and operation of the dropping mercury electrode

Dropping mercury electrode:



It acts as a small or micro-ploarizable electrode consists of mercury reservoir, can act as a cathode and anode. It is connected to fine capillary through rubber tubing. The mercury drop serves as the site for the electrochemical reaction. From reservoir mercury drops down (under gravity or slight pressure) as a small drops through a capillary bore , about 0.02 to 0.05mm, the capillary length is about 5 to 12 cm

The height of the reservoir is adjusted to set the drop time (i.e. time required to form every fresh drop of mercury from capillary) as required i.e. 1 to 5 seconds. Each drop has a fresh, smooth, and reproducible surface area, crucial for accurate measurements.

Drop weight: 10mg, surface area: 0.8mm2

Applied volt: 50 to 200mv/min

Flow rate of drop : 5 to 30 drops /min

Drop life : 2 to 12 seconds

Potential range : +0.4v to -2V

Reference electrode : Saturated Calomel electrode against which the working electrode's potential is measured

Auxiliary electrode or counter electrode: It completes the circuit by allowing the current to flow and donate or accepts electrons

Sample cell: The DME is dipped in glass cell in which analyte solution is kept and supporting electrolyte like KCl is added.

Pure nitrogen is bubbled through the solution to expel out dissolved oxygen.

Electrical circuit: Both anode and cathode is connected to appropriate end of battery

Working:

When a gradually increasing negative voltage is applied, analyte first diffuses to the DME and undergo reduction or oxidation reactions at its surface. As each drop detaches, a new drop forms, providing a refreshed electrode surface. Diffusion current is generated due to analyte is measured and graph is plotted between voltage applied(x axis) and current(Y axis)

Half wave potential: It is the potential at which the concentration of the oxidized and reduced forms at electrode surface becomes equal and is used for qualitative analysis and diffusion current measured is used for quantitative analysis

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6. Name the different types of redox titrations

1. Permanganometry
2. Cerimetry
3. Iodimetry
4. Iodometry
5. Bromatometry
6. Dichrometry
7.Titration with potassium iodate

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8. Classify redox indicators with suitable examples

1. Self-Indicator: Potassium permanganate
2. Internal indicator: Ferroin , diphenylamine indicator
3. External indicator: Potassium ferrocyanide
4. Instrumental methods: Potentiometry and polarography

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9. What distinguishes iodimetry from iodometry?

Iodimetry	**Iodometry**
Direct method	Indirect method
Iodine is used as a Tirant to determine the concentration of analyte with reducing properties	Sodium thiosulphate is used as a Tirant to determine the equivalent amount of liberated Iodine due to reaction between analyte and potassium iodide in presence of acid.
Potassium Iodide and acidic condition is not required for titration	Potassium Iodide and acidic condition is required for titration
Example: Ascorbic acid, Sodium	Example: Copper sulphate, chlorinated

bisulphate	lime

10. What is Bromatometry? Give any two applications

A quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration of Oxidizing agent, Potassium bromate which is required to react quantitatively with a measured volume of a solution of the substance to be determined which has Reducing properties is termed as Bromatometry.
Applications: Antimony or Arsenic, Sodium salicylate etc.,

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11. Write the role of Starch indicator in redox titrations

Starch (amylose component) is commonly used as an indicator in iodometric and iodimetric redox **titrations** because it forms a deep blue colored complex with iodine

Starch indicator is usually **added whenthe end point** of the titration approaches because at high iodine concentration, the starch–iodine complex becomes very stable. Therefore Iodine will not be available to react with sodium thiosulphate and results in inaccurate results

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